

Chapter 6

Classification and Operating Principles of Nanodevices

6.1 Classification

6.1.1 Correlations of the Fundamental Properties of Non-regular Materials

The analysis of the principles of nanosensorics, nanomemory and energy nanotransducers is based on the study of various correlations of the fundamental properties of non-regular nanomaterials with the elements of functionalization.

Consider the general scheme of modelling of non-regular materials [1–4] (see Fig. 6.1). The cycle of full-scale self-consistent calculations begins with the specification of the atomic structure $\{\mathbf{R}_i^{(0)}\}$ in the form of coordinates that fix the initial configuration. The potentials of the atoms must be known [1–4]. Then the statistical characteristics of the structure in the form of pair correlation functions $g(R)$ or, in more detail, in the form of a number of many-particle correlation functions $g(1, 2), g(1, 2, 3), g(1, 2, 3, 4), \dots$ are estimated. The postulated atomic structure is divided into clusters, the electron charge density ρ_{cr} is calculated, crystalline potentials V_{cr} are built, and a self-consistent EDOS $\rho(E)$ calculation is performed in the EMA-CPA framework. Then the total energy $E_{\text{tot}}^{(0)}[\rho(\mathbf{r})]$ is estimated as an electron charge density functional, which is minimized by the positions of atoms $\{\mathbf{R}_i\}$, and new positions $\{\mathbf{R}_i^{(1)}\}$ of atoms are defined. And again, the cycle of calculations $g^{(1)}(R) \rightarrow \rho^{(1)}(E) \rightarrow E_{\text{tot}}^{(1)}$ is carried out.

This is the basic meaning of the correlations of the atomic and electronic structure of the material. After that, the total energies $|E_{\text{tot}}^{(1)} - E_{\text{tot}}^{(0)}| = \Delta E$ are compared. It should be noted that in this formulation, the characteristics of the ground state of the system are estimated. If the convergence of the calculation cycle $g(R) \rightarrow \rho(E) \rightarrow E_{\text{tot}}$ is satisfactory with respect to a given value ΔE , then it is possible to proceed to the calculations of dynamic characteristics, such as

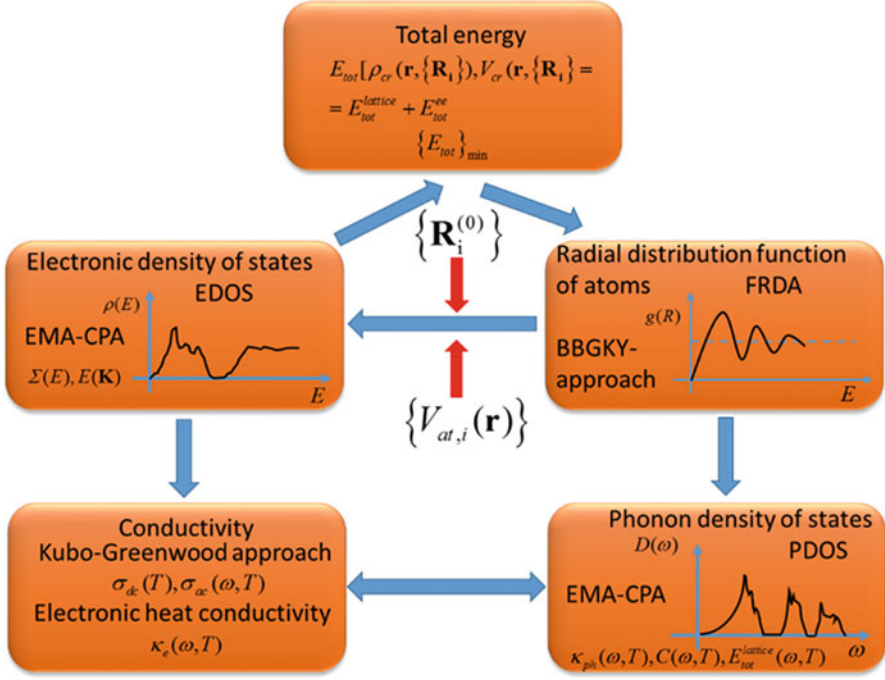


Fig. 6.1 Correlations of the fundamental properties of condensed non-regular materials

conductivity $\sigma(\omega, T)$, thermal conductivity $\kappa(\omega, T)$, heat capacity $C(\omega, T)$ and lattice total energy $E_{\text{tot}}^{\text{lattice}}(\omega, T)$, taking into account the temperature factor introduced by means of the Fermi–Dirac and Bose–Einstein distribution functions.

Therefore, further ways of modelling are:

1. $\rho(E) \rightarrow \sigma(\omega, T) \rightarrow \kappa_e(\omega, T)$;
2. $\{R_i\} \rightarrow g(R) \rightarrow D(\omega) \rightarrow \kappa^{\text{lattice}}(\omega, T) \rightarrow E_{\text{tot}}^{\text{lattice}}(\omega, T) \rightarrow C(\omega, T)$.

We note that in accordance with the adiabatic approximation, the electron and phonon factors are separated. However, it is also necessary to keep in mind the requirement of mixed excitations modelling, for example, the estimation of the electron–phonon thermal conductivity or conductivity factor, which is also reflected in the modelling scheme (see Fig. 6.1). It is also worth mentioning the more subtle practically significant changes in EDOS caused by the magnetic field $\mathbf{B}$, which are significant for nanospintronics, namely, $\rho_{\uparrow\downarrow}(\mathbf{E}) \xrightarrow{\mathbf{B}_{\uparrow}} \rho_{\uparrow}(\mathbf{E})$ and $\rho_{\uparrow\downarrow}(\mathbf{E}) \xrightarrow{\mathbf{B}_{\downarrow}} \rho_{\downarrow}(\mathbf{E})$. This is important for creating nanomemory devices.

However, the greatest practical values for creating nanosensors are correlations $\rho(E) \rightarrow \sigma(\omega, T)$. This means that EDOS-induced changes in the EDOS $\rho(E)$ are reflected in the conductivity changes of the nanosensor sensing element. A typical example of a theoretical description of this kind is the Kubo–Greenwood approximation:

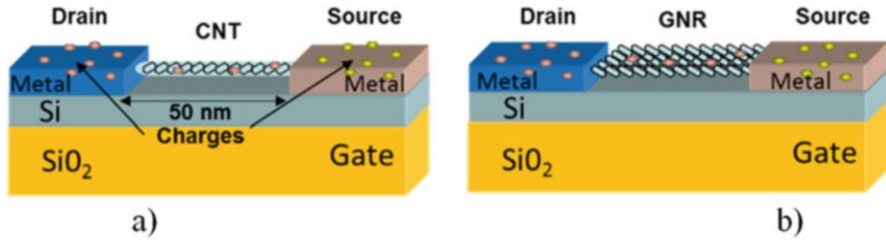


Fig. 6.2 Typical structure of a CNT-based FET (a) and GNR-based FET (b). The unperturbed field-effect transistors based on CNT and GNR are given CNT- or GNR-based FET which is mainly composed of a corresponding semiconducting carbon material suspended over two electrodes

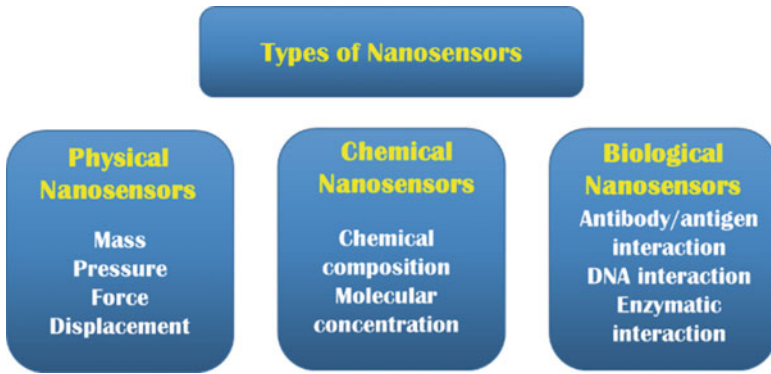


Fig. 6.3 Nanosensors types, which can be realized using FET-type technology

$$\sigma_E(\omega) = \frac{2\pi e^2 \hbar^2 \Omega}{m^2 \hbar \omega} \int [f(E) - f(E + \hbar\omega)] |D_F|^2 \rho(E) \rho(E + \hbar\omega) dE,$$

where $f(E)$ is the Fermi–Dirac function and $\rho(E)$ is the EDOS.

Practically, the correlation $\rho(E) \rightarrow \sigma(\omega, T)$ can be realized in FET-type nanodevices [5] (see Fig. 6.2), including sensing elements based on CNTs and GNRs. If it is necessary, CNTs and GNRs are provided with appropriate functional elements [6–10].

There are some important applications of CNT- and GNR-based interfaces with other materials for novel nanosensor devices. Usually, these devices are considered as integrated devices around 10–50 nm in size. The fundamental electron devices are field-effect transistors (FETs), which are very sensitive to various external influences of different nature such as mechanical, chemical, electrical, magnetic, etc. [5].

Variants of nanosensor realizations using FET-type nanodevices are presented in Fig. 6.3.

Source–drain current via gate voltage of typical CNT-based FET and GNR-based FET nanodevices is a monotonally growing function and sensitive on CNT or

GNR electrical properties and morphologies. Electrical properties of CNT and GNR are sensitive to the effects of various external influences, including mechanical, electromagnetic, chemical and biochemical factors, which induce charge transfer changes.

6.1.2 Nanosensing Paradigm

A sensor represents a device or instrument that converts a physical, chemical or biochemical stimulus into a quantity measurable form. The stimulus can be expressed in different ways. A physical phenomenon, presented in the absence of certain material, can perturb some environment, and the mentioned perturbation must be received in ‘understandable’ form for data acquisition system (DAS).

As a rule, converters of different stimuli are constructed using the generalized scheme shown in Fig. 6.4. A flow of photons or particles must be directed to the sensor (in some cases using certain optics equipment for the flow concentration purposes), and a sensor gives the response understandable for the DAS. The presented chart demonstrates macro- and microconverters.

A nanosensor (NS) represents a device working at the nanoscale space by means of previously described principles. The main task of a nanosensor is to recognize the presence of nanoparticles (nanospheres of nanoscale diameter, the size order of 10^{-9} m) and to create physical stimuli for translating to the macroscopic world (technically, to the data acquisition system).

In general, nanoparticles in the macroscopic world can drive the same surrounding information in comparison with macroactions. However, a miniaturization of devices or sensors increases the functionality and specificity and decreases the operating power. Such significant factors allow expanding the application area in biology: quantitative measurements in intracellular surrounding by negligible physical perturbation of the cell. In addition, the sensitivity of nanosensors can be in higher orders because of the insignificant resistance in electrical circuits.

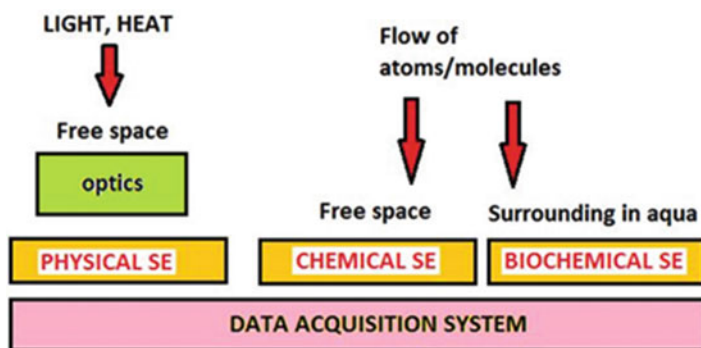


Fig. 6.4 Physical, chemical and biochemical sensors

An additional term *nanosensory point* is related to the nanosphere recognition. Three phenomena are important for the use of nanosensors: (1) small quantities of a sample could be recognized and analysed; (2) the physical limit of detection should be very low; and (3) in many cases, an intermediate reagent for detection is unnecessary (direct detection is possible). Nanosensors can be integrated into a practical macro device to continuously present the important current information on the chemical or biochemical parameters.

Another aspect of utilizing nanosensors is related to the surface/volume ratio (S/V) phenomena. When the size of a structure (atomic, molecular, macromolecular, cluster, polycrystalline, etc.) decreases, the surface/volume ratio increases significantly. Two models – cubic and spherical – are available as the first approach models. For example, Table 6.1 represents the comparison of parameters related to the volume and surface.

Decreasing the cube edge from 3 to 1 (in arbitrary units), the surface/volume ratio increases from 2 to 6. For a spherical particle, the surface/volume ratio increases from 1 to 3 when the sphere radius decreases from 3 to 1. This example illustrates the influence of the nanosensor driving reactivity on the particle size. For practical purposes, a small nanosensor size realizes a fast reaction rate (according to the Arrhenius equation for a chemical reaction) – ensures fast information readout (physical measurement).

According to that, the surface phenomena (physisorption) start to predominate over the chemistry (bonding). In that case, particles display new energetic properties related to the size.

Nanorobots represent a separate class of nanosensors (NS) working in an autonomic regime. Table 6.2 represents a classification of nanosensors according to the recognition type. According to the stimulus recognition process, nanosensors can be divided into two groups: (1) NS with transducing mechanism and (2) NS with recognition mechanism.

In NS with a transducing mechanism, many processes in different areas of physics and chemistry can be involved: electrochemical (potentiometric, amperometric, ion conducting, etc.), optical (absorption, fluorescence, phosphorescence, polarization) and mass detection (acoustic wave). Practically, all sensors with

Table 6.1 Cubic and spherical models of nanoparticle

Cube edge (arbitrary units)	$a = 3$	$a = 2$	$a = 1$
Sides (a)	3	2	1
Surface ($S = 6a^2$)	$6 \cdot 3^2 = 54$	$6 \cdot 2^2 = 24$	$6 \cdot 1^2 = 6$
Volume ($V = a^3$)	$3^3 = 27$	$2^3 = 8$	$1^3 = 1$
$S/V = 6/a$	2	3	6
Sphere radius (arbitrary units)	$r = 3$	$r = 2$	$r = 1$
Radius (r)	3	2	1
Surface ($S = 4\pi r^2$)	$4\pi \cdot 3^2 = 113.09$	$4\pi \cdot 2^2 = 50.24$	$4\pi \cdot 1^2 = 12.57$
Volume ($V = 1.33\pi r^3$)	$1.33\pi \cdot 3^3 = 113.09$	$1.33\pi \cdot 2^3 = 33.51$	$1.33\pi \cdot 1^3 = 4.19$
$S/V = 3/r$	1	1.5	3

Table 6.2 Classification of nanosensors (NS) according to recognition type

Physical NS	Chemical NS	Biochemical NS
Displacement (size)	Atoms	Enzymatic interaction
Force (pressure)	Molecules	DNA interaction
Mass	Cations/anions	Tracers
Charge	Species	Antibody/antigen
Optical	Specificity	Cytotoxicity
Thermal	pH	Vitamins
		Cell/tissue

transducing mechanism where mentioned processes are used belong to the group of physical NS.

In NS with a recognition mechanism, several sensitive processes from analytical chemistry (ion vaporization, volatile gases), biochemistry (DNA, enzymatic interaction, antibody/antigen) and macromolecular chemistry (cell/tissue recognition, vitamin recognition, cytotoxicity) are involved. Practically, all sensors with a recognition mechanism where mentioned processes are used belong to the group of chemical and biochemical NS.

Current NS devices are divided into two groups: nanocrystalline NS and nanostructured NS. Nanostructured NS are also divided into two groups: (1) polymer-based, such as pigment-conjugated, drug-conjugated dendrimers, micelles and nanoparticles, and (2) nonpolymer-based such as silica nanoparticles, classical porous silicon, metallic nanoparticles, single-walled and multiwalled carbon nanotubes, nanowires, nanoprobe and quantum dots. To manufacture nanosensors, three different technologies are possible: molecular self-assembly, bottom-up assembly and top-down lithography.

Hierold et al. [11] presented a very complete review of sensors at the nanoscale including device concepts, functional properties and realization type. Written in 2005, this review has not lost its importance nowadays. Nano-electromechanical sensors based on carbon nanotubes (CNTs) are described as multipurpose devices.

Nanosensing as a paradigm started at the end of the twentieth century with the recent development of micro- and nanotechnologies. Mechanical, optical, fibre optical and nanoelectrode-based nanosensors are known from the 1990s. Fullerenes, nanocrystal and quantum dot-based nanosensors start to pervade from the 2000s. For biological experiments *in vivo*, new types of nanosensors such as DNA-based nanosensors and nanogap nanoparticles have been introduced purposefully.

6.2 Physical Nanosensors

Physical nanosensors aim to recognize a certain motion (kinematical translation or rotation, changes of pressure, wave, etc.) as well as a certain radiation and to generate a specific output signal. A certain motion can be flow based, diffusion

based, walkway based, etc. Electromagnetic radiation (gamma, X-ray, UV, visible, IR) can be recognized according to the standard procedure of interactions between light and material.

Here, a prototype of physical nanosensor will be demonstrated from the initial idea till the molecular realization.

After significant achievements in solid-state physics, molecular electronics started developing in 1970s. The possibility to use low-cost mass production of molecular devices that are suitable for light conversion, catalysis of chemical reactions and drug/medication synthesis stimulated a rapid growth of molecular electronics and utilization of molecular devices.

With the development of lasers operating in near IR region (invisible for human eyes), the problem of creating a light sensor was quite serious. Solid-state crystalline detectors were manufactured to detect a sufficiently high flux density. An idea to use sensitive sensors for the detection of near IR radiation build-up by a polar molecular compound arises from multitasking experiments in chemical physics. Figure 6.5 represents a prototype of a physical sensor able to make the conversion from near IR to visible. For such a task, a polar molecular compound of the extreme stability with the well-expressed π -conjugated system must be found.

DMABI. Figure 6.6 represents N,N-dimethylamine benzylidene indan-1,3-dione (DMABI) as the prototype of a physical sensor. Two polar fragments, namely, indandione and diamino phenyl derivatives, are connected via the $[>C = CH-]$ bridge. The π -conjugated system is displaced along the long molecular axis. According to crystallographic studies [12], the DMABI molecule is practically flat. According to quantum chemical studies [13–15], the DMABI molecule is flat in the ground electronic state and twisted through the mentioned $[>C = CH-]$ junction in the excited electronic state.

Fig. 6.5 Physical sensor:
near IR conversion to
visible

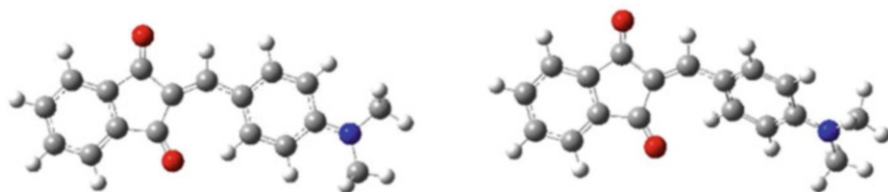
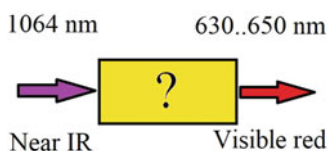


Fig. 6.6 Prototype of physical sensor: N,N-dimethylamine benzylidene indan-1,3-dione (DMABI). Plane structure (*left* conformation) and twisted by $[C-C]$ junction structure (*right* conformation)

As polar molecular compounds, DMABI crystalline derivatives (α , β , γ) exhibit the red fluorescence at 610÷680 nm spectral region by the excitation into molecular absorption band at 488 nm wavelength (typical autolocalized excitons) and also by the excitation at 1064 nm wavelength (anti-Stokes luminescence), with the typical time 8÷15 ns [16, 17]. A luminescence of DMABI dissolved in different solvents and DMABI deposited as crystalline films as well as Langmuir–Blodgett (LB) molecular films differs significantly [18, 19]. Stokes shift for DMABI dissolved in different solvents is equal to 30÷50 nm.

According to the quantum chemistry simulations (DMABI in flat conformation), an electronic charge redistribution was established for [HOMO] $\rightarrow$ [LUMO] allowable transition (see Fig. 6.7 – from ground to first excited electronic state) and for [HOMO-1] $\rightarrow$ [LU-MO + 1] forbidden transition (see Fig. 6.8 – from ground to second excited electronic state). Such two transitions represent the population of two spectroscopic states (first and second). For both transitions, an interfragmental charge redistribution takes place. Pure $\pi \rightarrow \pi^*$ -type transition is allowed along the long molecular axis in flat conformation. This conformation is typical for crystalline modifications and polycrystalline films (strong ordered derivatives). Otherwise, in twisting conformation, two types of transitions – $\pi \rightarrow \pi^*$ type and $n \rightarrow \pi^*$ type – are mixed. A twisted conformation is allowed for LB films and solutions in the excited electronic state (non-ordered derivatives).

The indandione fragment contains two carbonyl [$>C=O$] fragments, which are the sources of two pairs of n -electron. Also, the benzylidene fragment contains dimethylamino [$-N(CH_3)_2$] group, which is the sources of one pair of n -electron. For the electronic charge redistribution process, when the second excited electronic

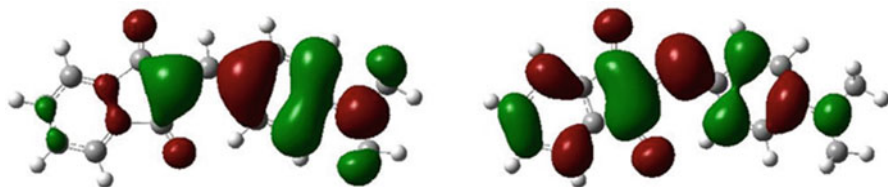


Fig. 6.7 DMABI: ground and first excited electronic states. Electronic charge redistribution for [HOMO] $\rightarrow$ [LUMO] transition

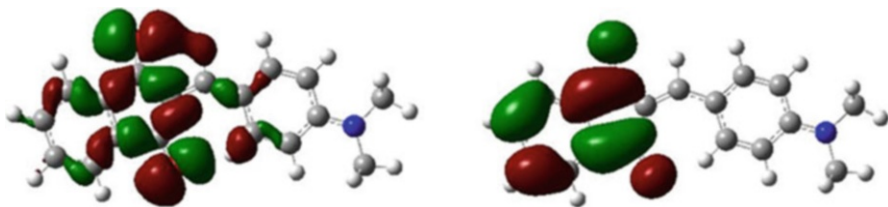
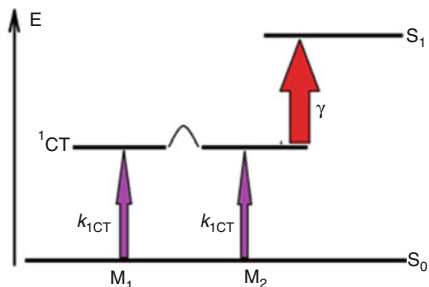


Fig. 6.8 DMABI: ground and second excited electronic states. Electronic charge redistribution for [HOMO-1] $\rightarrow$ [LUMO + 1] transition

Fig. 6.9 DMABI: energy diagram of CT exciton interaction model



state is populated, a charge redistribution is localized in the indandione fragment ($n \rightarrow \pi^*$ transition is significant). Unfortunately, a transition of this type is forbidden for flat configuration. For a twisted configuration, a transition of $n \rightarrow \pi^*$ type is partially allowed. In that case, n -electrons of carbonyls from indandione fragments take place in the charge redistribution process.

Generally, for a flat conformation, $\pi \rightarrow \pi^*$ transition is allowed, but $n \rightarrow \pi^*$ transition is forbidden. For a twisted conformation, $\pi \rightarrow \pi^*$ transition is partially allowed, and $n \rightarrow \pi^*$ transition is also partially allowed. A behaviour of two types charge redistribution allows receiving a spectral information related to the surroundings viscosity, polarity, etc.

Anti-Stokes red luminescence of strong ordered (crystalline) derivatives of DMABI shows quadratic dependence on the excitation intensity. At high excitation intensities, quadratic dependence changes to linear one. Figure 6.9 represents the energy diagram of CT exciton interaction model. Excitation of DMABI by IR quantum (1064 nm wavelength) means that population of ^1CT energy level (M_1 and M_2 molecular derivatives) takes place. The mentioned excitation is too low to populate S_1 state.

The suggested bimolecular reaction can be explained as ^1CT singlet-singlet annihilation reaction rate constant γ :



For bimolecular reaction, two kinetic equations are useful to describe the population of ^1CT and S_1 energy levels:

$$\frac{dn_{\text{CT}}}{dt} = I - k_1 n_{\text{CT}} - \gamma n_{\text{CT}}^2, \quad (6.2)$$

$$\frac{dn_S}{dt} = \gamma n_{\text{CT}}^2 - k_S n_S, \quad (6.3)$$

where the intensity of IR laser pulse is denoted as I , k_1 represents the linear decay constant of ^1CT state and n_{CT} and n_S represent population densities of ^1CT and S_1 states. The solutions of differential equations Eq. (6.2) and Eq. (6.3) are presented below:

$$n_{\text{CT}} = \frac{I}{k_1}, \quad (6.4)$$

$$n_S = \frac{\gamma I^2}{k_S k_1^2} = \frac{I}{k_S} \frac{\gamma I}{k_1^2}. \quad (6.5)$$

Now it is necessary to estimate the intensity. In case of:

$$\frac{\gamma I}{k_1^2} \gg 1, \quad (6.6)$$

$$I \gg \frac{k_1^2}{\gamma}, \quad (6.7)$$

$$\frac{\gamma I}{k_1^2} \ll 1, \quad (6.8)$$

$$I \ll \frac{k_1^2}{\gamma}, \quad (6.9)$$

and the expression of population density of S state n_S according to Eq. (6.4) becomes shorter:

$$n_{\text{CT}} = \frac{I}{k_1} \approx \sqrt{\frac{I}{\gamma}}. \quad (6.10)$$

Equation (6.10) shows the possibility to switch the quadratic dependence to linear one and in case of:

$$\frac{\gamma I}{k_1^2} = 1, \quad (6.11)$$

$$n_S = \frac{I}{k_S} \frac{\gamma I}{k_1^2} \approx \frac{I}{k_S}. \quad (6.12)$$

The value γ was estimated of the order of $10^{12} \text{ cm}^3 \cdot \text{s}^{-1}$, which is a typical value for excimer–excimer annihilation rate constant in organic molecular crystals.

The origin of ^1CT state is related to the exciton–phonon interaction. The analysis of vibrational spectra of different DMABI derivatives [17] allows the estimating behaviour of fragmental motion: symmetric stretch $[\text{C} = \text{O}]$ at 1698 cm^{-1} , skeletal scissoring of indandione and benzylidene fragments at 612 cm^{-1} and ring stretch deformation of benzylidene at 1663 cm^{-1} . The mentioned vibrations are responsible for the occurrence of ^1CT state, related with the charge separation in fragments. The occurrence of ^1CT state is related to the charge redistribution during fragmental motion. In the case of symmetric stretch $[\text{C} = \text{O}]$, the $n \rightarrow \pi^*$ -type charge redistribution in carbonyl fragment takes place. In the case of skeletal scissoring of indandione and benzylidene fragments, the $\pi \rightarrow \pi^*$ -type charge redistribution along the long molecular axis can be observed. The origin of self-trapped excitons was discussed in [19–21]. A detection limit of material can be established in order of $100 \text{ } \mu\text{m}$.

Fig. 6.10 Prototype of physical sensor: indan-1,3-dione pyridine betaine (IPB). Plane structure

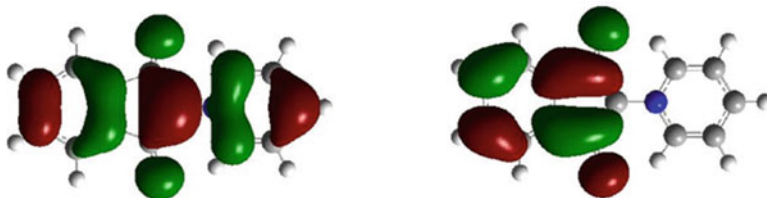
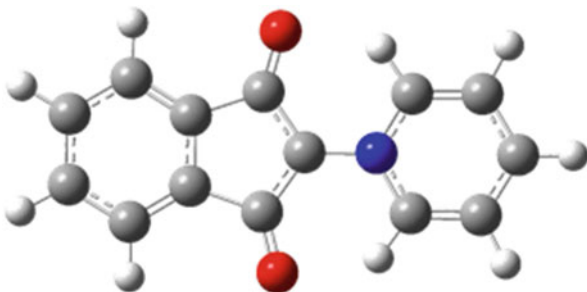


Fig. 6.11 IPB: electronic charge redistribution for $[HOMO] \rightarrow [LUMO + 1]$ transition, belonging to ground and first excited electronic states, respectively

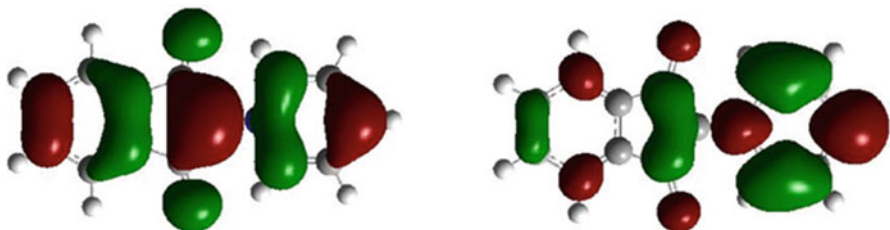


Fig. 6.12 IPB: electronic charge redistribution for $[HOMO] \rightarrow [LUMO]$ transition, belonging to ground and second excited electronic states, respectively

IPB. Another prototype of molecular sensor can be realized using the polar molecular compound indan-1,3-dione pyridine betaine (IPB), presented in Fig. 6.10. IPB consists of two fragments – indan-1,3-dione and pyridine betaine – connected via $[>C-N<]$ bridge. Both fragments are presented in plane surface, and this conformation is typical for ground and excited states.

According to quantum chemistry simulations [22] (IPB in flat conformation), an electronic charge redistribution has been established for $[HOMO] \rightarrow [LUMO + 1]$ forbidden transition (see Fig. 6.11 – from ground to first excited electronic state) and for $[HOMO] \rightarrow [LUMO]$ allowable transition (see Fig. 6.12 – from ground to second excited electronic states).

Such two transitions represent the population of two spectroscopic states (the first and second). For both transitions, an interfragmental charge redistribution

takes place. The pure $\pi \rightarrow \pi^*$ -type transition is allowed along the long molecular axis in flat conformation. This conformation is typical for crystalline modifications, polycrystalline films and LB films and solutions. The interfragmental twist is forbidden.

Unique properties of IPB derivatives are related to dipole moment phenomena. Dipole moments of a molecule in the ground state and first excited state are equal to (+3.7) D and (−4.5) D, respectively. After excitation, the direction of the change in the dipole moment is opposite [22]. This circumstance is very important for the surface manipulation purposes, when a fabrication of layers through a self-organizing procedure occurs. Analysing the charge redistribution between the ground and first excited electronic states, it is easy to recognize the important asymmetry: the excited state is populated after the charge redistribution to the local indandione fragment.

As in the case of DMABI, the analysis of vibrational spectra of different IPB derivatives [23] allows estimating a behaviour of the fragmental motion: out of plane skeleton bend 151 cm^{-1} , interfragmental stretch 305 cm^{-1} and in-plane skeleton bend 146 cm^{-1} .

From the chemical point of view, the IPB molecule and molecular derivatives including films, the Langmuir–Blodgett films, and molecular crystals are less stable in comparison with DMABI. The origin of self-trapped excitons has been discussed in [24].

Carbazole: Fluorene Compounds. Carbazole and fluorene compounds play a very important role in molecular electronics due to such circumstances: they are mechanically flexible, chemically stable at room temperature and electronically well π -conjugated. Carbazole as a tricyclic structure consists of nitrogen-containing pentaring and two six-membered benzene rings and belongs to the basic materials for the dye industry. Fluorene as a tricyclic structure consists of one pentaring and two six-membered benzene rings and belongs to a series of precursors in pharmaceutical industry.

Figure 6.13 represents carbazole and fluorene structures. Molecular substitutes in positions 2 or 3 represent a possibility to drive the velocity of charge redistribution. A population of excited state for 2,7- and 3,6-substituted carbazole derivatives and simulations using quantum chemistry methods shows the overlap of different

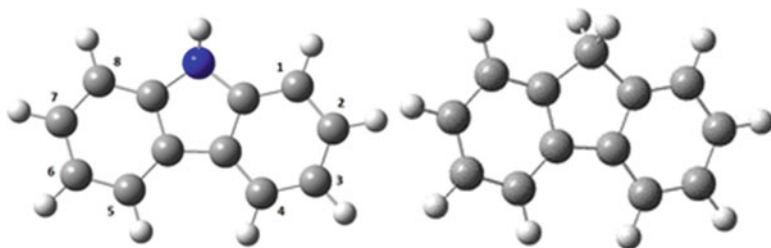


Fig. 6.13 Carbazole and fluorene compounds

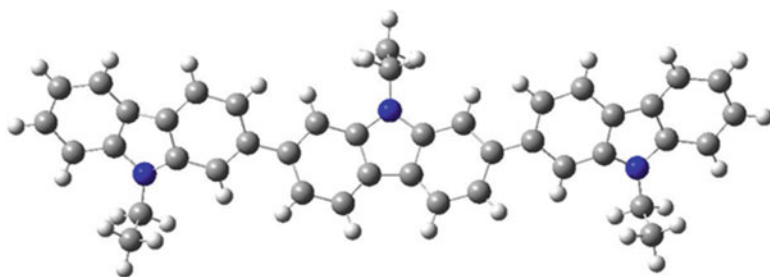
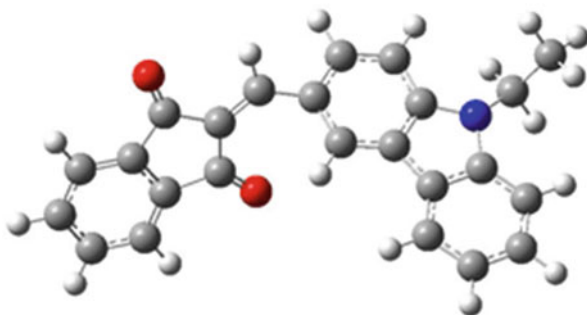


Fig. 6.14 Triad formed from carbazoles connected in 2–7 positions

Fig. 6.15 Indandione-1,3-carbazole compound



types of wave functions. For 3,6-substituted compounds, a partial charge localization in 3,6-bicarbazole core takes place; otherwise, for 2,7-substituted compounds, charge delocalization along the long axis is realized.

Baronas et al. [25] described the investigations of carbazole, namely, fluorene tetrads created using bicarbazole core with carbazole substitutes in 3–6 positions:

2-(9,9-diethyl-fluoren-2-yl)-6-[7-(9,9-diethylfluoren-2-yl)-9-(2-ethylhexyl)-3,4-dihydrocarbazol-3-yl]-9-(2-ethylhexyl) carbazole. A potential host material exhibits a large hole drift mobility (up to $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in the solution processed amorphous films.

Tomkeviciene et al. [26] studied 2-, 2,7-substituted carbazole dimers and trimers as charge carrier transport materials. Triad of carbazoles with connections in 2–7 positions is presented in Fig. 6.14. 2,7-Di(9-carbazolyl)-9-(2-ethylhexyl) carbazole was found to show very high electron mobility ($\mu_e = 2 \cdot 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at an electric field of $1.8 \cdot 10^5 \text{ V cm}^{-1}$) and reasonably high hole mobility ($\mu_h = 8 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at an electric field of $1.8 \cdot 10^5 \text{ V cm}^{-1}$). Dihedral angle between different carbazoles is equal to $\approx 40^\circ$. Pyrene-substituted and naphthalimide-substituted fluorene and carbazole derivatives [27, 28] also express a low-energy barrier for intramolecular twisting in the ground and excited states.

Karpicz et al. [15] investigated indan-1,3-dione and carbazole-based (IDC) compounds with single and four covalently connected chromophores (see Fig. 6.15). An intramolecular charge distribution takes place. Two types of charge

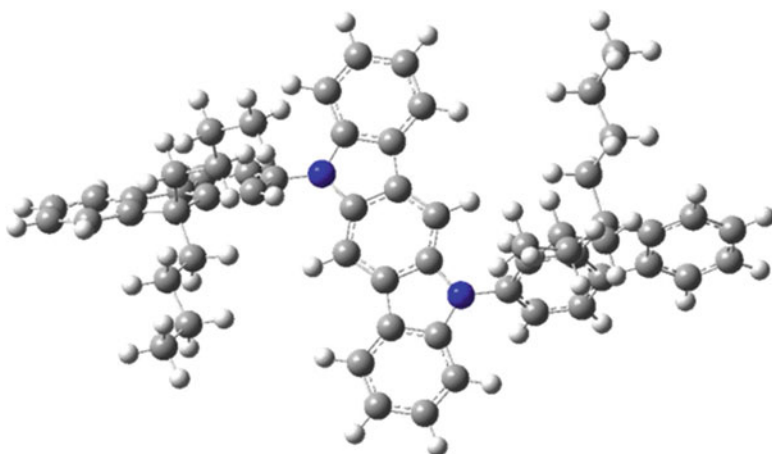


Fig. 6.16 Indolocarbazole derivative NN3

distribution ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$) also are observed. Carbonyl fragments of indandione fragments are sources of n -type electrons, and carbazole fragments are acceptors.

Due to the molecule twisting, opening transitions to $n \rightarrow \pi^*$ states, IDC chromophores in solutions express the ultra-fast excited state relaxation (time constant of about 2 ps, in solids and films, and about 300 ps in solid films).

Strečkaite et al. [29] studied the indole [3,2-b] carbazole derivatives. Figure 6.16 represents 5,11-bis(9-butyl-9H-carbazol-3-yl)-6-pentyl-5,11-dihydro-indolo[3,2-b] carbazole – NN3. Conformational motions of the substituents in solutions have been found to cause a significant acceleration of the non-radiative excited state relaxation.

Figure 6.17 represents the maps of electronic charge redistribution related to the transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$. The population of spectroscopic state S_1 is related to the allowed [HOMO] $\rightarrow$ [LUMO] transition, while charge redistribution is localized in indole core.

Otherwise, a population of spectroscopic state S_2 is related to the partially forbidden [HOMO-1] $\rightarrow$ [LUMO + 1] transition, when a charge redistribution is delocalized from the indole core to carbonyl substitutes. A similar effect is presented for fluorene substitutes. According to this mechanism, substituents influence the radiative relaxation rates.

Figure 6.18 represents the total energy distributions of NN3 on reaction parameter φ , namely, the orientation dihedral angle between indole core and carbazole substitute.

The ground state S_0 , first and second excited states S_1 and S_2 dependence contain minima at different φ value: for S_0 , 75° , and for S_1 and for S_2 , 50° . Transition $S_0 \rightarrow S_1$ is allowed: value of oscillator strength is quite high, about 0.1, but transition $S_0 \rightarrow S_2$ is partially forbidden. It means that the absorption $S_0 \rightarrow S_2$ is

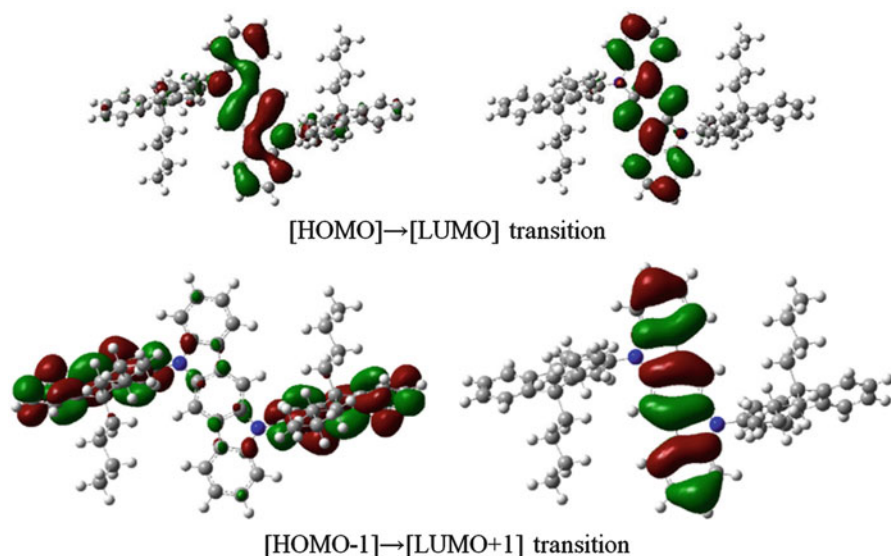


Fig. 6.17 Indolocarbazole derivative NN3. Maps of electronic charge redistribution related to the transitions $S_0 \rightarrow S_1$ (top) and $S_0 \rightarrow S_2$ (bottom)

related to the population of S_1 state using internal conversion processes. The absorption occurs from the twisted configuration ($\varphi = 75^\circ$). After excitation, the planarity of the molecule increases ($\varphi \rightarrow 50^\circ$).

A twist to a more planar conformation may cause an acceleration of the non-radiative relaxation. A twist to the pure planar position ($\varphi \rightarrow 0^\circ$) is forbidden due to the rotational barrier >0.2 eV. The green rectangle describes an energetically limited twist motion of carbazole-substituted groups in the range of $45 \div 75^\circ$.

Rimkus et al. [30] investigated spatial carbazole-type structures as a charge transport material. Figure 6.19 represents the structure of 8-alkyl-6,10-disubstituted 8H-16,17-epoxydinaphtho[2,3- c:2,3-g] carbazoles (EDNC).

The V-shape geometry (meaning a broke planar structure) through bridging fragments of nitrogen, sulphur and oxygen heteroatom produces the extended π -electron system. Also, an alteration of the molecular structure with conjugated or nonconjugated side groups enables the tuning of ionization potential from 4.7 to 5.5 eV. This ensures hole drift mobility for thick films up to $8 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 1 MV cm^{-1} .

Physical nanosensors are nanoscale devices, which are able to control masses of small particles, local pressure, force and temperature changes. Usually, schemes of these devices are based on the corresponding electric responses.

FET-Based Nanosensors. Physical nanosensors are used to measure magnitudes such as mass, pressure, force or displacement. The working principle is usually based on the fact that the electronic properties of both nanotubes and nanoribbons

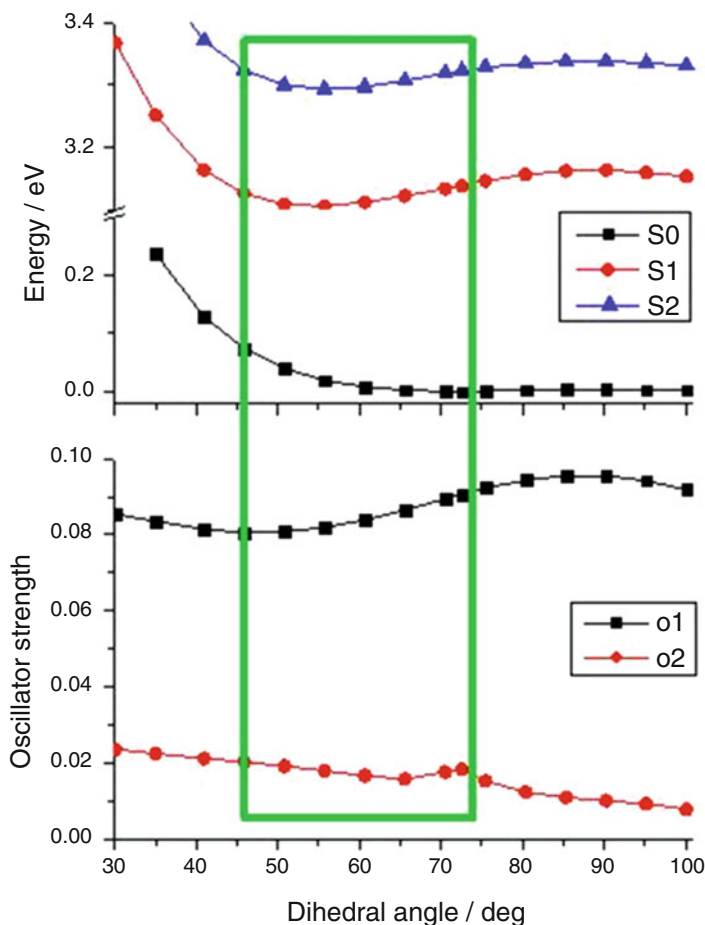


Fig. 6.18 Diagrams of total energy distributions of indolocarbazole derivative NN3. Ground state S_0 and the first and second excited states S_1 and S_2 dependence on orientation dihedral angle φ between indole core and carbazole substitute (*top*). The oscillator strength O_1 and O_2 dependence on orientation dihedral angle φ (*bottom*). Green rectangle describes energetically limited twist motion (in range 45° – 75°)

change when these are bent or deformed. For example, CNTs (or GNRs) can be used to build a field-effect transistor (FET) nano in size, whose on/off threshold depends on the tube dimensions, shape and temperature, among others. A local deformation of the tube/ribbon creates a change in the on/off threshold voltage of the transistor (see Fig. 6.20 and [5]).

Starting from this simple principle, different types of nano-electromechanical systems (NEMSs) have been proposed in the literature with different applications, such as pressure nanosensors [31], force nanosensors [32] or displacement nanosensors [33].

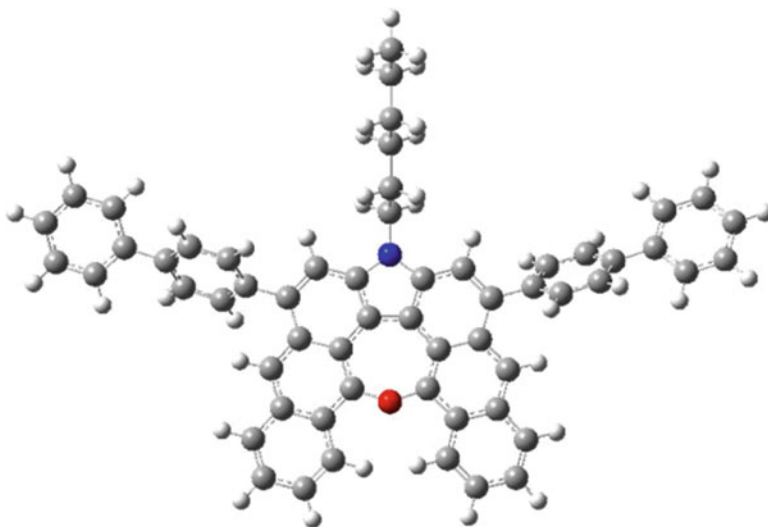


Fig. 6.19 8-alkyl-6,10-disubstituted 8H-16,17-epoxydinaphtho[2,3-c:2,3-g] carbazoles (EDNC)

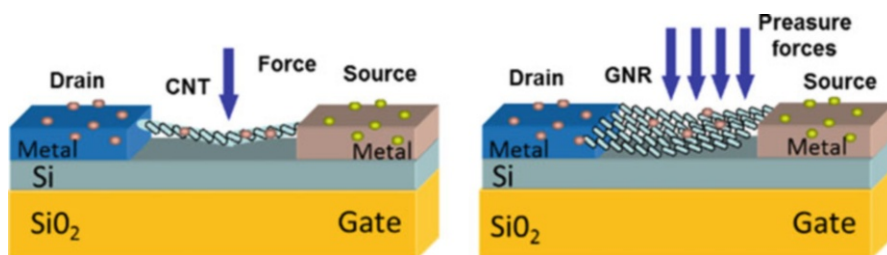


Fig. 6.20 Physical nanosensors: a conducting threshold can be altered when the tube (CNT) or graphene ribbon (GNR) is bent

6.3 Chemical Nanosensors

Chemical nanosensors are aimed at recognizing the unknown species of substances, for example, gaseous or liquid. The composition, concentration and presence of certain elements through the partial pressure in the form of chemical information should be generated and converted to a signal of another type (electrical, light, etc.). Different types of gases, including NO, NO₂, CO, explosive gases H₂, NH₃, etc., are objects of recognition in the well-known project – the *electronic nose*.

Figure 6.21 represents a principal scheme of a chemical sensor. Two components (a recognition system as a receptor and an electronic system as a transducer) represent a chemical sensor. Requirements for chemical sensors are the following: (1) direct contact with analytes, (2) transformation of chemical (non-electric) information into electric one and (3) quick response without any delay.

Fig. 6.21 Principal scheme of a chemical sensor: (1) chamber containing sensors, (2) layered receptor coating system and (3) transducer

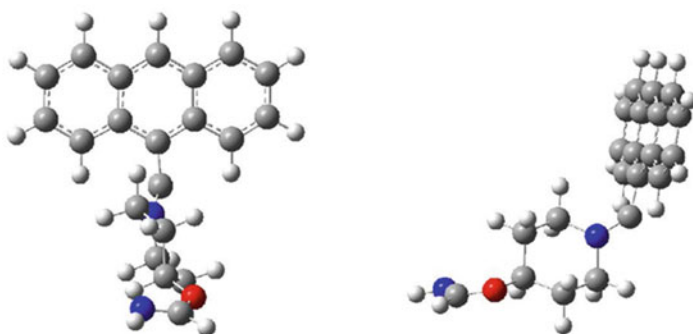
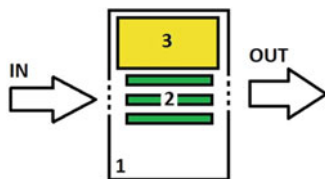


Fig. 6.22 Anthracene derivatives. Two projections

Molecular analytes such as explosive gases or poison gases must be pumped at the certain pressure through a chamber, containing sensor receptors (arrays IN and OUT). A layered receptor coating system must be selected according to the task. A layer of receptor can be manufactured for the selective respond to particular substances (analytes) or also to series of analytes. Metal lattice (Pd, Au, Ni, etc.) as well as polymer surface (poly-epoxy-propyl-X) changes its own properties after a physical contact to analytes. Main interaction processes useful for practical purposes are liquid–liquid extraction, ion exchange and surface adsorption.

Nowadays, transducers operate as amplifiers of an electric signal to a readable one. A response will be made by a transducer as a change of capacitance, conductance, light intensity, etc. Selectivity and sensitivity of the mentioned technique are distinguished on demand.

Sensors based on the photo-induced electron transfer (PET) effect are well known in photochemistry, physiology and medicine. De Silva et al. [34] observed basic principles of PET sensors when luminescence and PET effects are mixed together. A single-point receptor can be connected to a catalytically active peptide. Figure 6.22 represents a derivative constructed as a monoamine which is selective to a presence of protons in bonding distance [34].

The most sensitive materials for detection purposes are single-walled carbon nanotubes (SWCNT). Collins et al. [35] found a low barrier for detection of NO₂ (200 ppm). Chopra et al. [36] investigated selectivity of SWCNT for O₂, Ar and N₂, and a low barrier at 100 ppm has been distinguished (*ppm* parts per million).

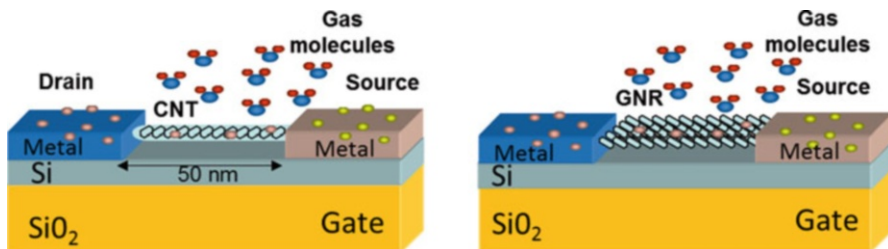


Fig. 6.23 Chemical nanosensors: a conducting threshold can be altered when the amount of free charges on the tube of graphene ribbon surface is increased or decreased by the presence of donor or acceptor molecules of specific gases or composites

Multiwalled carbon nanotubes (MWCNTs) in comparison with SWCNT show a lower barrier due to topological properties. Suehiro et al. [37] reported a detection of ammonia NH_3 of concentrations of 10 ppm.

FET-Based Nanosensors. Chemical nanosensors are used to measure magnitudes such as the concentration of a particular gas, the presence of a specific type of molecule or the molecular composition of a substance. The functioning of the most common type of chemical nanosensors is based on the fact that the electronic properties of CNTs and GNRs change when different types of molecules are adsorbed on their top, which locally increases or decreases the number of electrons able to move through the carbon lattice (see Fig. 6.23 and [5]).

Similarly to physical sensors, the presence of a specific type of molecules changes the on/off threshold voltage of the transistor when a nanotube or a nanoribbon is used in a transistor configuration. Various gas sensors based on nanotubes have been reported in the past few years. Modi et al. have developed a miniaturized gas ionization detector based on CNTs [38]. The sensor can be used in gas chromatography. Titania nanotubes have been incorporated in a wireless sensor network to detect hydrogen concentrations in the atmosphere [39]. Kong et al. have developed a chemical sensor based on nanotube molecular wires for the detection of gaseous molecules such as NO_2 and NH_3 in the environment [40].

6.4 Bio-nanosensors

Usually biosensors are constructed using three component schema:

$$\text{Bioreceptor} \rightarrow \text{transducer} \rightarrow \text{detector}. \quad (6.13)$$

A bioreceptor is an active biological structure (enzyme, NA, cell, etc.) which interacts directly to certain chemical component or virus. If a physical contact occurs, the bioreceptor generates a response signal, which through a transducer excites a detector in order to create the measurable signal (in electric circuit).

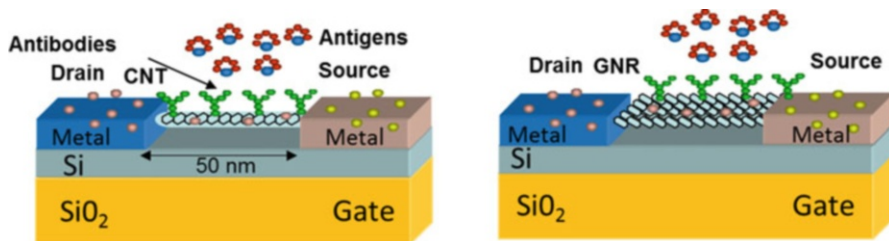


Fig. 6.24 *Biological nanosensors*: monitoring of biomolecular processes such as antibody/antigen interactions, DNA interactions, enzymatic interactions or cellular communication processes, among others

Biosensors for measuring glucose in blood represent about 90% of global market. Possibility of such detection is organized using glucose dehydrogenase also glucose oxidase [41]. Some enzyme categories are useful for determined functions, for example, ligases, for joining of two molecules; isomerases, for intramolecular rearrangement; and transferases, for intermolecular transfer motion of molecular groups.

Barone et al. [42] reported a usage of single-walled carbon nanotube (SWNT) for beta-D-glucose recognition in strongly absorbing media. Two different mechanisms of signal transduction (fluorescence and charge transfer) have been used. Results demonstrate new opportunities for nanoparticle optical sensors.

Das et al. [43] presented the study of affinity-based biosensors in the framework of scaling laws. Several parameters of physical importance (implications of scaling on the response time, signal-to-noise ratio and dynamic range of biosensor) were analysed using stochastic differential methods and particularly Fokker–Planck equation. Authors claim that scaling down significantly reduces the achievable signal-to-noise ratio and dynamic range of biosensors (miniaturization phenomenon takes place).

FET-Based Biological Nanosensors. Biological nanosensors are used to monitor biomolecular processes such as antibody/antigen interactions, DNA interactions, enzymatic interactions or cellular communication processes, among others (Fig. 6.24 and [5]). A biological nanosensor is usually composed of (1) a biological recognition system or bioreceptor, such as an antibody, an enzyme, a protein or a DNA strain, and (2) a transduction mechanism, e.g. an electrochemical detector, an optical transducer or an amperometric, voltaic or magnetic detector [44].

Electrochemical biological sensors work in a similar way as chemical nanosensors, but in this case, the change might be in the electronic properties of a protein, for example, or of any other chemical composite that binds itself to the functionalized nanotube. A specific antigen that binds itself to an antibody stuck to the nanotube. A single-stranded DNA chain binds itself to another DNA chain, which has been attached to the nanotube [45]. There are commercial nanosensors based on this principle. They are able to detect lung cancer, asthma attacks,

different common viruses such as the influenza virus or the parasites responsible for malaria [46].

The second subtype of biological nanosensors is based on the use of noble metal nanoparticles and the excitation using optical waves of surface plasmons, i.e. coherent electron waves at the interfaces between these particles. Simply stated, the resonant frequency of the surface plasmons, resulting from light irradiation, changes when different materials are adsorbed on and in between the particles. This technique, known as localized surface plasmon resonance (LSPR), is the underlying principle behind many biological nanosensors [47].

Polymer Ion Track-Based Bio-nanosensors Since 1960s, it has been known that energetic (with tens of MeV or more) heavy (with atomic masses being usually larger than that of Ar) ion irradiation ('swift heavy ions', SHI) introduces very narrow (~ some nm) but long (typically 10–100 μm) parallel trails of damage in irradiated polymer foils, the so-called latent ion tracks. The damage shows up primarily by the formation of radiochemical reaction products. Whereas the smaller ones readily escape from the irradiated zone, thus leaving behind themselves nanoscopic voids, the larger ones tend to aggregate towards carbonaceous clusters. Thus, emerging structural disorder along the tracks modifies their electronic behaviour.

In particular, a complicated biochemical kinetics of basic reaction of glucose detection depends on track qualities (e.g. track creation mechanism, foil material properties), enzyme (GOx) distribution on the track surface, geometry of the etched track, etc. All these factors are the subject for the nearest special research. Moreover, the detailed kinetics of reaction is the object of 3D modelling to design the optimal geometry of nanosensor active space. This allows creating optimal nanosensors with the increased efficiency.

The newly created intrinsic free volume enables electrolytes to penetrate into the polymer, thus forming parallel liquid nanowires. In case of tracks penetration through all the foil, the conducting connections emerge between the front and back sides of the foil. The ion track technology is particularly intended to biosensing applications. In this case, the ion tracks are functionalized directly by attaching organic or bioactive compounds (such as enzymes) to their walls [48–51].

6.5 Memory Nanodevices

Memory could be defined as an equipment or device for storing a certain amount of information for retrieving purposes. This task physically must be realized by a storing of the system state. A realization of memory can be very different: mechanical, electromagnetic, etc. There are four basic groups of memory devices: resistive, ferroelectric, charge trapping and phase change. Many physical characteristics of a system such as position, capacitance, resistance and inductance can be realized for such purposes. A storing time depends on the material structure as well as of the state overload.

A macro-realization of memory is related to the rapid growth of computer implementation. Random access memory (RAM) in the form of integrated circuits plays the general role for direct access purposes. Dynamic RAM (DRAM) and older static RAM (SRAM) are constructed as the device suitable to store and retrieve the electronic state of several (from six) memory cells built up by p - n - p or n - p - n transistors (SRAM) or capacitors (DRAM). Charging and discharging of corresponding cell structures create the high-energy state and low-energy state (informational 1 and 0, TRUE and FALSE). Some sort of bistability of any parameter must be allowed for a certain system. Generally, a paradigm of bistability is typical for many dynamic systems, and the simple differential equation can illustrate the phenomena of presence of several energy states:

$$\frac{\partial z}{\partial t} = z(1 - z^2). \quad (6.14)$$

Figure 6.25 represents the illustration of bistability from the physical point of view. The distribution of the potential energy E on the reaction parameter z contains two local minima, B and C, which are separated by the energy barrier D. The solution of the mentioned Eq. (6.14) represents a triplet of states: $z = 1$, $z = -1$ (two minima, B and C, stable states) and $z = 0$ (local maximum, D, unstable state). The bistability must be realized via the macro-approach (macro-circuit) or via the micro-approach (atomic, molecular system).

For example, the Schmitt trigger as a typical model of comparator circuit in macroelectronics is used as a model system. Figure 6.26 represents the energy diagram as the output voltage V_{out} via the input voltage V_{in} .

The output voltage levels L and $-L$ represent the states for information storing (informational 1 and 0, TRUE and FALSE); the switching between states must be realized by manipulating input voltage levels S and $-S$. It means that Schmitt

Fig. 6.25 Bistable system: distribution of potential energy E on reaction parameter z . Two local minima, B and C, are separated by energy barrier D

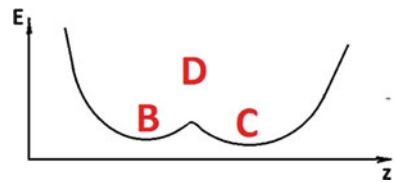
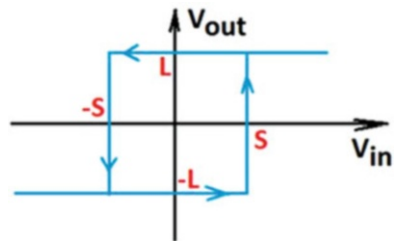


Fig. 6.26 Schmitt trigger: output voltage V_{out} dependence on input voltage V_{in} . S and L represent the voltage levels of input (switching) and output, respectively



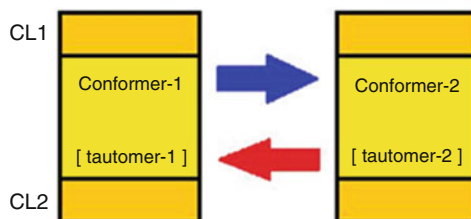


Fig. 6.27 Sandwich-type structure includes two conducting layers (CL1 and CL2) and bistable molecular structure (two conformers or two tautomers). Switching between two states occurs after external perturbation

trigger converts an analogy input signal (range from $-S$ and less until $+S$ and more) to a digital one – only L and $-L$ values without intermediates. A transfer function with a positive feedback is realized as hysteresis. It is necessary to point out that the metastable state (see Fig. 6.19, D) is not suitable for the storage realization.

Figure 6.27 represents a practical composition of sandwich-type structure, which includes two conducting layers (CL1 and CL2) and active material (solution or Langmuir–Blodgett film) consisting of bistable molecular structure (two conformers or two tautomers). A switching between two states occurs after an external perturbation of tautomers. Two tautomers when the proton transfer occurs from carbonyl the amino fragment represent one of simplest bistable systems (see Fig. 6.27). Limitations of memory in macro-realization are the following: (1) in crystalline structures, significant fluctuations of excited state relaxation time take place; (2) during operating period, significant thermal gradients occur; and (3) applications in micro- and nanosized structures (e.g. in cell biology, etc.) are not possible.

Molecular-Based Nanodevices. Bistability in a molecular system or a single molecule can be realized in a very simple way: by exciting the system from ground to the lowest excited state. In case, when the molecule contains the well-organized π -electronic system, the excitation energy is order of several eV. In the case of σ transition, this energy arises up to $\sim (5 \div 10)$ eV, and problems with the molecular stability occur. A decomposition of molecule into molecular fragments destroys the device. Also, the lowest excited state can be populated for several *ns* or *ps* only, and after that a molecule returns to the ground state. A switching of molecular behaviour (e.g. the creation of two tautomers through a proton transition, creation of two conformers by rotating two molecular fragments, etc.) realizes the idea of bistability in the ground electronic state. Two states (informational 1 and 0, TRUE and FALSE) can be realized for such a type of bistable molecule as, for example, low- and high-conductance states, respectively. A reason for reswitch could be induced by a laser pulse, by heating, by the occurrence of a redox reaction, by a mechanical deformation of a polymer, etc.

Franckevicius et al. [52] described the advanced research of the promesogenic unit containing the salicylideneimine chromophore groups. Figure 6.28 represents

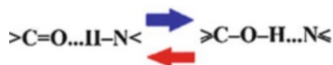


Fig. 6.28 Proton transfer motion in carbonyl-amine system

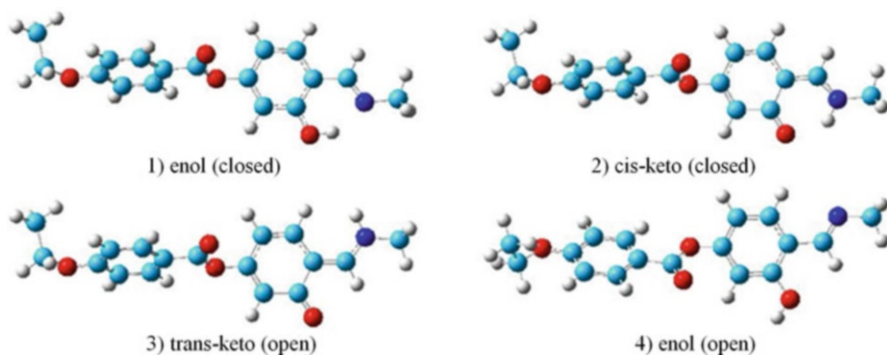


Fig. 6.29 Four tautomeric forms of 4-(4'-ethoxybenzoyloxy)salicylaldehyde chromophores

four tautomeric forms of 4-(4'-ethoxybenzoyloxy)salicylaldehyde chromophores which are the parts of PPI dendrimer chains.

Two forms – enol (1,4) and cis-keto (2,3) – can be formed by rotation about the phenyl long axis. Closed (1,2) and open (3,4) structures could be formed due to proton motion (related to oxygen or nitrogen). The closed form represents the more stable structure (of lowest total energy) due to hydrogen bonding (in enol (closed) structure [$>\text{C}-\text{O}-\text{H}\cdots\text{N}<$] and cis-keto (closed) structure [$>\text{C}=\text{O}\cdots\text{H}-\text{N}<$]) (see Fig. 6.29).

Such two circumstances predetermine the usage of the two most prominent structures: second, cis-keto (closed) and third, cis-keto (open). Figure 6.30 represents the charts of charge redistribution corresponding to $S_0 \rightarrow S_1$ electronic transition from ground to excited electronic state. For the second cis-keto (closed) and third cis-keto (open) forms, the charge redistribution is delocalized along all molecules. Both fragments are included in the mixed but not pure CT process of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ type. A twist of the fragment containing the nitrogen atom along the long axis is related to the creation of a new semi-ring (for cis-keto (closed)) and charge acceptor (electron donor) properties of the molecular fragment increases.

From the chemical point of view, the whole tautomeric structure must be stable and not reversible. In order to estimate a reversibility of structures, quantum chemical simulations have been carried out. Figure 6.31 represents the potential energy diagram (the ground state S_0 and first excited state S_1 energy dependence on reaction coordinate – the dihedral twisting angle φ), which determines tautomeric structure. The rotation of phenyl substitutes along the long axis realizes occurrence of two tautomeric forms: second form cis-keto (closed), $\varphi = 180^\circ$ and $\varphi = -180^\circ$,

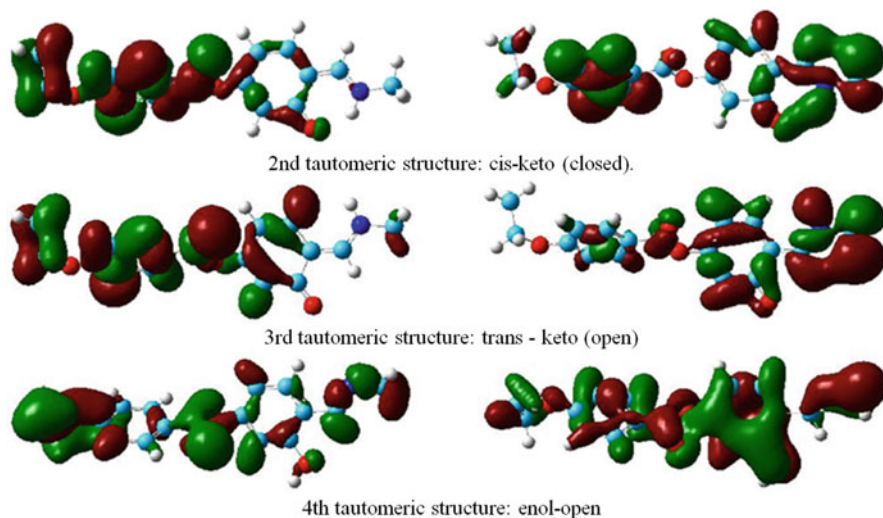


Fig. 6.30 Most important tautomeric structures: second, third and fourth. Charge redistribution corresponding to $S_0 \rightarrow S_1$ electronic transition: from ground state (left) to excited state (right)

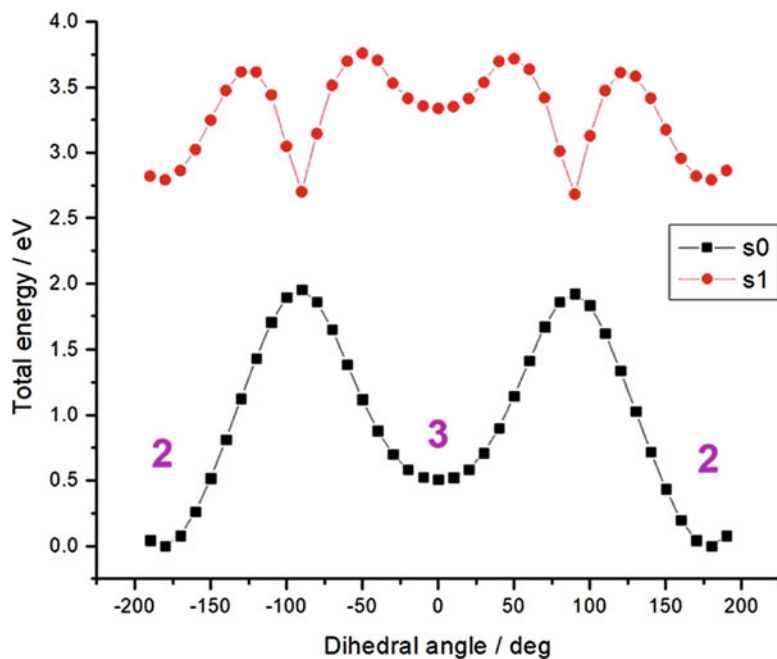


Fig. 6.31 Potential energy diagram. Ground state S_0 and first excited state S_1 energy dependence on dihedral twisting angle which determines tautomeric structure: second form cis-keto (closed) or third form trans-keto (open)

or third form trans-keto (open), $\varphi = 0^\circ$. The difference between ground state energies of such forms is equal >0.5 eV. The rotation barrier contains 2.0 eV, in comparison to kT factor for room temperature objects, which is equal to 0.03 eV. This means that both configurations – second form cis-keto (closed) and third form trans-keto (open) – can exist quite a long time in the ground state, and the transition from second to third can be made through the excited state only. A twist of molecular fragment occurs in the excited state only.

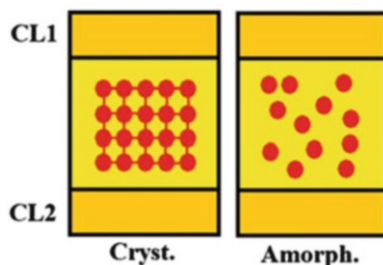
After excitation, the first excited state is populated after finishing internal conversion processes. A curve form of the ground state dependency and excited state dependency differs significantly. The presence of the minimum of the excited state dependency at $\varphi = 90^\circ$ realizes a possibility of relaxation to the ground state in a twisted configuration while the twisting continues until $\varphi = 0^\circ$.

The presented model is presumptive and can be used by choosing materials of demand properties.

Kim et al. [53] demonstrated the non-volatile memory cell element as the transistor, namely, the resistor hybrid-type device consisting of a silicon transistor and a resistive polymer memory. Organic memory has been constructed using polyfluorene-derivative poly[(9,9-bis((60-(N,N,N-trimethylammonium)hexyl)-2,7-fluorene)-alt-(9,9-bis(2-(2-methoxyethoxy) ethyl)-fluorene)] dibromide (WPFOxy-F). Actually, the authors claimed that the construction of difluorene derivative exhibits non-volatile memory properties. Zhao et al. [54] presented the active layer application built up by poly(9-vinylcarbazole) (PVK) with zinc oxide (ZnO). Cho et al. [55] presented the originally constructed organic-based device using titanium dioxide nanoparticles (TiO₂ NPs) embedded in poly(9-vinylcarbazole) (PVK) film. The presented structure exhibits the bistable resistance states and unipolar non-volatile memory effect. Kim et al. [56] described the reversible switching performance of metal–organic–semiconductor (MOS) memory devices containing a polyfluorene-derivative single-layer film.

Phase Change Nanodevices. Phase change nanodevices are based on the idea to use phase change (PC) switching between stable material states, e.g. conduction states for the electrical memory, or a large difference of the refractive index for optical memory. A sandwich-type structure can be composed from two conducting layers (CL1 and CL2) and PC material inside (see Fig. 6.32). Crystalline and amorphous states of material can be received after an internal perturbation

Fig. 6.32 Sandwich-type structure includes two conducting layers (CL1 and CL2) and phase transition material



(e.g. current pulse or laser pulse). A phase transition from the crystalline to amorphous state is related to the significant increase of the resistance, a refraction index, etc. Restoration of the crystalline order can be made by another type of pulse (refers to the properties of the material). Laser pulse duration, pulse energy and pulse polarization can be titled as driving factors for advanced phase transitions (from ordered to non-ordered and back).

Warren et al. [57] described $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST)-based phase change PC memory. Figure 6.33 represents phase transitions and the related state diagrams.

A crystalline state is stable with the temperature increasing from T_1 to T_3 . A volume of amount changes negligible (crystal heating process). After receiving the melting point at T_3 , the volume increases drastically from V_3 to V_4 (melting process occurs). After some time, a disordered state forms from a crystalline state. During the starting fast cooling process (4–5–6), a volume decreases, but not drastically, and a stable amorphous state forms at the temperature T_6 . Set operation (amorphous to crystalline) represents the phase change $6 \rightarrow 1$ – the heating to 500°C – and the reset operation (crystalline to amorphous) represents the phase change $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6$ – the heating to 600°C and fast cooling. Table 6.3 represents the scheme of memory state manipulation.

Nano-electromechanical (NEM) Switching Devices. A switch is an electrical equipment for manipulating of the electrical circuit. An interruption of current can be realized in several ways: significant increasing of conductivity or breaking the circuit. A mechanical degree of freedom (one, two, etc.) must be presented for a selecting mechanism of macroscale. Two-state logic schema can be realized by a spatial configuration of vibrating, rotating or generally moving objects (in micro- or macroscale).

Fig. 6.33 Phase transitions and the related state diagrams. 1–2–3, crystal state; T_3 , melting point; 3–4, melting process; 4–5, disordered state; 4–5–6, fast cooling; 6, stable amorphous state

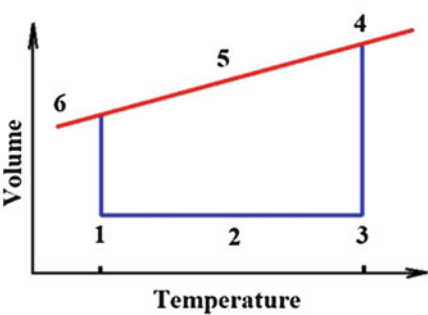


Table 6.3 The scheme of memory state manipulation. Adapted according to [57]

Operation		Reset		Set	
Memory state	1	$\rightarrow$	0	$\rightarrow$	1
Phase	Crystalline	$\rightarrow$	Amorphous	$\rightarrow$	Crystalline
Temperature, $^\circ\text{C}$		600		500	

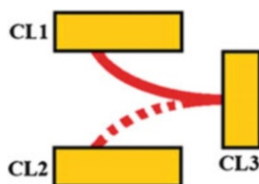


Fig. 6.34 Nano-electromechanical (NEM) switch. Sandwich-type structure includes two conducting layers (CL1 and CL2) and polymer chain (red). Applying the potential to conducting layer CL3, polymer chain changes mechanical position from CL1 to CL2. Reversible process is allowed by the absence of the potential to CL3

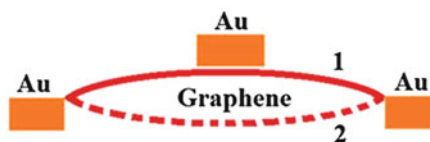


Fig. 6.35 NEM switch realized as double-clamped graphene beam. Conducting layers are built up by Au. Graphene bend (first or second position) is related to a potential

A nano-electromechanical (NEM) switch can be realized using a nanoscale equipment when the switch motion could be applied by programming electrical signal. A low voltage operation is possible in the region of 1 V. For a special equipment, a low-temperature processing is possible. For one of the best examples in nanoelectronics, information reading and erasing times can be distinguished in the range of <6 ns.

Figure 6.34 represents the principal scheme of nano-electromechanical (NEM) switch. A polymer chain is placed in the space with a possibility at different conditions to touch conducting layers CL1 and CL2. Applying the potential to the conducting layer CL3, a polymer chain changes a mechanical position from CL1 to CL2. A reversible process is allowed by absence of potential to CL3.

Peschot et al. [58] analysed a chip functionality from the energy point of view. NEM relays are promising candidates for low-power applications due to very low switching voltages. Hwang et al. [59] analysed NEM switching device based on carbon nanotube (CNT) and Cu electrode. The energy dependences on *In-Out* processes showed the hysteresis loop that has been induced by the adhesion of the CNT on the Cu (interatomic interaction).

Wang et al. [60] studied graphene–metal static contacts by fabricating the transmission line model (TLM) pattern on a graphene nanoribbon (GNR) and dynamic contacts by GNR nano-electromechanical (GNEM) switches. They checked that all the dynamic contacts in GNEM switches show clear pull-in operations, which are not reversible.

Kulothungan et al. [61] reported the NEM switch as a double-clamped graphene band (see Fig. 6.35). The authors showed the possibility of achieving a pull-in voltage as low as 2 V. The presence or absence of the potential is related to a graphene bend (first or second position).

Flash Memory Nanodevices. Flash memory can be designed using two approaches: charge transfer material (organized at the sub-macro level) or using the circuits containing field-effect transistors. Firstly, the sandwich-type structure can be composed of two conducting layers (CL1 and CL2) and a material containing silicon nitride inside (see Fig. 6.36).

Polysilicon–oxide–nitride–oxide–silicon (SONOS) and titanium–aluminium–nitride–oxide–silicon (TANOS) are medium for the charge transfer (CT) realization, which can be performed using an insulating layer (operating potential from the conducting layer CL2).

Kim et al. [62] investigated polyfluorene-derivative polymer as the hole device. The device showed excellent resistive switching behaviours such as device-to-device switching uniformity and good retention times.

Secondly, the field-effect transistors using single-walled carbon nanotubes are known from the pioneering Tans publication [63, 64]. Martel et al. [65] reported the fabrication of field-effect transistors, as the multiwalled carbon nanotube device. Holes are dominated in the charge transport motion through the nanotubes.

Nanodevices of Memristor Type. Memristor or memory resistor represents a nonlinear electronic device. A resistance of memristor depends on history of current. Generally, a resistance depends on the amount of charge, which passes through it. When the voltage is turned off, the memristor must remember its state (as most recent resistance) until voltage is turned on again. The practical realization of memristor can be performed as follows. The sandwich-type structure is created in this case from two conducting layers (CL1 and CL2) and a layer of resistive oxide inside (see Fig. 6.37).

Fig. 6.36 Flash memory nanodevice: two conducting layers (CL1 and CL2) and silicon nitride inside

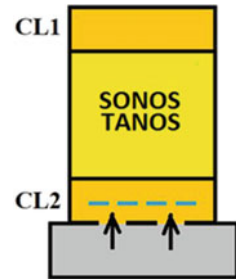


Fig. 6.37 Memristor-type nanodevice: two conducting layers (CL1 and CL2) and resistive oxide inside

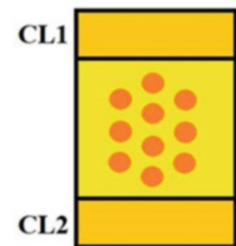
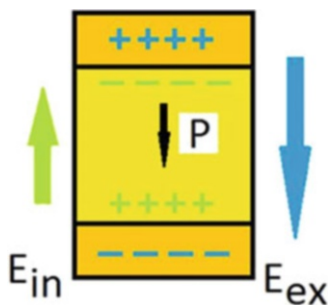


Fig. 6.38 Ferroelectric memristor: two conducting layers (CL1 and CL2) and ferroelectric material inside



The external voltage pulse drives the electronic state of device. FALSE state (0) corresponds to a high resistance state, TRUE state (1) – to a low resistance state. One of the oldest reports about TiO_2 phenomena was published by Argal [66]. Thin films of anodized TiO_2 can be made to switch between three distinct conductivity states.

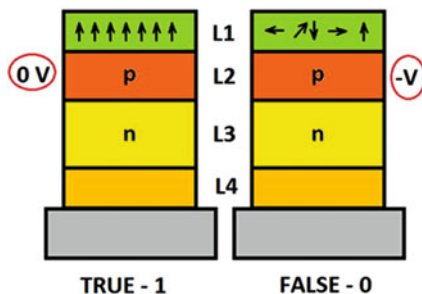
Alibart et al. [67] reported a novel device called firstly as nanoparticle organic memory field effect transistor (NOMFET). A device has been composed from organics and nanoparticle to exhibit the memristor properties. Additionally, a behaviour of a biological spiking synapse appears. Secondly, a name was expanded to a synapstor (synapse transistor).

Ferroelectric Nanodevices. This type of nanodevices belongs to a class of memristors, when a bistable ferroelectric material is used. Due to difficulties to perturb ferromagnetic material by an external source and to keep a material in the same crystalline phase (any phase transition of first or second type must occur!), polarization phenomena could be used. Figure 6.38 represents ferroelectric memristor: two conducting layers (CL1 and CL2) and ferroelectric material inside. A memory manipulation can be provided by applying a positive or negative voltage which switches the positive polarization states to negative (computational states FALSE ‘0’ to TRUE ‘1’). A reversible action is allowed. Chanthbouala et al. [68] describe the practical implementation of the device with a speed 10 of ns .

Spintronic Nanodevices. Spintronic (or spin transport electronics) devices are driven by the processes of intrinsic electron spin and associated magnetic moment. A class of magnetic semiconductors represents a significant part of the spintronic system. Practical applications of a spintronic system are presented in Fig. 6.39.

Gallium manganese nitride magnetic layer (L1) is intended for spin manipulating purposes. A traditional pn junction (L2, L3 layers) is placed on a gallium nitride substrate (L4). A closed electric circuit must be organized through the pn junction. With the negative voltage, the concentration of holes in the p layer significantly decreases, and spins of manganese atoms (from L1 layer) become disoriented. The creation of state ‘0’ is finished. With a zero voltage, the concentration of holes in the p layer significantly increases, and spins of manganese atoms become aligned due to the interaction of holes and manganese atoms. The creation of state ‘1’ is finished.

Fig. 6.39 Spintronic system. L1, gallium manganese nitride magnetic layer; L2 and L3, pn junction; L4, gallium nitride substrate



6.6 Biomolecular Rotary Machines

All biological systems represent various embodiments of molecular machines. Richard Feynman pointed out in his pioneering work [69] the idea about the biological cells organization through self-replication structures at the nanoscale.

All biological complexes as machines transduce the energy from one form to another (generally, from chemical to mechanical). A metabolic breakdown of glucose through the phosphorylation reaction can be treated as the main source of energy in cells. All organisms use the reaction of adenosine triphosphate ATP^{4-} hydrolysis to ADP to drive the metabolic breakdown of glucose $G^\circ = -30.5 \text{ kJ mol}^{-1}$:



Many molecular motors can be divided into several groups according to their biological importance.

1. *Nucleic acid motors*. DNA polymerase for the single-stranded DNA converting to the double-stranded DNA. RNA polymerase for transcription of RNA from the template.
2. *Rotary motors (proteins)*. They convert the chemical energy from ATP to the electrochemical potential energy of a proton gradient across a membrane.
3. *Cytoskeletal motors*. Myosin responsible for the muscle contraction.
4. *Synthetic molecular motors*.

Vicario et al. [70] reported the light-driven unidirectional molecular motor, where a fluorene core is connected through an alkene double bond [$>\text{C}=\text{C}<$] to helicene (pentaring substituted) (see Fig. 6.40). This system is titled as one of the fastest systems; rotation motion is realized by thermal helix inversion, when half-life of process is 0.005 s.

Katoono et al. [71] reported the propeller-shaped dynamic helicity, which was realized in a hexakis (phenylethynyl) benzene framework (see Fig. 6.41).

Fig. 6.40 Synthetic molecular motor built up using fluorene core

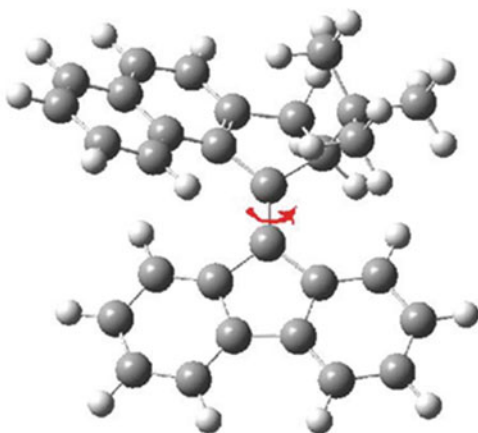
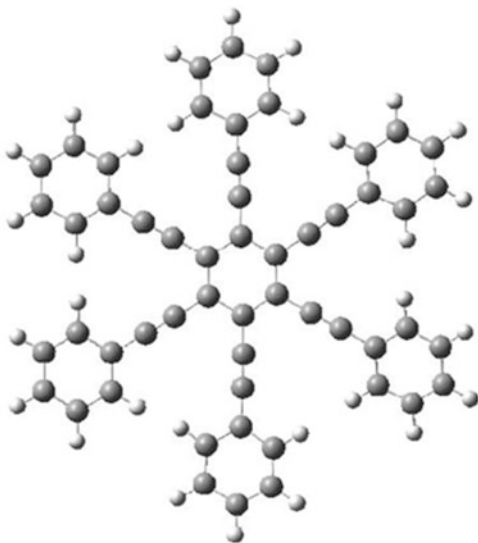


Fig. 6.41 Hexa-derivative of benzene



6.7 Nanotransducers

A nanotransducer is a device that converts one form of energy into another in the nanoscale range. Note that human sense facilities include the corresponding nanotransducers which convert external influences into neuron (bioelectric and biochemical) signals. Nanotransducers are the necessary parts of nanosensor systems (see Fig. 6.42).

A neuron network communication with the different human brain parts is presented in Fig. 6.43. Using the human brain researches, we can develop various applications for the human body enhancement and prosthetics. Outline the main *goals of human enhancement*:

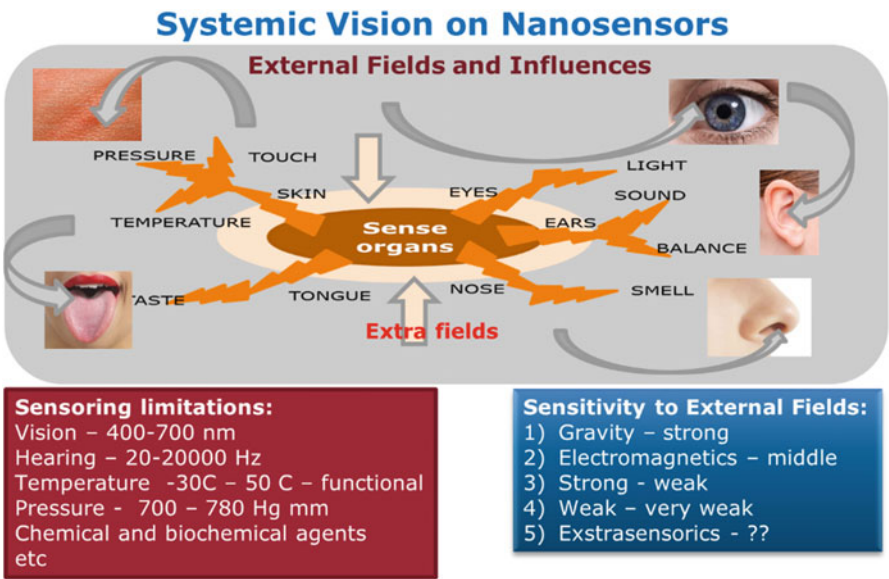


Fig. 6.42 Description of typical external influences on the human body in connection with the human sensing abilities and limitations

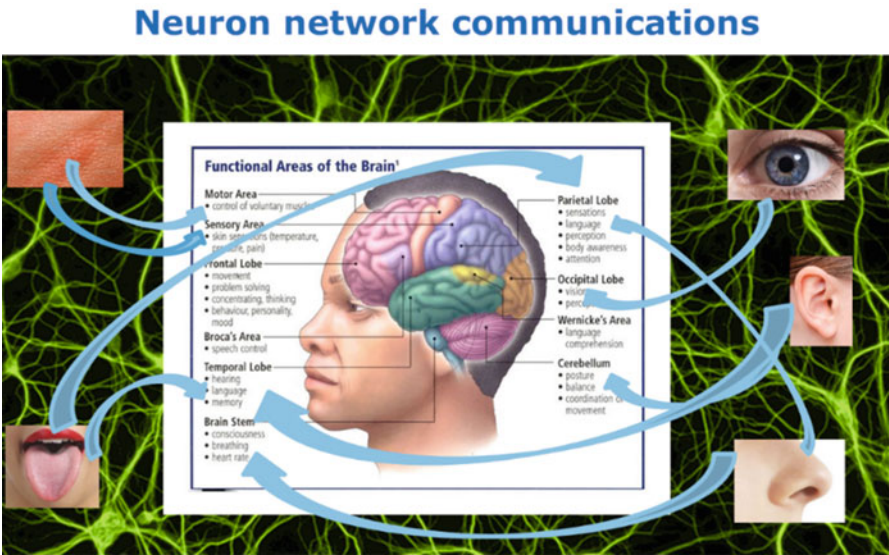


Fig. 6.43 Connections of human sensing with the corresponding human brain areas

Table 6.4 Nanosensing techniques review

Signal transduction techniques	Measurements details
Optical sensing and measurements	Luminescence, absorption, surface plasmon resonance
Electrochemical sensing and measurements	Redox reactions potentiometric, amperometric, etc.
Electrical sensing and measurements	FET-type devices, nanowires, conductive gels
Mass-sensitive sensing and measurements	Surface acoustic wave Nanocantilever-based sensing: 1. Cantilever surface is covered by receptor layer (functionalization) 2. Biomolecular interaction between receptor and target molecules (molecular recognition) 3. Interaction between adsorbed molecules induces surface stress change for cantilever bending.
Magnetic sensing and measurements	Magnetic fields sense magnetic nanoparticles attached with biological molecules

- Enhance cognitive abilities: *cognitive stimulants, neurotechnology, neurochips*
- Enhance physical abilities: *modified biological functions, prosthetics/exoskeleton*
- Modify psychology: *stimulants/medication, neurotechnology*
- Get non-human abilities [lifespan enhancement]: *night-vision technology, prosthetics/implants modified biological functions, genetic engineering, etc.*

Some special nanodevices for artificial systems based on nanotransducers can be also created.

Basic and practically essential energy types for transducing include electrical, mechanical, electromagnetic (including light), chemical, acoustic, thermal energies, etc. We can concentrate our attention on a set of particular signal transduction techniques (see Table 6.4).

While the term *transducer* commonly implies the use of a sensor/detector, any device which converts energy can be considered a transducer. Transducers are widely used in measuring instruments. Future sensor systems will incorporate nanoscale transducers that use multiple physical phenomena to sense a broad range of processes to be analysed.

6.7.1 Optical Nanotransducers

Optical nanoconverters are nanodevices that measure light and, conversely, convert various impacts into light. Reversibility of transformations of influence signals (e.g. light $\rightarrow$ chemical reaction and, conversely, chemical reaction $\rightarrow$ light) is a

fundamental property of nanotransducers. This applies, as a rule, to other types of nanotransducers, namely, mechanical, magnetic, electrochemical and so on.

Chemical Reaction → Light. Optical transduction which utilizes changes in optical properties such as phase, amplitude and frequency is manifested because of the selective binding of an analyte with the biorecognition element; i.e. it converts chemical energy to light. Photometric devices for the light intensity measure the photon output for luminescent or fluorescent processes, which can be detected with photomultiplier tubes or photodiode systems.

Light → Chemical Reaction. Colourimetric devices for the colour analysis measure a change in light adsorbed when reactants are converted to products.

Surface Plasmon Resonance. SPR is an optical phenomenon due to a charge density oscillation at the interface of a metal and a dielectric, which has dielectric constants of opposite signs. Some particular research details in the SPR technique are presented by Rupert et al. [72] and Kari et al. [73]. For example, a thin layer of gold on a high refractive index glass surface can absorb laser light, producing electron waves (surface plasmons) on the gold surface. This occurs only at a specific angle and wavelength of incident light and is highly dependent on the surface of the gold, such that binding of a target analyte to a receptor changes the resonant frequency which produces a measurable signal.

Fluorescence. Fluorescence is a molecular absorption of light at one wavelength and its instantaneous emission at longer wavelengths. Some molecules fluoresce naturally, and others, such as DNA, can be modified for a fluorescence detection by the attachment of special fluorescent dyes. This process can be considered as nanotransducing.

Light-Induced Actuating Nanotransducers. Ding et al. [74] presented the light-induced actuating nanotransducers (LIAN). Temperature responsive polymers to charged Au nanoparticles, storing elastic energy that can be rapidly released under light control for repeatable isotropic nanoactuation, are developed in [74]. Optically heating above the critical temperature $T_c = 32^\circ\text{C}$ using plasmonic absorption of an incident laser causes the coatings to expel water and collapse within a microsecond to the nanoscale, millions of times faster than the base polymer. This leads towards rational design of diverse colloidal nanomachines.

Nanotransducers for Photoactivation Applications. Idris et al. [75] analysed the remote activation of photoactivable therapeutic compounds by light providing a high spatial and temporal control for activating the therapeutic agent. However, photoactivable compounds are mostly responsive towards ultraviolet (UV) or visible light radiation that has poor tissue penetration depth besides being unsafe to the body in the case of UV light. Nanoparticles with energy upconversion hold potential in overcoming this limit by using safe and deeply penetrating near infrared (NIR) light. These upconversion nanoparticles (UCNs) act as versatile nanotransducers. Their highly unusual optical properties to fluoresce with near-

Table 6.5 Actual applications of optical nanotransducers

Nanotransducing	Application
DNA sensors	Genetic monitoring, disease (e.g. Schwartz et al. [76]) Immunosensors: HIV, hepatitis, other viral disease, drug testing, environmental monitoring Cell-based sensors: functional sensors, drug testing Point-of-care sensors: blood, urine, electrolytes, gases, steroids, drugs, hormones and proteins Bacteria sensors (<i>E. coli</i> , <i>Streptococcus</i> , other): food industry, medicine, environmental Enzyme sensors: diabetics, drug testing
Quantum dots	Quantum dots are used as inorganic fluorophores (e.g. Jamieson et al. [77]). QDs have fairly broad excitation spectra – from ultraviolet to red – that can be tuned depending on their size and composition. They are being used in virus tagging and cancer cells imaging for diagnostics purposes
Luciferase luminescence	Nanotransducer is based on luminescence firefly luciferase (<i>Photinus-luciferin</i> 4-monooxygenase: ATP-hydrolysing) to detect the presence of bacteria in food or clinical samples [78]. Bacteria are specifically lysed, and the ATP released (roughly proportional to the number of bacteria present) reacted with D-luciferin and oxygen in a reaction which produces yellow light in high quantum yield <i>luciferase</i> $\text{ATP} + \text{D-luciferin} + \text{O}_2 \rightarrow \text{oxyluciferin} + \text{AMP} + \text{pyrophosphate} + \text{CO}_2 + \text{light (562 nm)}$

zero photobleaching, photoblinking and background autofluorescence are unique and have an added benefit when used simultaneously as optional imaging agents.

Some actual application descriptions are presented in Table 6.5.

6.7.2 Mechanical Nanotransducers

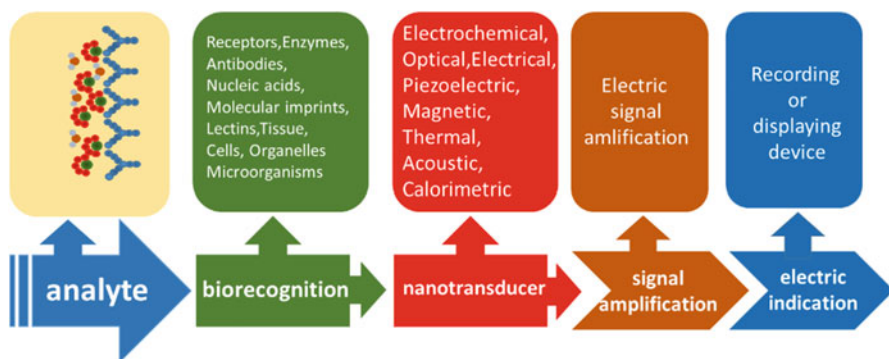
Mechanical nanotransducers detect changes in motions and convert mechanical energy into electrical energy. Mechanical transducers are usually cantilever shaped. The smaller size of mechanical transducers provides an outstanding mass resolution in a single atom, which is an advantage of a quartz crystal. Biomolecules form a monolayer on the upper side of the micro-cantilever that generates a surface stress creating a static mechanical bending with curvature, which causes cantilever to oscillate relative to the equilibrium position [79]. Some actual application descriptions of mechanical nanotransducers are presented in Table 6.6.

6.7.3 Electrochemical Nanotransducers

Electrochemical nanotransducers convert chemical reactions into electrical signals (see also Fig. 6.44).

Table 6.6 Actual applications of mechanical nanotransducers

Nanotransducing	Application
Biosensors	Biosensors based on mechanical transducers can specifically detect single-base mismatches in oligonucleotide hybridization. Nucleic acids are immobilized on a side of a cantilever (active side). Exposure of the cantilever to a sample containing complementary nucleic acid gives rise to a cantilever bending (deflection) of a few nanometres. Deflection can be measured by an optical system in which a laser beam reflects on cantilever [79]
Boron–carbon–nitride (B–C–N) nanotubes BCN NTs	Nanotube-based materials with piezoelectric properties have been invoked highly valuable tools for next generation transducers [80] Future expectations are mainly focused on nanocomposites with tuneable physical properties, as well as nanotube-based electronic textiles. However, both the high electrical resistivity of BCN NTs and the poor control over bandgap parameters in CNTs can represent shortcomings for their factual application in nanoelectronics. To overcome these limiting factors, ternary boron carbon nitride (B–C–N) nanotubes (BCN NTs), in which boron, nitrogen and carbon atoms are disposed within a honeycomb hexagonal lattice, have recently been proposed as highly sensitive torsional electromechanical nanotransducers [81]

**Fig. 6.44** General nanotransduction and nanosensing scheme using electrochemical techniques

Consider some special techniques of nanotransduction and nanosensing.

Nanoelectrode Techniques. The development of electrochemical nanosensors in recent years has been of growing interest. The enhanced chemical and physical properties arising from discrete nanoelectrode devices or microelectrodes modified with nanomaterials make these devices an attractive option for the improvement of current electroanalytical applications. Individual electrodes with nanoscale dimensions, which offer fundamental improvements over micro- and macroelectrodes, have been developing at a growing rate. In particular, single gold nanowires

fabricated on silicon substrates using electron-beam (e-beam) lithography have shown to exhibit enhanced mass transport due to radial diffusion. Steady-state currents observed in these electrodes allow the use of increased scanning rates and, as a result, shorter analysis times. The double layer capacitance in these electrodes also shows an improvement over micro-/macroelectrodes due to their very small surface area. The major application fields are health, security, law enforcement, environment and food safety. Nanoelectrode devices offer an attractive option in this field due to their small footprint and the potential for high sensitivity. As a result of the versatility and variety of nanoelectrode devices, they have been employed for the detection of a large range of medically relevant analytes ranging from small molecules such as dopamine and histamine to larger, more complex targets like bacteria or pharmaceutical drugs. Enzyme-based biosensors have long been of interest because of the selectivity of enzymes as biorecognition elements [82–86].

Electrochemical biosensors are some of the most widely used biosensors in the market, mainly due to glucose monitoring. Electrochemical biosensors are easily miniaturized, inherently inexpensive and require simple electronics for conditioning and read-out, making them ideal for point-of-care applications. Amperometric biosensors measure currents due to electroactive species, often using mediators to enhance electron transfer. Electrochemical impedance spectroscopy-based biosensors are some of the most promising electrochemical sensors for systems with well-defined charges, such as DNA. Electrochemical nanobiosensors with extremely low limits of detection are nowadays being developed thanks to the extraordinary properties of nanomaterials such as carbon nanotubes and graphene [87].

Nanoparticle Techniques. An effective detection of biological agents can be realized in the electrochemical impedance spectroscopy (EIS) with the emphasis on using nanoparticles and nanotechnology. Rapid, selective and sensitive detection technologies for biological agents are critical in clinical diagnosis, environmental monitoring and food safety. Recent developments in nanomaterial create many opportunities to advance DNA sensing and gene detection. The fact that gold nanoparticles are able to provide a stable immobilization of biomolecules that retain their bioactivity is a major advantage for the preparation of biosensors. However, there are a lot of researches reporting electrode modification by different nanomaterial to improve the DNA biosensor performance; the preparation of nanomaterial or the electrode modification strategy is often relatively complex. Furthermore, some DNA biosensors based on nanomaterial modification are still very limited for the improvement of DNA biosensor performance [88–92]. The emerging nanotechnology has opened novel opportunities to explore analytical applications of the fabricated nanosized materials. Recent advances in nanobiotechnology have made it possible to realize a variety of enzyme electrodes suitable for sensing application. In coating miniaturized electrodes with biocatalysts, undoubtedly the most of the potential deposition processes suffer from the difficulty in depositing process and reproducible coatings of the active enzyme on the miniature transducer element [93–96].

Molecular Imprinting Technique. Molecular imprinting technique (MIT) is a method of preparing polymer scaffolds that function as synthetic receptors [97]. Imprinted polymers that can selectively bind organic compounds have proven useful in developing sensors. Although creating synthetic molecular imprinting polymers that recognize proteins remains challenging, nanodevices and nanomaterials show promise in this area. Molecular imprinting sensors, specific for human ferritin and human papillomavirus-derived E7 protein, have been developed [98]. The molecular imprinting-based nanosensor can also discriminate between Ca^{2+} -induced conformational changes in calmodulin. This ultrasensitive, label-free electrochemical detection of proteins offers an alternative to biosensors based on biomolecule recognition [98].

6.7.4 Magnetic Nanotransducers

Nanowire Transducers. Magnetic nanotransducers are already central to data storage and sensor devices, and more recently they are penetrating various new areas including life sciences and biomedical applications. Magnetic nanowires offer unique properties, due to a high aspect ratio and shape anisotropy. They are characterized by a single magnetic domain, rendering them nanopermanent magnets. This feature allows energy-efficient and remote operation of the nanowire transducers, i.e. induce motion, produce heat or sense their location [99, 100].

Magnetomotive Nanotransducers. Resonant acoustic spectroscopy of soft tissues using embedded magnetomotive nanotransducers and optical coherence tomography performing dynamic elastography of soft tissue samples is demonstrated in [101]. By sensing nanoscale displacements with optical coherence tomography, a chirped, modulated force is applied to acquire the mechanical spectrum of a tissue sample within a few seconds. This modulated force is applied via magnetic nanoparticles, named ‘nanotransducers’, which are diffused into the tissue and which contribute negligible inertia to the soft tissue mechanical system. Excised tissues that exhibit mechanical resonance modes which are well described by a linear damped harmonic oscillator have been observed. Results are validated by using cylindrical tissue phantoms of agarose in which resonant frequencies (30–400 Hz) are consistent with longitudinal modes and the sample boundary conditions. Magnetomotive resonant acoustic spectroscopy (MRAS) has been developed. Nanotransducers consist of magnetic nanoparticles (~20 nm diameter iron oxide, –COOH terminated, Ocean NanoTech, LLC) in an aqueous solution that are either diffused into the tissues or premixed into tissue phantoms before gelation. To mechanically drive the nanoparticles, a solenoid is placed 1–2 mm above the tissue to apply a temporally modulated magnetic field from $B \approx 0\text{--}600\text{ G}$ along its central axis (z). The resulting gradient force on the nanoparticles $\mathbf{F} \propto \nabla |\mathbf{B}|^2$ is directed primarily towards the solenoid along $+z$ [101–104].

Targeted Magnetic Nanoparticles. Hysteretic heat dissipation by magnetic nanomaterials can be used to remotely trigger activity of neurons expressing heat-sensitive ion channels. Since the alternating magnetic fields in the low radiofrequency range interact minimally with the biological tissues, the magnetic nanoparticles injected into the brain can act as transducers of wireless magnetothermal deep brain stimulation. Similarly, local hysteretic heating allows magnetic nanoparticles to disrupt protein aggregates associated with neurodegenerative disorders [102–104].

Heat-Assisted Magnetic Recording (HAMR). Integrating magnetic thin-film heads with plasmonic nanotransducers has gained importance in magnetic data storage concepts because of its promise to overcome the superparamagnetic limit. Integrated heads offer significant advancement in the performance of hard disc drives by lowering the coercivity of magnetic grains via localized heating of the grains during the recording process. The magnetization of the grains can then be changed by the applied magnetic field of the integrated head, which has paved the way for heat-assisted magnetic recording (HAMR). HAMR is an emerging technology that has increased the areal density of conventional recording techniques for hard disc drives. Integrated heads have enabled this increase through localized heating of the recording media during the recording process. One of the problems in integrating magnetic heads with plasmonic nanotransducers is the resulting losses. In particular, multilayer configurations with gold thin films near magnetic thin films are investigated to minimize radiative and load-induced losses. The effect of load-induced damping of the magnetic film and evanescent coupling is identified with the intensity enhancement near the magnetic films. A higher intensity enhancement can be obtained by minimizing radiative and load-induced losses through adjusting layer thicknesses in multilayer configurations [105–107].

Magneto-Plasmonic Nanoantennas. Plasmonic nanoantennas are a hot and rapidly expanding research field. Here we overview basic operating principles and applications of novel magneto-plasmonic nanoantennas, which are made of ferromagnetic metals and driven not only by light but also by external magnetic fields. Magneto-plasmonic nanoantennas enhance the magneto-optical effects, which introduces additional degrees of freedom in the control of light at the nanoscale. This property is used in conceptually new devices such as magneto-plasmonic rulers, ultrasensitive biosensors, one-way subwavelength waveguides and extraordinary optical. Magneto-plasmonic nanoantennas may also be used to achieve spectral tuning or enhance nonlinear effects [108]. However, their advantage over nonmagnetic nanoantennas is that they can additionally exhibit nonlinear magneto-optical properties. It was shown that the nonlinear magneto-optical Kerr effect and the SHG effect can be enhanced at the frequencies of plasmon modes supported by arrays of ferromagnetic metal nanorods or magnetic multilayer heterostructures. The inverse magneto-optical effects are important for ultra-fast all-optical control of magnetisation, which may be useful in data storage systems and generation of spin waves with light pulses transmission structures, as well as in novel biomedical imaging modalities.

6.8 Nanoaerogels and Nanofoams

6.8.1 Introduction to Aerogels

Aerogel is a synthetic porous ultralight material derived from a gel, in which the liquid component of the gel has been replaced by a gas. The result is a solid with extremely low density and thermal conductivity. Nicknames include *frozen smoke*, *solid smoke*, *solid air* or *blue smoke* owing to its translucent nature, and the way light scatters in the material. However, it feels like expanded polystyrene (*styro-foam*) to the touch.

Nanofoams are a class of nanostructured, porous materials (foams) containing a significant population of pores with diameters less than 100 nm. Aerogels are one example of nanofoam.

Table 6.7 presents the evolution of aerogels, steps and stages of the process.

CNTs and Aerogels. There are several different ways how nanotubes and aerogels come together:

- Aerogels can be made out of carbon nanotubes.
- Carbon aerogels can be reinforced with embedded carbon nanotubes.
- Metal oxide aerogels can be used as catalysts to grow carbon nanotubes.
- Metal-doped carbon aerogels can act as catalysts for growing carbon nanotubes.

Remark. Fluffy masses of nanotubes formed during *nanotube yarn* production and sheets of entangled carbon nanotubes are sometimes incorrectly referred to as aerogels.

Carbon–Carbon Nanotube Aerogels. In 2008, Ted Baumann and Marcus Worsley at Lawrence Livermore National Laboratory developed a composite material made of double-walled carbon nanotubes dispersed uniformly throughout a carbon aerogel. The resulting carbon–carbon nanotube aerogels have improved electrical conductivities over regular carbon aerogels. For 8 wt % nanotube loading and bulk density of 0.139 g cm^{-3} , these aerogels have about twice the conductivity of regular carbon aerogels ($5 \Omega^{-1} \text{ cm}^{-1}$ vs $2 \Omega^{-1} \text{ cm}^{-1}$).

Graphene Aerogels: Main Properties and Qualities.

- Graphene aerogels demonstrate densities approaching 10 mg/cm^3 .
- Graphene aerogels demonstrate an improvement in bulk electrical conductivity of more than two orders of magnitude ($1 \cdot 10^2 \text{ S/m}$) compared to graphene assemblies with physical cross-links alone ($5 \cdot 10^{-1} \text{ S/m}$).
- The graphene aerogels also possess large surface areas ($584 \text{ m}^2/\text{g}$) and pore volumes ($2.96 \text{ cm}^3/\text{g}$), making these materials viable candidates for use in energy storage, catalysis and sensing applications.

Table 6.7 Aerogel evolution and application development

Evolution period	Description
1930s–1940s <i>1929–1931, Samuel Stephens Kistler [109]</i>	A discovery of many different types of aerogels, including transparent silica aerogels with densities as low as $0.030 \text{ g} \times \text{cm}^{-3}$, alumina aerogels, tungsten oxide aerogels, iron oxide aerogels and tin oxide aerogels
1940s–1970s <i>The early days of aerogels</i>	Aerogels were even commercialized as early as the 1940s by Monsanto Corporation (till 1970s). A powdered silica aerogel product called ‘Santocel’ for use as a thickening agent for paints, makeup and napalm, as cigarette filters and as insulation for a national line of freezers
1970s–1980s	<i>The 1980s</i> brought forth safer techniques for producing aerogels, ways of making aerogels 30 times lighter than had ever been accomplished before, and a new class of organic and carbon aerogels that would demonstrate aerogels of different substances could do amazing and very different things <i>In early 1980s</i> , particle physics researchers realized that silica aerogels would be an ideal medium for the production and detection of Cherenkov radiation <i>In the 1980s</i> , the alkoxide sol-gel process was made less toxic by using a safer alkoxide compound, and the supercritical drying technique was made safer by replacing supercritical alcohol with supercritical carbon dioxide [110]
1980s–1990s	<i>The 1990s</i> was the decade of aerogel increased publicity. Moreover, aerogel synthesis evolved to include ways to speed up or even eliminate supercritical drying and to extend aerogels to metal oxides across the periodic table
1990s–2000s <i>Commercialization trends</i>	Mechanically strong aerogels, aerogels of strange new materials and, finally, commercially available aerogels changed the way of thinking for aerogels application from energy transducing to lightweight structures and nanosensors
2000s–2020s <i>The nearest future</i>	<i>Actual and prospective developments trends:</i> ▪ Mechanically strong aerogels, aerogels of new compositions for sensors and energy production ▪ Aerogels applications for use as hydrogen storage media ▪ Metal aerogels ▪ More advanced supercapacitors that rival today’s batteries ▪ Hydrogen production using cleverly engineered semiconductor aerogels changing the way of thinking about energy and fuel ▪ Smart materials with the unique combinations of materials properties There are endless possible applications of aerogel materials

Ohm’s Law and Hooke’s Law Analysis The analysis of graphene/MWCNTs hybrid aerogels [111] is that these materials demonstrate Ohm’s law behaviour. It is very important that Hooke’s law behaviour also is observed. However, the linearity of *compressive stress* via *compressive strain* is very ‘deep’ (till 50%). This is larger than for simple elastic materials. This property also gives possibilities to create pressure and force nanosensors.

6.8.2 Aerogels Forms and Characterization

Silica Gels. *Silica gels* are produced through the sol-gel process, in which nanoparticles suspended in a liquid solution (i.e. a sol) are invoked to interconnect and form a continuous, porous, nanostructured network of particles across the volume of the liquid medium (i.e. a gel). Silica aerogels have found a wide array of uses, mostly in high-tech science and engineering, but are beginning to enter the commercial mainstream. Below are a few examples of where silica aerogels have helped out. There are some known applications: *Insulation on the Mars Exploration Rovers, Hypervelocity Particle Capture in the Stardust Probe, High-Energy Cherenkov Radiation Particle Counters, Remediating Oil from Water, Transparent Window Insulation* and *Thermal Insulation Without the Chlorofluorocarbon (CFCs)*.

Metal Oxide Aerogels. *Metal oxide aerogels* are the inorganic cousins of the more common silica aerogel – each type with its own unique properties. These aerogels are important, as they can act as catalysts for various chemical transformations, matrices for explosives and precursors for other materials (such as carbon nanotube catalysts), can be magnetic and are often quite colourful. Up until the 1990s, metal oxide aerogels had been historically much more difficult to synthesize than silica aerogels, largely because there were no good synthetic routes for making metal oxide gels. This is mostly due to the difficulty associated with handling metal alkoxide compounds (as they hydrolyse readily), or in some cases simply because of there aren't any or any good metal alkoxides for a particular metal. One of the most notable differences between metal oxide aerogels and silica aerogels is that many metal oxide aerogels are often brilliantly coloured. It is important to remember that the bluish cast characteristic of a silica aerogel is the result of the Rayleigh scattering by nanoparticles (which make up the aerogel backbone) and that silica itself is not blue. There are some colour realizations of metal oxide aerogels (see Table 6.8).

Organic and Carbon Aerogels. Organic aerogels have been around as long as any aerogel. In fact, the first aerogel which Samuel Kistler is believed to have prepared was aerogel made from jelly (which is composed of the organic heteropolysaccharide pectin). Kistler also prepared aerogels of gelatin and rubbers,

Table 6.8 Colour realizations of metal oxide aerogels

Metal oxide aerogels	Colour palette
Silica, alumina, titania, zirconia	Clear with Rayleigh scattering blue or white
Iron oxide	Rust red or yellow opaque
Chromia	Deep green or deep blue, opaque
Vandia	Olive green, opaque
Neodymium oxide	Purple, transparent
Samarium oxide	Yellow, transparent
Holmium oxide, erbium oxide	Pink, transparent

both of which are composed of organic polymers. There are numerous examples of organic aerogels which have been prepared in the literature, many of which are biological in nature. Supercritical drying has been used by biologists for many decades to preserve biological specimens or prepare them for electron microscopy – in essence making aeroinsects, aerobacteria and even aeroorgans. Organic aerogels made from polymers of not only resorcinol but also melamine, phlorglucinol and acetic acid are used to prepare carbon aerogels.

Semiconducting Metal Chalcogenide Aerogels. Semiconducting metal chalcogenide aerogels are a new, exciting class of aerogels materials. First prepared in 2002, these aerogels possess a unique combination of porosity, optical translucency and photoluminescence and show great promise for use as chemical sensors (*artificial nose*) and energy applications such as photovoltaics (solar cells) and extraction of hydrogen from water using sunlight as the energy source. Metal chalcogenide aerogels exhibit a property called photoluminescence, that is, the glow when irradiated with a black light (ultraviolet lamp). In fact, metal chalcogenide aerogels have a bandgap, like other semiconductors, and that bandgap corresponds to the colour of light they will emit under the black light. Bulk CdS has a bandgap around 2.05 eV (meaning the crystal will photoluminesce orange), but nanosized CdS quantum dots can have a very different bandgap depending on their diameter. In general, aerogels made from quantum dots have about the same bandgap as the quantum dots they are made out of, so CdS aerogels made from CdS quantum dots that have a bandgap of 2.73 eV (blue) will photoluminesce blue as well, although a bit greener of a blue (the bandgap of aerogels is usually ‘redshifted’ compared to quantum dots). Interestingly, if the aerogel is annealed at 300 °C, the aerogel’s bandgap decreases to 2.22 eV (green). The main application directions are *photocatalysts, photovoltaic cells, chemical and biological sensors and quantum dot metal chalcogenide aerogel*.

Nanoporous Metal Foams. There are now a number of ways to make nanoporous metal foams. There are three major approaches: *combustion synthesis of metal nanofoams, dealloying of templated Au alloys and nanosmelting of iron aerogels*.

One method for making nanoporous metals is called dealloying. In this method, an alloy of gold and a less noble (more reactive) metal is prepared (usually an alloy of copper and gold or silver and gold), where enough less noble metal is present in the alloy that forms a continuous percolating network throughout the gold.

Iron aerogels are made through a nanosmelting process. Fe aerogels are both magnetic and electrically conductive just like iron is. They have surface areas ranging from ~ 95 to $300 \text{ m}^2\cdot\text{g}^{-1}$ and densities of about $0.046 \text{ g}\cdot\text{cm}^{-3}$ (about 20 times less dense than water and 172 times less dense than bulk Fe metal).

The main applications are *hydrogen storage, antimicrobial scaffolds, irregularly shaped magnetic media and X-ray optics*.

Strong and Flexible Aerogels. Although it is true that a typical silica aerogel could hold up to 2000 times its weight in applied force, this only holds if the force is gently and uniformly applied. Also, keep in mind that aerogels are also very light,

and 2000 times the weight of an aerogel still might not be very much. Additionally, most aerogels as produced are extremely brittle and friable (i.e. they tend to fragment and pulverize). As a result, structural applications of aerogels were for a long time totally impractical.

There are four general ways to enhance the mechanical properties of aerogels: *liquid-phase crosslinking*, *vapour-phase crosslinking*, *fibre reinforcing* and *reduced bonding*.

6.8.3 Aerogels Commercialization

Mechanically Strong and Flexible Aerogels. If you can dope polymers with nanomaterial fillers, could you dope a filler material with a polymer? [112] – this was a question. It was shown that the lowest density form of silica available is silica aerogel and proceeded to see what kinds of materials you could make if you doped them, that is, crosslinked them, with polymers. Discovered x-aerogels, a new class of flexible, mechanically robust aerogels, have been developed. Diffusing crosslinking agents such as diisocyanates (used in making polyurethane) into the pores of a silica aerogel have been obtained. The hydroxyl groups on the surface of the particles that make up the aerogel framework to create polymer bridges between particles – the structural weak spots in the aerogel structure – have been used. Later, a set of x-aerogels from many more substances than just silica, including most of the transition metal and lanthanide oxides and many organic aerogels, have been prepared.

Quantum Dot Aerogels and Beyond If aerogels of metal oxides could be made, why should other chalcogenides, such as sulphides and selenides be searched for? [113] – this was a question. Gels of cadmium sulphide and selenide have been prepared. The result is a novel class of photoluminescent, semiconducting aerogels with unusual and exciting properties. Many metal sulphides and selenides as well as nitrides and phosphides gels have been prepared, and applications of these types of aerogels in photoelectrolysis of water and chemical sensors have been demonstrated.

Metal Aerogels. The development of a technique for producing monoliths of nanoporous gold was the essential technological step [114, 115]. Cast bimetallic alloys of gold and another metal (such as Cu or Ag) over micron-diameter polystyrene spheres, which served as a template for a foam structure, were created. After dissolving the template, the less noble metal in the alloy was then etched away through a technique called dealloying. The remaining structure was a macroporous foam with nanoporous walls, closely approximating a *gold aerogel*. The foams had two levels of porosity, micron-diameter pores leftover from the template and nanometre-size pores from dealloying. However, these materials did not exhibit significant mesoporosity, that is, pores between 2 and 50 nm in diameter, which is more typical of aerogels.

Bryce Tappan [116] found that ignition of pressed pellets of these compounds under an inert atmosphere left behind incredibly low-density metallic foams. It was discovered that the foams, although largely macroporous, contained significant mesoporosity as well, approximating the expected structure of a metal aerogel. The group eventually extended the technique to prepare foams of Fe, Co, Ni and Cu, among other metals. The polymer that smelted the iron oxide component of the aerogel, leaving behind an aerogel of ‘pig iron’ – iron rich in carbon content but magnetic and metallic as characterized by X-ray diffraction [117] was created.

Carbon Nanotube Aerogels. It was shown that carbon nanotubes could be assembled into a gel structure using polyvinyl alcohol as a ‘binder’ [118]. Then these gels were supercritically dried to prepare carbon nanotube aerogels. The next new technology (Marcus Worsley and Sergei Kucheyev 2008) gave a hybrid of carbon nanotubes and carbon aerogel, with the amazing ability to compress 80% and elastically return undeformed. The materials also showed high electrical conductivity.

Acid-Catalysed Carbon Aerogels. Acid-catalysed carbon aerogels – an intriguing variation on carbon aerogels with incredibly enhanced strength – were developed [119]. Although technically not aerogels because of their primarily macroporous bone-like structure, these materials exhibit compressive strength and stiffness much higher typical of most aerogels and different from any other carbon material. A way to make these materials nanoporous by etching them with CO₂ at high temperatures, resulting in ultrahigh surface area carbon aerogels with promise for hydrogen storage applications, was demonstrated [120].

6.8.4 Functionalization

Functionalization is the process of adding new functions, features, capabilities or properties to a material by changing the surface chemistry of the material. It is a fundamental technique used throughout chemistry, materials science, biological engineering, textile engineering and nanotechnology. Functionalization is performed by attaching molecules or nanoparticles to the surface of a material, sometimes with a chemical bond but sometimes just through adsorption (i.e. the thing you’re trying to attach sticks to the surface without forming a covalent or ionic bond).

Functionalization can:

- Make a water-absorbing material waterproof
- Change the colour of a material
- Render a surface antibiotic
- Make chemical sensors (‘artificial noses’)

- Make nonmagnetic materials magnetic
- Make sophisticated batteries

Flat surfaces such as silicon wafers or glass are commonly functionalized to make useful and interesting materials and devices. However, aerogels, with ultrahigh surface areas wrapped up inside their porous skeletal frameworks, can also be functionalized to make materials with even more amazing properties than ordinary aerogels (see also Table 6.9).

6.9 Biocomposites

6.9.1 *Biocomposite Concepts and Definitions*

Polymer nanocomposites represent a new alternative to conventional polymers. Polymer nanocomposites are materials in which nanoscopic inorganic or organic particles, typically 1–100 nm in at least one dimension, are dispersed in an organic polymer matrix in order to improve the properties of the polymer dramatically.

Owing to the *nm* length scale, which minimizes scattering of light, nanocomposites are usually transparent and exhibit properties that are markedly improved over those of pure polymers or their traditional composites. They have increased modulus and strength, outstanding barrier properties, improved solvency, heat resistance and generally lower flammability, and they do not have detrimental effects on ductility [121]. There are three basic classes of *biopolymers*:

1. *Bioresources*: natural biopolymers (plant carbohydrate like starch, cellulose, chitosan, alginate, agar, carrageenan, etc. and animal- or plant-origin proteins like soy protein, corn zein, wheat gluten, gelatin, collagen, whey protein and casein)
2. *Chemical synthesis*: synthetic biodegradable polymers
3. *Microorganisms*: biopolymers produced by microbial fermentation

Table 6.10 demonstrates the evolution biocomposite material concepts from traditional forms till absolutely new and prospective.

Bio-nanocomposites which are obtained from 100% bio-based materials, in which both the fillers and the matrix are obtained from renewable resources. Four different nanofillers are extensively used for the preparation of bio-nanocomposites presented in Table 6.11.

6.9.2 *Bio-nanocomposites from Renewable Resources*

A variety of nanofillers allow the creation of large four classes of bio-nanocomposites.

Table 6.9 Aerogels functionalization

Aerogel function	Description
<i>Aerogels are 3D surfaces</i>	While aerogels are generally three-dimensional materials, they contain a tremendous amount of surface area. The surface of each and every nanosized strut that makes up the open porous skeleton of the aerogel can potentially serve as a surface for molecules or particles to be attached to. There is a lot of surface area wrapped inside an aerogel, a typical piece of silica aerogel, say with a density of 0.1 g/cm^3 , and easily has a surface area of $750 \text{ m}^2/\text{g}$, which means an ice cube-sized piece having 2.2 cm sides (a little less than a cubic inch) has 750 m^2
<i>Aerogels are great things to functionalize</i>	Aerogels offer lots of advantages in functionalization: • Aerogels pack tremendous surface into a small volume (i.e. they have a high surface-to-volume ratio) • Aerogel backbones can be made of many different substances, providing tremendous chemical flexibility • Aerogels can frequently made through ambient temperature bench-top processes • The open pore network of aerogels enables movement (mass transport) of stuff through the aerogel, providing avenues for getting things you might want to detect or adsorb to the functional groups that will sense or adsorb them
<i>Waterproof aerogels: an example of functionalization</i>	One classic example of functionalization of aerogels is the making of hydrophobic (waterproof) silica aerogels. Silica aerogels are normally hydrophilic; that is, they readily absorb moisture from the air (which causes them to shrink and become cloudy over time) and wick up liquid water on contact (which causes them to shrivel up and densify). This is because of surface hydroxyl (-OH) groups that cover the struts of the aerogel's skeleton—sticky, polar groups to which water can readily stick by hydrogen bonding. To make a waterproof silica aerogel, we can replace the hydrogen on these sticky -OH groups with a much less sticky, non-polar group called trimethylsilyl (-Si(CH ₃) ₃). Transforming just 30% of these -OH groups into -OSi(CH ₃) ₃ groups is enough to make the struts of the aerogel repel water, allowing the aerogel to float in water indefinitely without wicking water into its pore network (which would cause the aerogel to shrivel up).
<i>How to functionalize an aerogel</i>	There are three points in the process of making an aerogel where you can functionalize its surface: during gelation of the precursor gel, after gelation of the precursor gel and after supercritical drying.
<i>Cool stuff using functionalization</i>	• Make brittle silica and metal oxide aerogels superstrong and tough by functionalizing the surface with polymers • Make precursors for metallic aerogels by functionalizing metal oxide aerogels with carbon-rich polymers • Make carbon aerogels into battery-like materials by functionalizing with electrochemical coatings such as manganese dioxide

(continued)

Table 6.9 (continued)

Aerogel function	Description
	• Make silica aerogels into oxygen sensors by functionalizing with oxygen-sensitive fluorophores • Make carbon aerogels into efficient catalysts by functionalizing with precious metals • Make silica or carbon aerogels into hydrogen storage materials by functionalizing with metals that form hydrides • Make aerogels that absorb 20× their weight in oil by functionalizing with oleophilic groups • Make aerogels that filter biomolecules like DNA by functionalizing with the complementary DNA sequence

Table 6.10 Bio-nanocomposite concepts evolution [122]

Concept	Definition
Bioplastic	A plastic that is made from biological/renewable resources or degrades by the action of microorganisms/biological activity or both
Bio-based plastic	A plastic that is obtained totally or partially from biological resources, i.e. all the monomers or any of the monomer used in the synthesis is derived from biological resources
Degradable plastic	A plastic, which undergoes major structural changes under prescribed environmental conditions
Biodegradable plastic	A plastic which degrades by the action of microorganisms or undergoes lowering of its molecular weight by biological activity
Compostable plastic	A plastic that undergoes biodegradation in composting environment to yield carbon dioxide, water, inorganic compounds and biomass at a rate equivalent to standard compostable materials and leaves no toxic materials
Biocomposite	Composite that consists of either filler or polymer matrix derived from biological resources
Nanocomposite	Polymer composites that have fillers with at least one dimension in nm
Bio-based nanocomposite	Nanocomposite in which either fillers or polymer matrix has been obtained from biological resources
Bio-nanocomposite	Nanocomposite in which both fillers and polymer matrix obtained from biological resources
Bio-degradable nanocomposite	Nanocomposites that degrades by the action of microorganisms
Bio-compatible	Refers to the ability of a material to carry out its intended function without any adverse reactions or unintended responses

Cellulose Nanocomposites. The importance of cellulose nanocomposites arises from the unique properties of cellulose nanomaterials such as structural stability against various processing windows, excellent mechanical properties in terms of Young's modulus (~138 GPa) compared to other lignocellulosic natural fibres (35–45 GPa for flax fibre) and very low coefficient of thermal expansion in

Table 6.11 Nanofillers for bio-nanocomposites

Nanofillers	Descriptions and characterizations
Cellulose-based nanofillers (CBN)	CBNs are widely available and low-cost material which is both renewable and biodegradable. Cellulose microfibrils and nanocrystalline celluloses or cellulose nanowhiskers (CNW) are the two types of nanoreinforcements obtained from cellulose. Cellulose microfibrils consist of bundles of molecules that are elongated and stabilized through hydrogen bonding [123]. The typical dimensions of these nanofibrils are 2–20 nm in diameters, while lengths in micrometer range
Carbon nanotubes	Carbon nanotubes find many applications that include polymer nanocomposites, electrochemical energy storage/conversion, catalysis, hydrogen storage, health and environmental hygiene products and electronics. In polymer nanocomposites they have been utilized as high-performance functional fillers, which not only improved thermal/mechanical performance but also provided additional functionalities such as fire retardant, moisture resistance, electromagnetic shielding and barrier performances. The field of polymer nanocomposites with carbon nonmaterial has highly diversified; carbon nanotube (CNT)-based polymer composites have been widely explored in many aspects as described elsewhere [124]
Nanoclays	Layered silicates also known as nanoclays are most commonly utilized nanofillers in the synthesis of polymer-layered silicate nanocomposites. Among these layered silicates, phyllosilicates (2:1) are extensively used in preparing clay-based nanocomposites. The crystal arrangement in the silicate layers is made up of two tetrahedrally coordinated atoms amalgamated to edge-shared octahedral sheets. The layers have thickness of 1 nm, and their tangential dimensions range from 30 nm to a few microns. The variation in the dimensions depends on clay source, particulate silicate and preparation technique [125]
Functional nanofillers	A wide range of biocompatible materials such as metal, alloys, ceramics, polymers and composites is used for medical implants. Among them, bio-nanocomposites that are fabricated using the combination of biopolymers and various nanostructured inorganic/organic functional fillers receive extensive attention due to their diversified biomedical as well as biotechnological application. Nanostructured fillers play an important role in biocomposite fabrication, since they bring various desired functionalities to the composites. Functional nanofillers such as cellulose nanofibres, hydroxyapatite (HAp), layered double hydroxides (LDH), silica nanoparticles and polyhedral oligomeric silsesquioxanes (POSS) are most investigated for this proposes [126–128]

longitudinal direction (10^{-7} K^{-1}). Structures of cellulose nanofibres are stabilized by hydrogen bonds with high levels of crystallinity, which makes cellulose nanofibres an ideal reinforcing material in polymeric materials. Cellulose nanocomposites made using renewable resource-based biopolymers exhibit superior thermal, mechanical and barrier properties with minimum reinforcement

(~5 wt %) compared to macro reinforcements with the added advantages of recyclability and biodegradability [129].

CNT Nanocomposites. Carbon nanostructures (including carbon nanotubes, nanofibres and graphene sheets) exhibit a range of properties, such as higher electrical conductivity, enhanced mechanical strength and better thermal behaviour, which make them desirable reinforcing materials for polymer nanocomposites [130]. Especially, carbon nanotubes receive more attention due to their uniqueness in efficient load transfer, which arises from the enormous surface area and high aspect ratio. Mechanical behaviour of carbon nanotubes composites is influenced by carbon nanotubes type, geometry of the carbon nanotubes and polymer nature (amorphous/crystalline/semicrystalline) and the processing method (in situ polymerization/solvent casting/melt processing) [131].

Clay Nanocomposites. Bioplastic–clay nanocomposites have been receiving extensive attention due to their improved thermal, mechanical and barrier properties as well as reduced flammability compared to their respective virgin polymers. Other positive aspect of nanoclay reinforcement is that it does not hamper the biodegradation of biodegradable polymers [132]. These clay materials were classified into many types based on their chemical nature, structure and their unique properties of swelling as well as exfoliation [133].

Functional Nanocomposites. Bio-based polymers with functional fillers such as HAp and LDH found a wide range of applications specially towards tissue engineering, drug deliver and gene therapy due to their compatibility and also non-cytotoxic and noninflammatory towards with biological system [134, 135]. Yamaguchi et al. reported fabrication of chitosan/hydroxyapatite nanocomposites using co-precipitation method. They reported the formation of flexible composites with homogenous dispersion of hydroxyapatite. Heat treatment of this composite caused the formation of hydrogen bonds between chitosan molecules and results in the enhanced mechanical properties [136].

6.9.3 Bio-nanocomposite Applications

Packaging. Bioplastics suffer from three main disadvantages: performance, processing and cost compared to the petro plastics [137–139].

Food packaging. General requirements for food packaging materials are to ensure gas barrier (O_2 , CO_2), antimicrobial function, mechanical properties, vapour barrier, optical properties, aroma barrier, thermal properties and environmentally friendly. Bio-nanocomposites open an opportunity for the use of new, high-performance, lightweight green nanocomposite materials making them to replace conventional nonbiodegradable petroleum-based plastic packaging materials. The most studied bio-nanocomposites suitable for packaging applications are starch and cellulose derivatives, polylactic acid (PLA), polycaprolactone (PCL), poly(butylene succinate) (PBS) and polyhydroxybutyrate (PHB). Bio-nanocomposites mostly

use nanoscale fillers being layered silicate nanoclays such as montmorillonite and kaolinite. The main goal is the development of high barrier properties against the diffusion of oxygen, carbon dioxide, flavour compounds and water vapour. Some bio-nanocomposites are useful to provide active and/or smart properties to food packaging systems, as exemplified by antimicrobial properties, oxygen-scavenging ability, enzyme immobilization or indication of the degree of exposure to some detrimental factors such as inadequate temperatures or oxygen levels. An important trend of food packaging applications is the enhancement of packaging performance of the green materials as well as their biodegradability, antimicrobial properties and mechanical and thermal properties [140–142].

Electronics, Sensor and Energy Applications. Polymers reinforced with engineered/functional nanostructures provide additional electrical, optical and electromagnetic shielding and magnetic properties and lead to the development of various advanced devices including light emitting, diodes, sensors, solar cells, display panels and other medical devices [143].

Bio-nanocomposites for Medical Applications. The versatility and adaptability of bio-nanocomposites enable these materials to be utilized for biomedical applications. An essential characteristic of medical biomaterials is biocompatibility, the ability to function appropriately in the human body to produce the desired clinical outcome, without causing adverse effects [134].

Bio-nanocomposites for Tissue Engineering. Bio-nanocomposites are well suited for regeneration of native tissue structures, as nanocomposite materials mimic the natural morphology of the extracellular matrix that surrounds cells. The extracellular matrix exhibits three key characteristics [144]:

1. The extracellular matrix is composed of a combination of macromolecules, such as proteins and polysaccharides, and inorganic matter.
2. Macromolecules in the extracellular matrix are typically present in a fibre form and possess an axial (length/diameter) ratio greater than 100.
3. Macromolecules in the extracellular matrix typically have nanoscale diameters of less than 500 nm.

Bio-nanocomposites for Drug Delivery. Bio-nanocomposites designed for implantation and tissue replacement/regeneration can simultaneously serve as reservoirs for drug delivery. A hydroxyapatite/collagen-alginate bio-nanocomposite has been developed as a bone filler and drug delivery vehicle; the composite is loaded with bone morphogenetic protein, a growth factor that stimulates bone formation [145]. Porous hydroxyapatite/collagen scaffolds have additionally been designed as carriers for fibroblast growth factor 2; these drug-releasing scaffolds are efficacious in stimulating both bone regeneration and cartilage regeneration in animal models of large osteochondral defects [146].

Bio-nanocomposites for Gene Therapy. Natural nucleic acid biopolymers can be intercalated into layered double hydroxides. Such composite materials can be utilized for gene therapy; for example, an ion exchange method has been used for

intercalation of DNA between the interlayers of LDH, leading to the formation of bio-nanocomposites. The DNA chains are arranged in a double helix conformation, oriented parallel to the basal plane of the LDH [147].

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