



Review Of Research



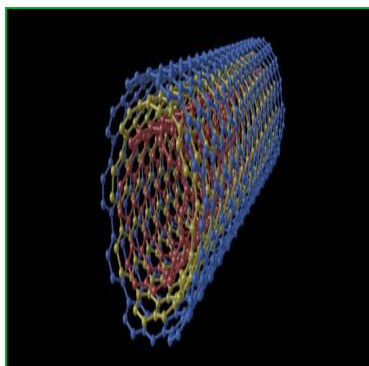
STUDIES ON NANOMATERIALS WITH CHEMICAL AND ENVIRONMENTAL APPLICATIONS

Shree Narayan Jha

Professor and Head , Dept. of Chemistry , C.M.Science College, Darbhanga .

ABSTRACT

Unusual physicochemical properties of semiconductor nanoparticles gave rise to various speculations concerning their practical implementations. Sensors and systems of light energy storage, electronics and photodetoxication of waste waters, non-linear optics and catalysis, and lithography and lasers are considered as possible fields of uses of semiconductor nanoparticles.



However, in most cases it is premature to discuss practical application of semiconductor nanoparticles. Only investigations in the field of photocatalysis carried out so far make it possible to consider the possibilities of practical use of nanoparticles.

Key-words : Nanoparticles , Semiconductor nanoparticles & Photocatalysis

INTRODUCTION

A decrease in the size of semiconductor nanoparticles results in a shift of the conduction and valence bands towards more negative and more positive potentials, respectively. It seems to be tempting to use the possibility of controlling the redox properties of nanoparticles by changing their size in photocatalytic systems of water decomposition and the, synthesis and destruction of organic compounds. Additionally, the fact that nanoparticles have a large specific surface area is of importance for carrying out photocatalytic processes on the surface of semiconductors. The small size of semiconductor nanoparticles can provide high efficiency of surface trapping of light-generated electrons and holes, thus increasing the probability of a photocatalytic process on the surface of the semiconductor.[1-3]

Indeed, typical recombination time of electrons and holes in semiconductors, τ , is about 10^{-10} s. For typical diffusion coefficient of electrons and holes $D \approx 0.1 \text{ cm}^2/\text{s}$, we have that during the lifetime electrons could diffuse over $R_s \approx \sqrt{\tau D} \approx 300 \text{ nm}$. Thus, most electrons and holes generated inside crystal could reach its surface only if the size of the crystal is less than 300 nm. And finally, the absorption coefficient of semiconductors is about 10^5 cm^{-1} . That means that light intensity drops substantially inside the crystal in a thin 10^{-5} cm layer.[4]

Thus only 100 nm thin layers semiconductors or nanocrystals with an average size of 100 nm provide efficient participation of semiconductor molecules in light absorption. However, it should be noted that the semiconductor nanoparticles used in photocatalytic studies are, as a rule, rather large ($\geq 10^2$ nm) and no pronounced quantum size effects are observed for them. A correlation between the photocatalytic activity of TiO₂ nanoparticles and their size was found only in one study.[5-6]

PHOTOCATALYTIC PROCESS WITH SEMICONDUCTOR NANOPARTICLES

High quantum efficiencies of photocatalytic processes with the participation of nanoparticles, are achieved by designing specifically ordered structures based on these particles. The idea of using nanoparticles for photocatalytic water decomposition was first proposed by A. Henglein about twenty years ago who has demonstrated the possibility of photoreduction of methyl viologen in colloidal solutions of semiconductors (TiO₂, and metal chalcogenides). Various dyes could also be photoreduced by nanoparticles.

For dyes, photoexcitation of nanoparticles results in one electron reduction of dye molecules followed by the formation of a leuco-product. The possibility of using nanoparticles in photocatalytic synthesis of organic compounds has also been demonstrated. Photocatalytic synthesis of an amino acid and the Kolbe reaction were carried out by the interband excitation of TiO₂ nanoparticles coated with platinum. Photocatalytic processes of oxidation of a number of alkanes, arenes, amines, and alcohols on the surface of nanoparticles are also known.

Light-generated holes can be used in photooxidation of various substrates on the surface of nanoparticles until their complete destruction. The use of semiconductor nanoparticles for photochemical purification of water from various contaminants seems to be rather tempting and attracts particular interest of researchers in recent years. Systems based on TiO₂ seem to be the most promising for photocatalytic mineralisation of organic compounds in waste waters. Of the three major structural modifications of TiO₂ (rutile, anatase, and brookite), anatase is the most photocatalytically active.

The difference in the photocatalytic activity of different TiO₂ modifications is most likely due to their different crystal structures. Anatase has a bandgap of 3.2 eV and UV radiation needs to be applied for the electronic excitation of this compound; hence, only a small portion of the sunlight can be used for the photocatalytic processes involving anatase to occur. Nevertheless, among a wide variety of semiconductor materials, TiO₂ is most often used as a photocatalyst due to the high oxidation ability of its photogenerated holes ($E^\circ = 2.9$ V vs. NHE at pH0), its stability in aqueous solutions, safety for living organisms, and low price.

DISCUSSION

Titanium dioxide has long been used in paint industry as the photocatalyst in the oxidation of organic substances. This property of TiO₂ has determined its wide use as the white pigment. Later, attempts were made aimed at using TiO₂ for photodecomposition of water. However, its efficiency appeared to be low because of a low quantum yield of charge photoseparation. Recently, the problems of the environment protection forced many researchers to direct their attention again to the systems based on TiO₂ and to make efforts to use TiO₂ for photocatalytic mineralisation of ecologically hazardous organic compounds both in aqueous media and gases.

The scheme of the photocatalytic process involving semiconductor nanoparticles is shown in Figure 1. The absorption of a light quantum with an energy of $h\nu$, that exceeds the bandgap of the semiconductor, results in the primary charge separation. In this case, the nanoparticle can be considered as a short-circuit electrode initiating the processes of oxidation and reduction of the substrate molecules adsorbed on the surface. The oxidation and reduction of nonadsorbed substrate molecules is possible if the primary electrons and holes are transformed into stable intermediates on the surface of nanoparticles. Good results have been obtained for the detoxication of wastewaters containing hydrocarbons, phenols, chloroaromatic compounds, surfactants, and nitro compounds.

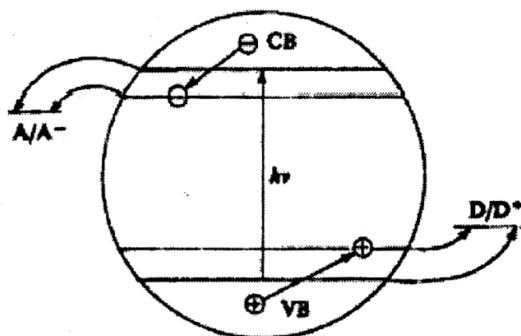
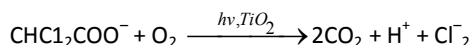


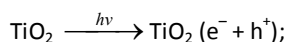
Figure 1. Schematic view of charge separation processes in a semiconductor nanoparticle.

A typical example of photocatalytic mineralisation is the oxidation of the dichloroacetate ion by oxygen in water:



The detailed mechanism of the processes of the photoreduction of acceptors and photooxidation of donors with the participation of TiO₂ nanoparticles includes a large number of events occurring both in the bulk and on the surface of nanoparticles; the basic events are outlined below (Figure 2):

Photostimulated generation of electrons and holes in the conduction and valence band, respectively

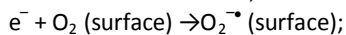
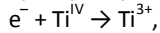
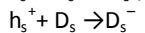
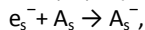
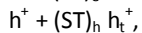
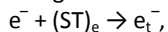


charge carrier migration to the surface of the nanoparticle



(e_s⁻, h_s⁺) → surface-migration;

charge carrier trapping by acceptor centers and into shallow traps (ST)



charge carrier recombination (radiative and nonradiative)

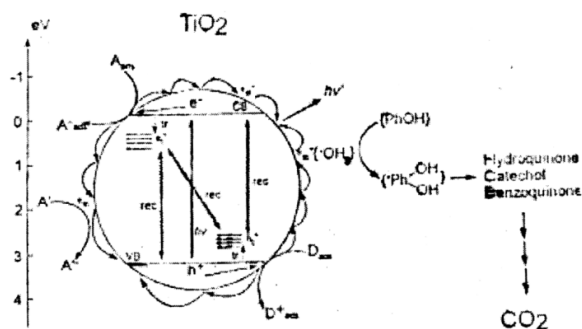
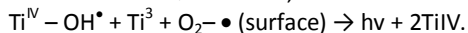
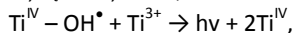
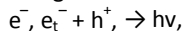


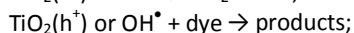
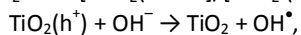
Figure 2. Schematic view of processes of photoreduction of electron acceptors and photooxidation of electron donors by TiO₂ nanoparticles.

It is usually assumed that the photooxidation of organic substrates in aqueous suspensions of TiO₂ can occur by both the direct interaction of the holes with the substrate molecules and the formation of the OH• radicals in the reaction of the holes with H₂O or OH⁻.

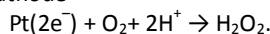
An idealised illustration of photocatalytic processes occurring on the surface of a conducting electrode with the participation of films composed of heteronanoparticles is exemplified in Figure 3 with TiO₂/SnO₂ films.

The position of the bottom of the SnO₂ conduction band is lower than that of the TiO₂ conduction band (0 and -0.5 V vs. NHE at pH 7, respectively). This causes the light-generated electrons to transfer from TiO₂ to SnO₂. The holes move in the opposite direction and are accumulated on the TiO₂ nanoparticles. As a result, an increase in the quantum efficiency of charge photoseparation and, hence, in the efficiency of the oxidation of donor molecules in solution can be observed in the structure under consideration. High efficiency of the TiO₂/SnO₂ film was demonstrated experimentally in the example of photocatalytic degradation of dyes. The overall processes occurring at the anode and cathode can be described by the following scheme:

at the photoanode



at the cathode



Porous nanostructured films possess high adsorption capacity to organic dyes and organometallic compounds. Large specific surface area of such films allows adsorption of a considerable amount of a dye. The use of these properties of the nanostructured films makes it possible to increase substantially their photocatalytic efficiency due to sensitisation into the visible region.

Nanomaterials have numerous commercial and technological applications. Table 1 summarises different applications of nanoparticles and nanomaterials.

Table 1. Nanomaterials and their applications in science and technology

Nanostructures	Applications
Quantum dots	Catalysis
Nanoclusters /nanoparticles	Sensors
Nanotubes	Separation technologies
(Ultra)thin films / layers	Electronics (Q computer)
Nano- or mesoporous materials	Information storage
Nanowires	(magnetic, electronic,
DNA and other biological structures	optical, electrooptical
Nanoreactors (e.g. micelles)	devices or switches...)
Nanocomposites/hybrid materials	Adhesives and Coatings
Nanoactuators	Medicine (drug delivery
Nanostructured	layers or interfaces systems...)
	Materials (ceramics,...)
	Energy (batteries, fuel cells, solar
	cells,...)
	Optics
	Paints and Dyes
	Cosmetics

CONCLUSION

Colloidal solutions of nanoparticles are suitable objects for the demonstration of the possibility of their utilisation in photocatalysis. However, the practical use of colloidal solutions is difficult because of the need to separate nanoparticles from the solution after the completion of the photocatalytic process. Thin layers of nanoparticles

adsorbed on a carrier seem to be much more promising, especially the films composed of hetero-nanoparticles shown in Figure 3. These films have many advantages over films composed of nanoparticles of the same nature, namely, the expanded spectral sensitivity region of the large-bandgap semiconductor nanoparticles, increased quantum efficiency of charge photoseparation and high efficiency of spectral sensitisation of films by dyes.

REFERENCES

1. Arnold W. H. "CMOS device fabrication and the evolution of optical lithographic exposure tools" *Microelectron. Eng.* 46 7–9. 1999
2. Binning G., Rohrer H., Gerber Ch., and Weibel E. "Surface Studies by Scanning Tunneling Microscopy" *Phys. Rev. Lett.* 1982
3. Cai X., Klauke N., Glidle A., Cobbold P., Smith G. L., and Cooper J. M. "Ultra-Low-Volume, Real-Time Measurements of Lactate from the Single Heart Cell Using Microsystems Technology" *Anal. Chem.* 2002
4. Chang, W., G. Skandan, H. Hahn, S. C. Danforth, B. H. Kear, *Nanostructured Mater.* 1994, 4, 345 Chou S. Y., Krauss P. R. and Renstrom P. J. "Nanoimprint lithography" *J. Vac. Sci. Technol. B* 1996
5. Choy K. L. "Chemical vapour deposition of coatings" *Prog. Mater. Sci.* 2003
6. Drazic S., G., Gogolides E., Argitis P., and Cefalas A. C., "The challenges of 157 nm nanolithography: surface morphology of silicon-based copolymers" *Mater. Sci. Eng. C* 23 995–999. 2003