SEMICONDUCTORS AND THEIR MODIFICATION FOR THE EFFECTIVE PHOTODEGRADATION OF POLLUTANTS FROM AQUEOUS SOLUTION

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Abstract

Semiconductors play an important role in photocatalysis. This review highlights the role of various semiconductors in the photodegradation of hazardous pollutants from aqueous solution, and their modification for achieving better efficiency towards the application of effective photocatalytic degradation of pollutants from its aqueous solution.

Introduction

The removal of organic dyes in waste effluents is of great environmental importance because they are widely used in industries such as textiles, paper, rubber, plastics and cosmetics. It is estimated that about 15% of the total world production of dyes is lost during the dyeing and finishing operations and is released in the textile effluents. The colour produced by organic dyes in water, is aesthetically unpleasant, affects the plant life and thus the ecosystems become slowly destroyed[1-3].

There are many processes extensively used for removing the dye molecules from wastewater such as incineration, biological treatment, ozonation, adsorption on solid phases, coagulation, foam floatation, electrochemical oxidation, Fenton or Photofenton oxidation, membranes, *etc.* [4,5]. However, the above processes have some kind of limitations, *viz.* the incineration can produce toxic volatiles; biological treatment methods demand long period of treatment and bad smells; ozonation presents a short half-life. In ozonation the stability of ozone is affected by the presence of salts, pH and temperature and adsorption which results in phase transference of contaminant, not degrading the contaminant and producing sludge. Most of these methods are non-destructive, but they generate secondary pollution, because in these techniques the dyes are transferred into another phase and not degrading the pollutants and this phase has to be regenerated[6-8]. All the above effects dictate us the necessity to find an alternate method for effective treatment of wastewater contaminated by organic dyes.

Now-a-days, heterogeneous photocatalytic processes are the most efficient method for destroying organic pollutants in aqueous media. Different semiconductor photocatalysts have been used in the field of pollutants degradation such as TiO_2, ZnO, ZnS, CdS, CuO, CeO_2, WO_3, Fe_2O_3, SiO_2, Al_2O_3 etc. Among the various semiconductors employed, TiO_2 and ZnO are known to be good photocatalysts for the degradation of several environmental contaminants due to their high photosensitivity and large band gap, *i.e.* high driving force for reduction and oxidation processes[5–10].

Basic electron energy features of a semiconducting material.

Promotion of an electron from the valence band to the conduction band can be brought about by the absorption of a photon of ultra-bandgap light, i.e. $hv \geq E$BG. The subsequent fate of this photogenerated electron–hole pair, e^-h^+, is determines largely the overall photoactivity of the semiconductor material. More often, the electron–hole pairs recombine to generate heat, and if this is the only process that occurs, the semiconductor will show no photoactivity. Electron–hole recombination is promoted by defects in the semiconductor materials and thus most amorphous semiconductor materials show little if any photoactivity. The major processes that occur on a semiconductor particle upon absorption of a photon of ultra-bandgap light, i.e. $hv > E$BG. Thus, the initial absorption process creates an electron, in the conductance band (CB), and a hole in the valence band (VB) which can then diffuse and/or migrate to the surface where they can react. The possible fates of the photogenerated electron–hole pairs include:

(i) recombination in the bulk, i.e. process

(ii) or at the surface, process

(iii) reduction of a suitable electron acceptor (A) adsorbed on the surface by the photogenerated electron, process (c), and

(iv) oxidation of a suitable electron donor (D) adsorbed on the surface by the photogenerated hole, process (d).

separate ways to the surface of the semiconducting material then it is possible for them to interact with surface species. Under these circumstances, if an electron donor, i.e. D such as ethanol, methanol, and EDTA, is present at the surface, then the photogenerated hole can react with it to generate an oxidised product, D^+. Similarly, if there is an electron acceptor present at the surface, i.e. A, such as oxygen or hydrogen peroxide, then the photogenerated

conductance band electrons can react with it to generate a reduced product, A^-. The overall reaction can be summarised as follows:
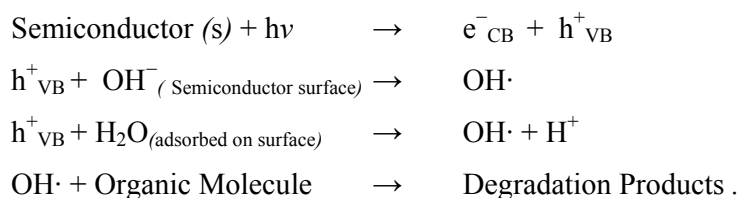
$$A + D \quad \xrightarrow[hv \geq E\text{BG}]{\text{semiconductor}} \quad A^- + D^+ \qquad (1)$$
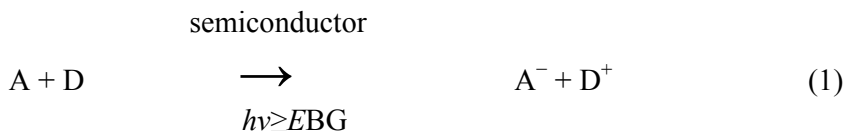
If the change in Gibbs free energy for reaction (1) is positive, the overall process is an example of semiconductor photosynthesis[11]. If, as is more usually the case, the change in Gibbs free energy gives free energy is negative, then it is an example of semiconductor photocatalysis[11]. Semiconductor photocatalysis is one of the major aspects of semiconductor photochemistry currently undergoing heavy commercial exploitation. Many of the current commercial systems that utilise reaction (1) employ the semiconductor photocatalyst to drive oxidation of organic pollutants by oxygen[12].

$$\text{i.e. organic} + O_2 \quad \xrightarrow[hv \geq E\text{BG}]{\text{semiconductor}} \quad CO_2 + H_2O + \text{mineral acids}$$
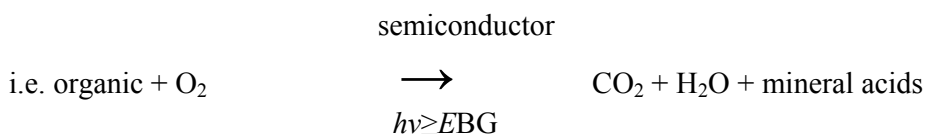
Semiconductor photocatalyst under light radiations

Heterogeneous photocatalysis is capable of degrading many classes of pollutants, but requires ultraviolet light source and thus may be energy intensive. Photocatalytic oxidation processes are usually referred to as advanced oxidation processes (AOP). When a photon with an energy which matches or exceeds the bond gap energy of the semiconductor is incident on a semiconductor surface, a conductive band electron will jump to its valence band leaving a positively charged hole behind. The initial step in this type of photo-oxidation process is believed to be the formation of free hydroxyl radicals[13-15]. Hydroxyl radicals are generated by the oxidation of water (OH^- ions) at the valence band positively charged holes.

Semiconductor (s) + hv $\rightarrow$ e^-_{CB} + h^+_{VB}

h^+_{VB} + $OH^-_{(\text{Semiconductor surface})}$ $\rightarrow$ $OH\cdot$

h^+_{VB} + $H_2O_{(\text{adsorbed on surface})}$ $\rightarrow$ $OH\cdot + H^+$

$OH\cdot$ + Organic Molecule $\rightarrow$ Degradation Products .

On the other hand, the dissolved O_2 molecules are transformed to anionic superoxide

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$(O^-_2\cdot)$ radicals *via* electrons from conductive band.

$$e^-_{CB} + O_2 \text{ (adsorbed on surface)} \rightarrow O^-_2\cdot .$$
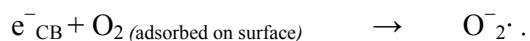
The most commonly studied photocatalysts are TiO_2, ZnO, ZnS and CdS. Additionally, In_2O_3, $SrTiO_3$, SnO_2 and WO_3 have also been used as photocatalysts but all showed lower levels of photoactivity, and SiO_2 and MgO are found to be inactive. Since most metal oxides and sulphides can undergo irreversible photocorrosion on the surface, these types of semiconductors are not suitable for long term treatment processes. However, TiO_2 is an inert oxide and can be reused for several times[16].

Anatase-type TiO_2 since its photocatalytic activity gives promising possibilities for the decomposition of various organic pollutants. An efficient way to improve the catalytic performance could be by supporting TiO_2 on some inorganic substrates[17-19]. The undesirable recombination of electrons and holes, and low efficiency of non-modified semiconductors under irradiation in the visible region indicate the needs to developing the modified semiconductors. Some types of modification of semiconductors for enhanced the photocatalytic efficiency of semiconductors given as follows.

Modification of semiconductor

Coupled semiconductors

The coupling of two semiconductors possessing different redox energy levels for their corresponding conduction and valence bands provides an attractive approach to achieve more efficient charge separation, increase the lifetime of the charge carriers and enhance the efficiency of the interfacial charge transfer to adsorbed substrates.

If two semiconductors are coupled, a photoelectron will be generated on semiconductor-1 can be injected into the (inactivated) another semiconductor-2 conduction band while the photohole remains on the semiconductor-1. Simultaneous activation of both semiconductors may lead to simultaneous electron transfer from Semiconductor-1 to Semiconductor-2 and hole transfer from Semiconductor-2 to Semiconductor-1. Several coupled systems have been examined by a variety of photochemical and photophysical methods[20].

Photosensitization

The sensitized photocatalytic process has some possible advantage over direct photocatalysis. When molecules are adsorbed onto the surfaces, their translational mobility is

considerably reduced. This reduction in dimensionality has important consequences in reaction kinetics. It extends the range of excitation energies of the semiconductor into visible region, making them for complete use of solar energy and could promote selective removal of colored pollutants. In systems with low concentrations of colored pollutants it may increase the sensitivity of the photocatalytic process for removal of colored pollutants. It may have the ability to drive other reactions, which may make sensitized photocatalysis which is a large-scale process[21].

Three basic processes are involved in the dye sensitizing semiconductor. First, dye sensitizer adsorbs onto the surface of semiconductor; second, adsorbed dye is excited by visible light; and finally, electrons are injected from the excited dye with high mobility into the conduction band of semiconductor. Conjugated polymer was used as a photosensitizer to modify semiconductor. Photoinduced electron transfer from p-conjugated polymers to nanocrystalline semiconductor was experimentally demonstrated by photoinduced absorption (PIA) spectroscopy and photoinduced electron spin resonance (ESR). Although there are plenty of conjugated polymers, so far little work has been done on using conjugated polymer modified TiO_2 to degrade organics. This may be due to two challenging problems: (1) the stability of conjugated polymers is poorer than that of dyes (for example, poly (p-phenylenevinylene) (PPV) (PPV) is readily oxidized under room light in the air[22] is readily oxidized under room light in the air. (2) The electron mobility of conjugated polymers is much lower than that of dyes[23,24].

Metal doped semiconductors

Commercial worldwide interest in the technology of metal doped semiconductor is explicit, but is still in pilot, or lab development, in most cases. The process fundamentals consist in hitting the semiconductor with radiation of energy near to, or greater than its band gap energy, generating high energy electron–hole pairs, which initiate the heterogeneous photocatalytic reactions. However, undesirable recombination of electrons and holes, and low efficiency under irradiation in the visible region are the two main drawbacks associated with the use of non-modified semiconductor. To overcome these limitations, one possible solution consists in doping the semiconductor with d-metal ions/oxides.

The modification by transition metal has been proved as an effective technique to improve the separation of photo-induced electron–hole pairs and extend its photoresponse to

visible region by modifying its surface structure, surface properties, and composition and so as to improve its photocatalytic activity in visible/solar light[25].

Transition metal doping with semiconductor enhances the interfacial charge-transfer reactions of semiconductor bulk phase and colloidal particles can also increase the photocatalytic activity of TiO_2. Although some transition metal ion doping is somewhat difficult to generalise for all systems (for e.g. Fe^{3+}, V^{4+}, Cr^{3+} doping), the co-deposition of noble metal islands on TiO_2 has been shown to be useful in improving the efficiency of photocatalysis. Au, Pt, Pd, Rh and Ag loading have been performed in several studies[16, 26-29].

Modification of semiconductor with metals and metal oxides such as Pt, Au, Pd, Ni, Ag, and also with carbon nanotubes and graphene has been found to enhance the catalytic and photocatalytic properties and has been exploited in antimicrobial coatings, photocatalytic hydrogen generation from alcohol, and in removal of xylene from air. Partial substitution of O in the lattice with Nor C leads to a shift of the absorption edge towards visible wavelengths thus, enhancing further the photocatalytic efficiency.

Non-metal doped semiconductors

However, the photocatalytic activity of metal doping was impaired by bad thermal stability and increased carrier-recombination possibility, another approach, from which TiO_2 obtained the desired narrow band gap, is the doping of TiO_2 with non-metal elements including C, N, S, F, B, and I or co-doping with N and F. By these methods, the absorption edge of TiO_2 could shift to the visible region and the doped TiO_2 showed photocatalytic activities under visible light irradiation. But, the inorganic modified TiO_2 could not adequately utilize visible light due to their poor visible absorption. Recently, more and more attention has been paid to organic modification on TiO_2 surface to prepare visible-light responsive TiO_2 photocatalysts. Generally, there are two types of organic modification methods. One is based on the chemical/physical adsorption of dye molecules on TiO_2 surface for construction of dye-sensitized photocatalysts that can work under visible light irradiation. Another approach utilizes the chemical reaction betweean Ti–OH and phenolic hydroxyl of organic compounds (not dye), such as catechol, salicylic and binaphthol to form surface complexes on TiO_2 surface and to realize visible light absorption. So produced organic modified TiO_2 was also a visible light activated photocatalyst. However, there were some disadvantages in the above mentioned organic modified methods. As to the dye-sensitized

TiO$_2$ photocatalysts, the dye molecules are only adsorbed on TiO$_2$ surface and no stable chemical bonds are formed between them. As a result, the dye molecules are easy to desorb from TiO$_2$ surface during photocatalytic process, which can decrease its photocatalytic activity. For the later method, although organic molecules are grafted on TiO$_2$ surface *via* firm covalent bonds, the obtained organic modified TiO$_2$ showed very weak absorption in visible region. Thus, if a synthetic strategy can inherit all the advantages of above two methods, it can be very desirable to enhance the visible photocatalytic performance of TiO$_2$[30-32].

Carbon doped semiconductors

Carbon nanotubes, since first found by Iijima[33], has attracted great interest for its superlative mechanical, thermal and electronic properties[34]. It is a novel adsorptive material for toxic chemicals, e.g., phenol, aniline[35,36], hydroxyl/amino-substituted aromatics[37], and other related polar and nonpolar organic chemicals[38]. Moreover, when placed in microwave field, multiwalled carbon nanotubes (MWCNTs) show strong microwave absorption capacity[39, 40]. Titania coated carbon nanotube film or particles prepared by various methods have been proposed for many years, e.g., electrospinning[41], sol-gel[42], metal-organic chemical vapor deposition[43], vapor phase method[44] and hydrothermal method[45]. The hydrothermal method for preparing titania could produce perfect particles with anatase phase at lower annealing temperature. To date, studies on titania coated carbon nanotubes have been focusing on the properties such as heterojunction[46,47] or photosensitization[48], for these catalysts could widen light response range by photosensitization effect of carbon nanotubes and minimize recombination tendency by Schottky barrier between TiO2 and carbon nanotubes[49].

A priori, it is believed that nanotitania coated carbon nanotubes could enhance the microwave-assisted photocatalytic efficiency than titania due to stronger microwave adsorption of carbon nanotubes. Organic chlorine compounds as a group of common pollutant in water, are always chosen to be target compounds for pollution control in recent years[50-53].

β-Cyclodextrin modified semiconductors

TiO$_2$ can only use less than 5% of the available due to its large band gap (3.2 eV). Furthermore, the high electron-hole recombination rate also makes it a relatively inefficient photocatalyst. Successful improvement of TiO$_2$ performance requires the lowering of the

band gap to use visible light and restricting the charge-hole recombination to enhance quantum efficiency.

Dye pollutants can be bleach under visible irradiation through photosensitized degradation on a semiconductor surface. However, only an adsorbed dye molecule can inject the charge from its excited state to the semiconductor's conduction band. Thus, the degradation is usually inefficient. Cyclodextrin (CD) modified TiO_2 has attracted renewed interest since Willner and colleagues observed that β-CD could stabilize TiO_2 colloids and facilitate interfacial electron transfer processes[54-56]. Excellent literature has been published to elucidate the effect of β-CD on TiO_2 photochemical properties[57-61]. All previous work suggests that β-CD plays electron-donating and hole-capturing roles when linked to TiO_2 colloids, which lead to charge-hole recombination restriction and photocatalytic efficiency enhancement. Some previous papers have reported the stimulative effect of cyclodextrin on the photocatalytic degradation of organic pollutants in TiO_2 suspensions[62-65].

However, it is difficult to recover cyclodextrin after the reaction because β-CD is an expensive reagent. Furthermore, synthesizing β-CD modified TiO_2 colloids is complicated and time-consuming, and the colloids were only stable in acidic conditions. Therefore, it is worthwhile to synthesize a β-CD grafted TiO_2 hybrid powder using a new method and investigate its catalytic performance[66].

Conclusion

Semiconductors have been widely investigated and are promising materials for efficient photocatalytic degradation. Therefore it is necessary to developing the modified semiconductors and improves the efficiency of the semiconductor. It is still need to find alternate modification methods.

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