

A Review-Catalytic Activity of Metal-fullerene/TiO₂

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Abstract: The present review paper seeks to offer an overview of the dramatic trend in the use of the Metal-fullerene/TiO₂ composites for catalytic activities. In this review, discolourization effect of iron treated fullerene based titania composites. Its main objective is to report on the different contents of iron of Metal -fullerene/TiO₂ composites, under different environment for different dyes.

Keyword: Metal -fullerene/TiO₂, catalytic activity, TEM, fullerene/TiO₂

1. Introduction

Wastewater effluents from textile and other dyestuff industry contain a large number of toxic dyes and industrial dyestuffs which constitute the largest groups of organic compounds, they are represent an increasing environmental danger.^[1,2] If these effluents are improperly treated, they will pose badly threats to all species on the earth because the hydrolysis of the pollutants in the wastewater can produce a great deal of toxic products.^[3] So the disposal of dyestuff wastewaters is necessary to settle the problem of environmental pollution.^[4,5] Physical, chemical, and biological methods are available for treatment of such waste; however, they are not sufficient and advantageous. Therefore applying photocatalytic oxidation (PCO) technique seems to be reasonable. PCOs are attractive in providing a promising and competitive solution for the abatement of numerous hazardous compounds in wastewater including fenton or photo-assisted fenton process, ozone or/and peroxide photolysis, and semiconductor photocatalysis process. What is the photocatalytic oxidation (PCO) technique?

The treatment of air borne pollutants by semiconductor photocatalysis is one of the fast growing areas in term of academic research and commercial activity. The key material in PCO technique is an agent named TiO₂. TiO₂ particles are used as photocatalyst because it is non-toxic, chemically stable, and possesses relatively high photocatalytic activity. Laboratory studies have demonstrated TiO₂ as the most efficient photocatalyst for organic oxidative degradation for the reason that it features:

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- (1) Deep and thorough action under low temperature: Just in room temperature, TiO_2 is active enough to completely oxidize organic contaminants in water, air and soil into harmless carbon dioxide, water, and simple mineral acids. This is different from the traditional catalyzed oxidation, which requires a temperature at least hundreds of degrees high.
- (2) Effective for a wide spectrum of organic contaminants: TiO_2 has been proved to be effective for kinds of organic varying from hydrocarbon to carboxylic acid. The 114 kinds of pollutants published by the US EPA (Environmental Protection Agency) all can be treated by TiO_2 . Atomic organic compounds, such as dyes, nitrides and organic pesticides are also within the capability of TiO_2 .
- (3) Strong oxidation ability: Even some of those organics which are hardly oxidized by ozone, such as trifluoro methane, carbon tetrachloride and hexachlorobenzene can also be dealt with by PCO. This is because the oxidation ability is far stronger than that of ozone, hypochlorous acid, potassium permanganate. This feature is rather meaningful for the degradation of obstinate organics.
- (4) Permanent function: TiO_2 is not consumed in PCO reactions for it can deoxidize itself under UV irradiation and resumes its high oxidation efficiency. It can be used permanently without refilling.

The photocatalytic process with using TiO_2 photocatalyst is very promising for application in the water purification, because many hazardous organic compounds can be decomposed and mineralized by the proceeding oxidation and reduction processes on TiO_2 surface. Among the photocatalysts, TiO_2 (in anatase phase) has been most widely used because it is easily available, inexpensive, non-toxic, and shows relative high chemical stability. However, TiO_2 has some typical shortcomings to render its wide application in partice:

- (1) It is difficult to separation of TiO_2 from aqueous phase so the TiO_2 powders are easy to lose and not suitable for recucling. This problem is somewhat overcome by attempts to immobilize TiO_2 on different supports, such as glass fibers, glass, quartz, and stainless steel, etc.
- (2) Rate of the electron or hole induced redox reaction.
- (3) Relatively low quantum yield due to the rapid recombination of charge carriers. The rapid recombination of photogenerated electron (e^-)/hole (h_{VB}^+) pairs, which significantly diminishes the efficiency of photocatalytic reactions.

For the first problem a great effort has been spent to prevent the recombination of charge carrier in the semiconductor and to improve the photocatalytic efficiency of TiO_2 including: (1) doping metal ions, in particular transition metal ions (iron, chromium, copper, vanadium and cobalt) into the TiO_2 lattice,^[6] (2) dye photosensitization on the TiO_2 surface^[7] and (3) deposition of noble metals^[8] and so on.

- (4) TiO₂ photocatalysts are active under UV light irradiation shorter than 390 nm; thus only a small fraction (3–5%) of the solar irradiation can be utilized for the degradation of environmental pollutants, because of their wide band gap.

Although the TiO₂ membrane immobilized on the glass surface has the advantages such as high photodegradation efficiency, its major shortcoming is that the adhesion force between the TiO₂ membrane and the glass is very weak, so the TiO₂ is easy to fall off, which causes the declining of the photodegradation efficiency. The kind of metal supporter is expensive in cost and has difficulty for immobilization. During the recent years, some sorbents as the supporter of photocatalyst have drawn the attention of researchers. These sorbents used often contain silica gel, zeolite and activated carbon.^[9-11] Compared with silica gel and zeolite, activated carbon has the superiority of lower cost and higher adsorption capacity.

To widen the area of their practical application to indoor use, it has been considered that photocatalysts which can be activated under visible light with high yields would be indispensable. TiO₂, having an energy band gap of about 3.2eV, mostly absorbs the ultraviolet portion of the solar spectrum and only a small amount of visible light.^[12] Thus, for efficient photocatalytic activity it is necessary to extend the photoresponse of TiO₂ to the visible spectrum by modification of its optical properties. Another problem is the high recombination rate of photo-generated electron-hole pairs which can be limited by introducing charge traps for electrons and/or holes, thus prolonging the recombination time. Many methods have been proposed to solve these problems, but doping TiO₂ with foreign ions is one of the most promising strategies for sensitizing TiO₂ to visible light and also for forming charge traps to keep electron-hole pairs separate.^[13]

Two approaches have been applied to extend the shift of photoresponse toward the visible range of the titania materials: one direction is the doping of metal ions, anions and synthesis of the reduced form of TiO_x photocatalysts;^[14-16] and the other is ion implantation.^[17] However, the ion implantation is quite expensive and possible only with high crystalline TiO₂. Metal element doping is a typical approach to extend the spectral response of the titanium dioxide to the visible-light region by providing defect states in the band gap. Some metal elements such as Fe, Cu, Mn, Cr and Ni have been employed to tune the electronic structure and enhance the photocatalytic activity of the titanium dioxide.^[18-20] Doping with metal ions may extend the photo-response of TiO₂ into the visible spectrum by introducing additional energy levels in the band gap of the TiO₂. Among these transition metals, Fe, Cu, and Mn are able to trap both electrons and holes, while Cr and Ni are capable of trapping only single-charge carriers. The Fe³⁺ ion with the band gap of 2.6 eV seems to be an interesting dopant for extending the absorption threshold toward the visible range. The prepared Fe³⁺ ion doped titania showed a high activity for the photocatalytic under visible light due to the red shift toward the visible range.

2. Fullerene

A fullerene is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube. Spherical fullerenes are also called buckyballs, and cylindrical ones are

called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings.^[21]

The first fullerene to be discovered, and the family's namesake, buckminsterfullerene (C_{60}), was prepared in 1985 by Richard Smalley, Robert Curl, James Heath, Sean O'Brien, and Harold Kroto at Rice University. The name was an homage to Buckminster Fuller, whose geodesic domes it resembles. The structure was also identified some five years earlier by Sumio Iijima, from an electron microscope image, where it formed the core of a "bucky onion."^[22] Fullerenes have since been found to occur (if rarely) in nature.^[23]

The discovery of fullerenes greatly expanded the number of known carbon allotropes, which until recently were limited to graphite, diamond, and amorphous carbon such as soot and charcoal. Buckyballs and buckytubes have been the subject of intense research, both for their unique chemistry and for their technological applications, especially in materials science, electronics, and nanotechnology.

C_{60} have attracted extensive attentions for their various interesting properties due to their delocalized conjugated structures and electron-accepting ability. One of the most remarkable properties of C_{60} in electron-transfer processes is that it can efficiently arouse a rapid photoinduced charge separation and a relatively slow charge recombination.^[24]

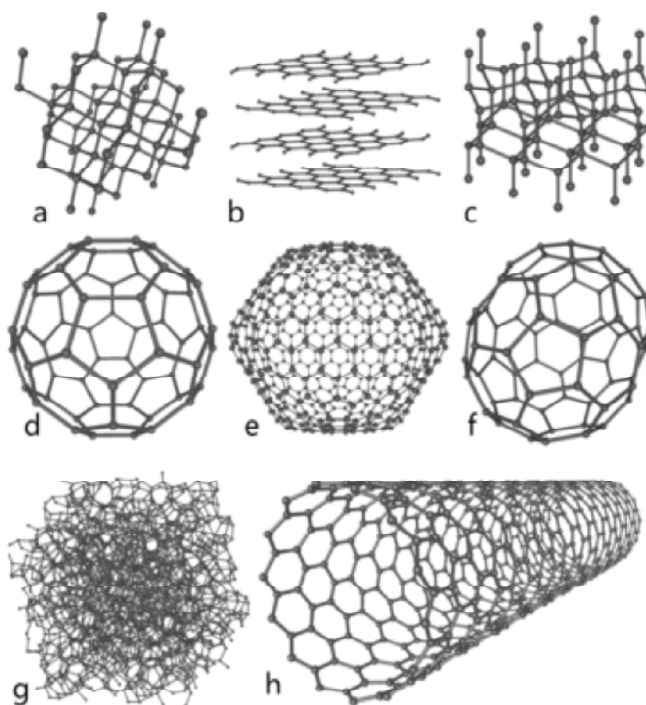


Figure 2: Some allotropes of carbon: (a) diamond; (b) graphite; (c) ionsdaleite; (d-f) fullerenes (C_{60} , C_{540} , C_{70}); (g) amorphous carbon; (h) carbon nanotube.

Thus, the combination of photocatalysts and C₆₀ may provide an ideal system to achieve an enhanced charge separation by photoinduced electron transfer. Some of the fullerene-donor linked molecules on an electrode exhibited excellent photovoltaic effects upon photo-irradiation.^[25–27]

Conjugated two-dimensional π -system, they are suitable not only for synthetic light-harvesting systems, but also for efficient electron transfer, because the uptake or release of electrons results in minimal structural and solvation change upon electron transfer. In contrast with the two-dimensional porphyrin π -system, fullerenes contain an extensively conjugated three-dimensional π system. Fullerene is described as having a closed-shell configuration consisting of 30 bonding molecular orbitals with 60 π -electrons, which is also suitable for the efficient electron transfer reduction because of the minimal changes of structure and solvation associated with the electron transfer. C₆₀ is one of the promising materials because of its band gap energy, about 1.6–1.9 eV. It has strong absorption in the ultraviolet region and weak but significant bands in the visible region. It is well established that C₆₀ films exhibit a fairly high photosensitivity. Fullerene based solids have been discussed as prospective materials for photovoltaic cells, and heterojunctions of C₆₀ with many organic semiconductors or conductive polymers have shown promising photovoltaic effects. The C₆₀ film is an n-type semiconductor and many organic semiconductors are p-type, thus by fabricating organic semiconductor/C₆₀ in contact, a p-n junction should be formed. However the quantum efficiencies of these devices are still considerably lower than unity.^[28,29] Although there are many publications on C₆₀ with organic hole conductors, to date there has been no report concerning the fabrication of devices comprising C₆₀ with inorganic hole conductors. However, fullerene possesses poor light-harvesting capability, exhibiting only low values of the incident photo-to-photocurrent efficiency. In order to overcome these problems, we used the properties of metal-oxide-based inorganic surfaces as metal doped fullerene. The doping of alkali metals, alkali-earth metals, and other elements brings about a rich variety of phenomena: superconductivity, ferromagnetism, antiferromagnetism, etc. And have become attractive for optical, electronic, photovoltaic, artificial photosynthesis, and solar cell applications.^[30] Fullerene cage is expected to be charged as a result of electron transfer from the metal atom. It is in fact known that electron transfer plays an important role in the superconductivity of metal-intercalated fullerene materials, such as Rb₃C₆₀ and K₃C₆₀.^[31]

This report is a short overview of discolourization effect of different metal treated fullerene based titania composites. Its main objective is to report on the different metal treated fullerene/TiO₂ composites, under different environment.

3. Oxidation for Fullerene

The FT-IR spectrum of fullerene is rather simple and suggests extensive oxidation. The spectra of crystalline material gave well distinguished and sharp bands, while amorphous spectra were less resolved. The hydration results established the importance of defined conditions for FT-IR (Figure 1) measurements and showed that fullerene could be successfully oxidized. They suggest that this kind of study can be performed on oxidize fullerene.

The strong C-O band at around approximately 1280 cm^{-1} was present in the spectrum, and the strong C=C band at 1590 cm^{-1} . The functional group C=O and C-OH was present at around approximately 1800 and 1080 .

This outcome confirms that the artificial ageing is actually occurring in the exposed film, and that the types of structural changes that can be inferred from the spectra are consistent with the mechanism proposed in literature: the formation of O-H bonds resulting from the oxidation of the hydrocarbon triterperpenic molecules by direct binding of O- and O-O radicals, followed by further oxidation to carbonylic functions.

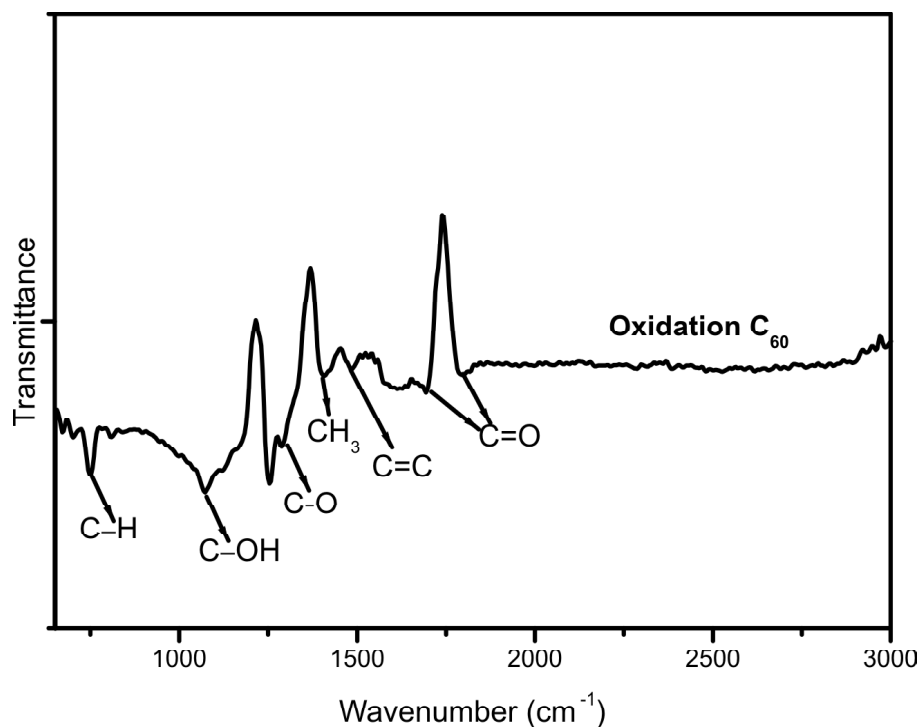


Figure 1: FT-IR patterns of oxidize fullerene.^[32]

A comprehensive overview of the chemistry of fullerenes with inorganic and organic metallic complexes has recently been published and the reader is referred there for detailed information on this area.^[33] Figure 2 is the routes to the formation of metal-fullerene/TiO₂ compounds, (a) is oxidize fullerene with different functional groups, (b) is metal complexes bound to the fullerene due to the functional groups, (c) is metal-fullerene bound to the TiO₂ to modify the TiO₂ nano-particles. Some of that is covered in Figure 2 which highlights routes to the formation of metal complexes bound to the outer surface of fullerene. We report herein, a new type of metal-fullerene based on composite nanoclusters of modified TiO₂ nano-particles. Fullerene modified with carboxylic acid group in order to be assembled on TiO₂ nanoparticles, in Figure 2.

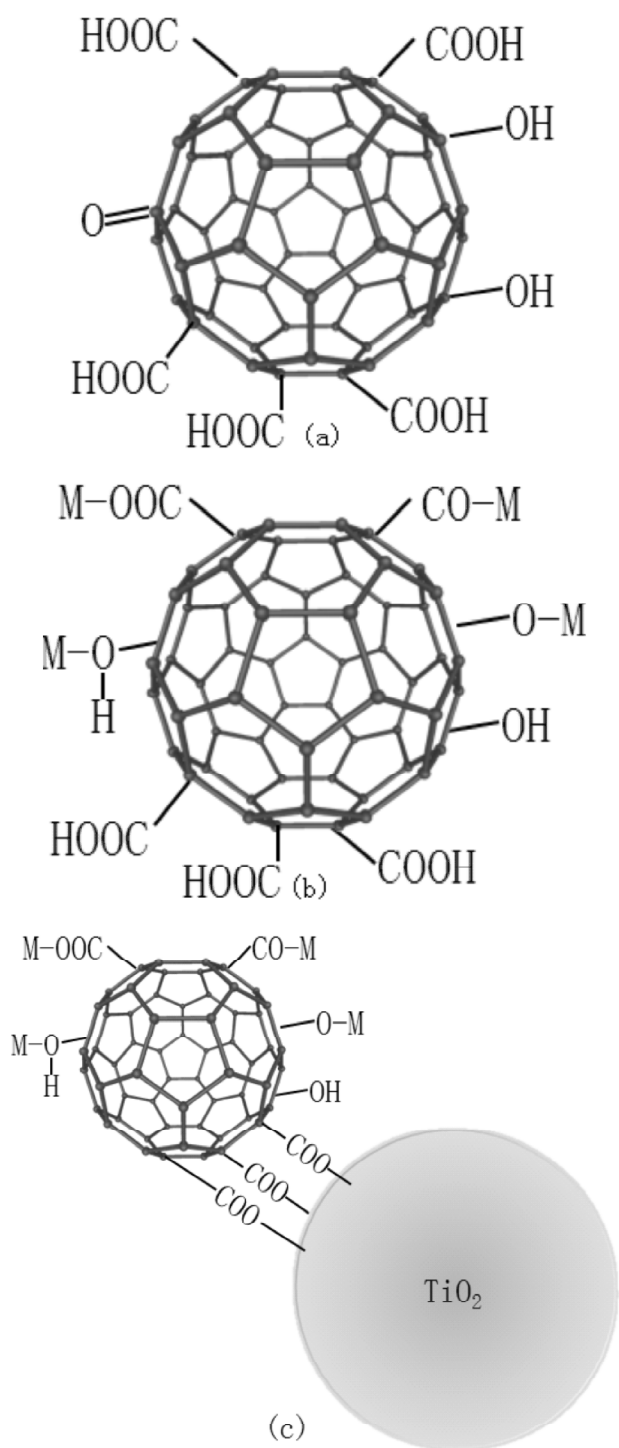
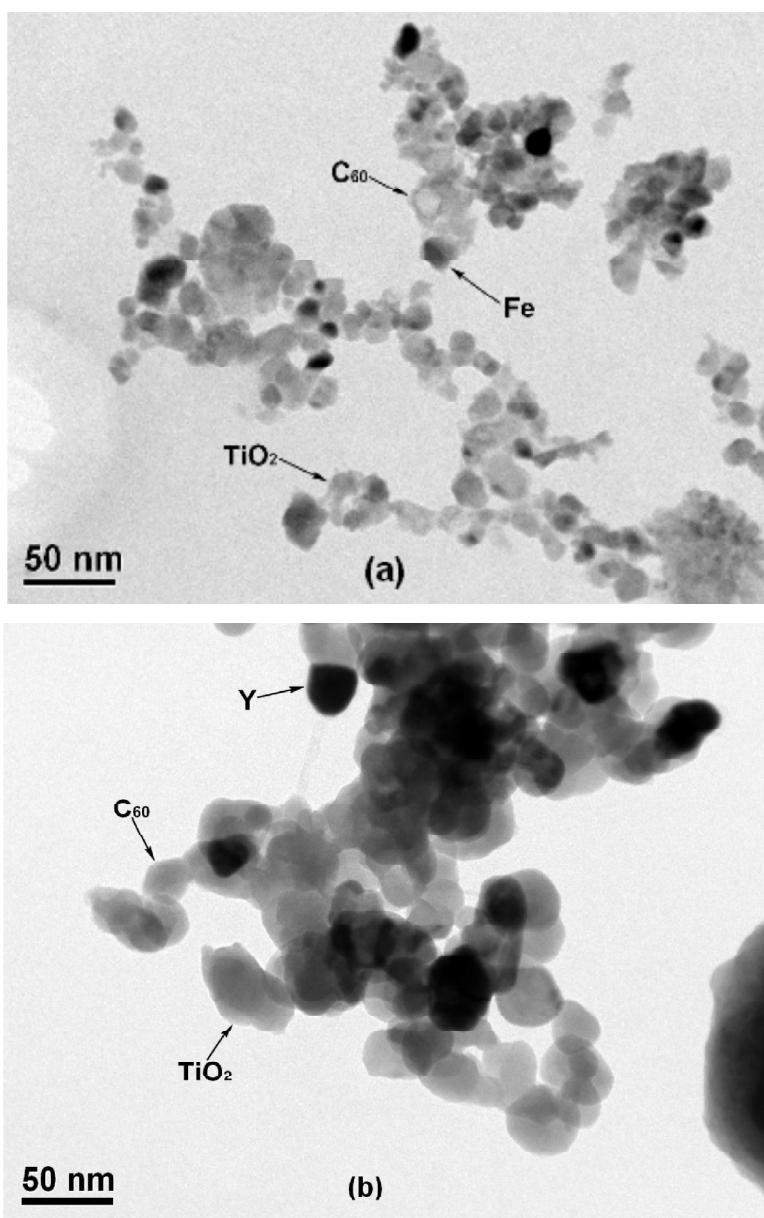


Figure 2: Routes to the formation of metal-fullerene/TiO₂

Figure 3 presents TEM images of the M-fullerene/ TiO_2 compounds. Fullerenes with a diameter of approximately 15-20 nm were clearly shown from this picture. Figure 3 shows large clusters with an irregular agglomerate dispersion of TiO_2 . The fullerene were distributed uniformly outside surface of TiO_2 nanoparticles with size about 10-20 nm, and metals were completely distributed uniformly attached on the surface of the fullerene and TiO_2 although this caused partial agglomeration to form blocky particle. TEM also revealed the presence of metal nanoparticles on the fullerene particles. Figure 3 shows that the metal ions not only intermingle with fullerene but also intermingle with the TiO_2 particles.



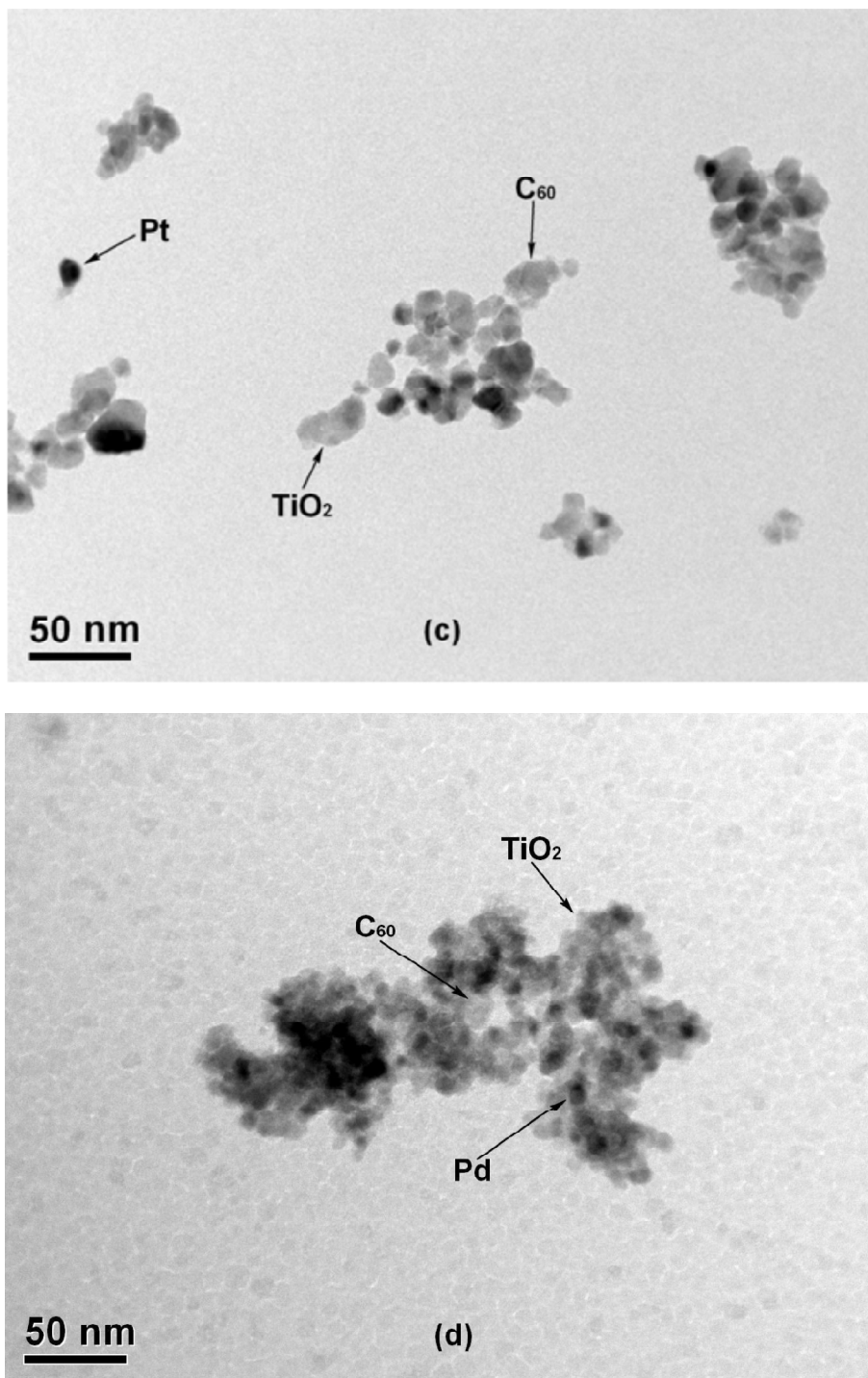


Figure 3: TEM micrographs of metal- fullerene /TiO₂ composites: (a) Fe-fullerene/TiO₂^[34] (b) Y-fullerene/TiO₂^[33] (c) Pt-fullerene/TiO₂^[32] (d) Pd-fullerene/TiO₂

4. Degradation Activity

4.1. Adsorption Effect of *M*-fullerene/ TiO_2

Figure 4 is the adsorptive effect of different metal treated fullerene/ TiO_2 for MB solutions. From Figure 4 we can see different metal treated fullerene/ TiO_2 has different adsorptive effect and Pd-fullerene/ TiO_2 has the best adsorptive effect, the adsorptive effect of Fe-fullerene/ TiO_2 is the lowest. Because Pd-fullerene/ TiO_2 composite had the largest BET surface area this can affect the adsorption effect.

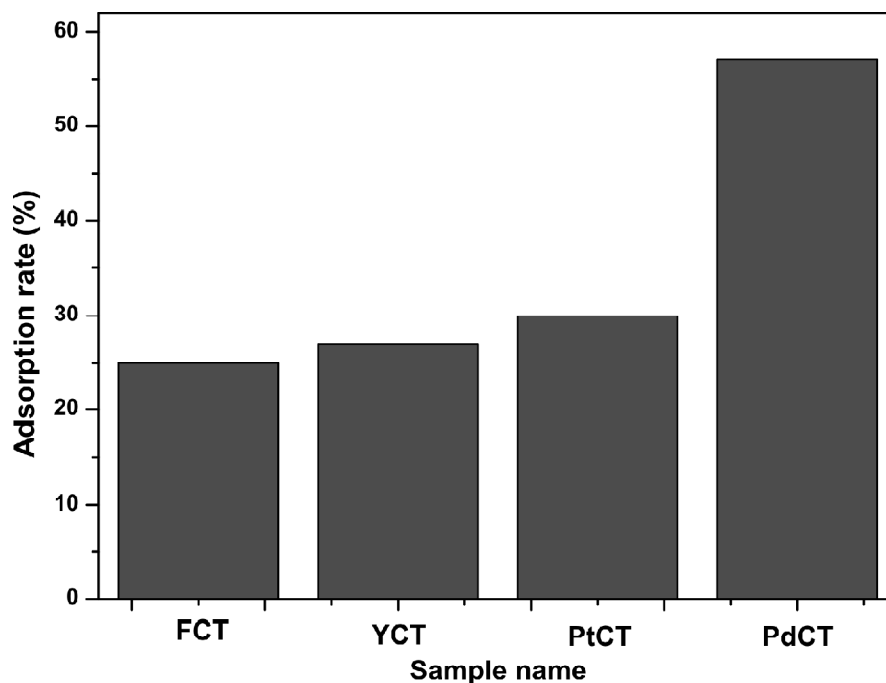


Figure 4: Adsorption rate for different metal-fullerene/ TiO_2 composites.^[35]

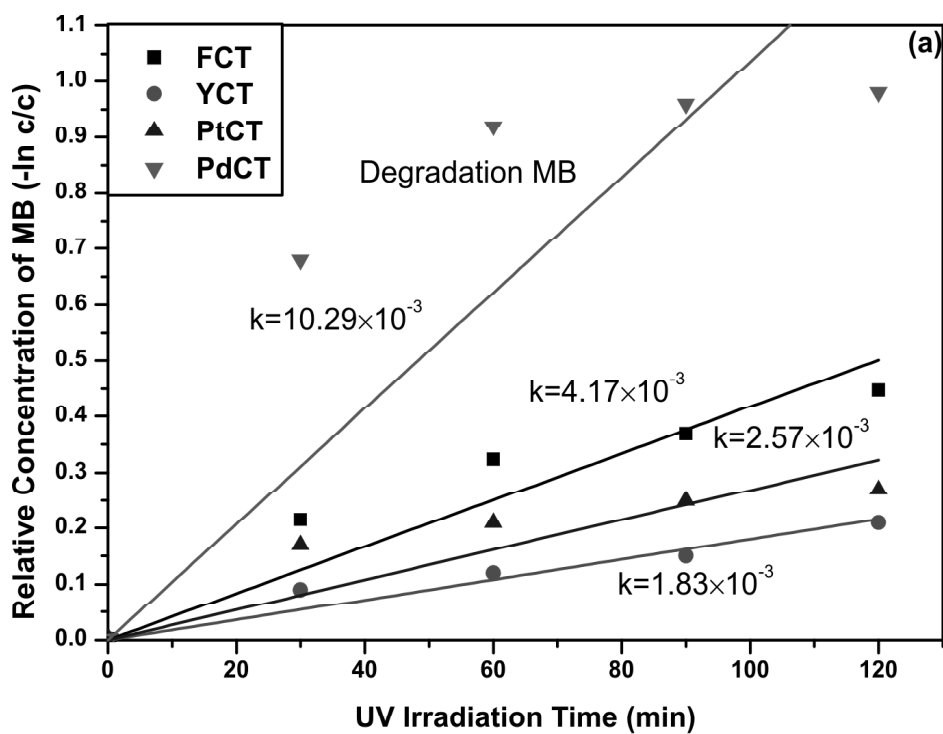
4.2. Photodegradation effect of *M*-fullerene/ TiO_2

Figure 5 shows the different degradation effect of *M*-fullerene/ TiO_2 clearly. The values corresponding to different initial concentrations along with the regression coefficients are listed. The picture (a) is degradation MB solution under UV light irradiation, (b) is degradation MB solution under visible light irradiation and (c) is degradation MB solution under ultrasonic irradiation.

From Figure 5 we can see Pt-fullerene/ TiO_2 produced a significantly higher photocatalytic under visible light irradiation, while the photocatalytic activity under UV light irradiation was not better than under visible light. The loading of noble metals such as metallic Pt on the TiO_2 surface were traditional ways to inhibit electron-hole pair recombination and widely investigated for many contaminations. Also Zang^[36] reported that the platinum(IV) chloride was an effective electron-hole separator in the liquid phase

photocatalytic oxidation of 4-chlorophenol. It could be easily concluded that for the photocatalytic degradation of MB in this experiment, the dopants as Pt oxide was an effective hole–electron separator and improved the photocatalytic degradation efficiency of MB. Pt oxide was a p-type semiconductor with a narrower band gap compared with TiO₂, while TiO₂ was a n-type semiconductor with a band gap range from 3.02 to 3.2 eV (anatase: 3.2 eV, rutile: 3.02 eV). However, the characteristic depth of UV light penetration into TiO₂ is about some hundreds nanometers, which is close to sizes of TiO₂ particles used. Therefore, platinum particles are able to absorb only the UV light fraction equal to their surface coverage on TiO₂. It can be know that the superior performance to dyes on pure TiO₂ is attributed to the presence of Pt on the exterior surface of the films. The relatively poor performance of dye ·Pt(in) ·TiO₂ in comparison to the dye ·Pt(on) ·TiO₂ is attributed to the bulk electronic structure modification of TiO₂ films in the presence of Pt in the bulk TiO₂ framework. So the Pt-fullerene/TiO₂ has better photocatalytic activity under visible light irradiation.

Compare the photocatalytic activity for this four kind of metal-fullerene/TiO₂, we come to conclusion that Pd-fullerene/TiO₂ has the best photocatalytic activity, as shown in Figure 5. Reactivity of TiO₂ depends on many factors: the adsorption of dye on catalyst surface, band-gap energy, surface area, crystal size, crystallinity, and electron–hole recombination rate, therefore an explanation of reactivity order is complicated. The addition of metals on the nanocrystalline TiO₂ photocatalyst surface can enhance the photocatalytic degradation activity due to the lower crystal size, higher surface area, higher efficiency



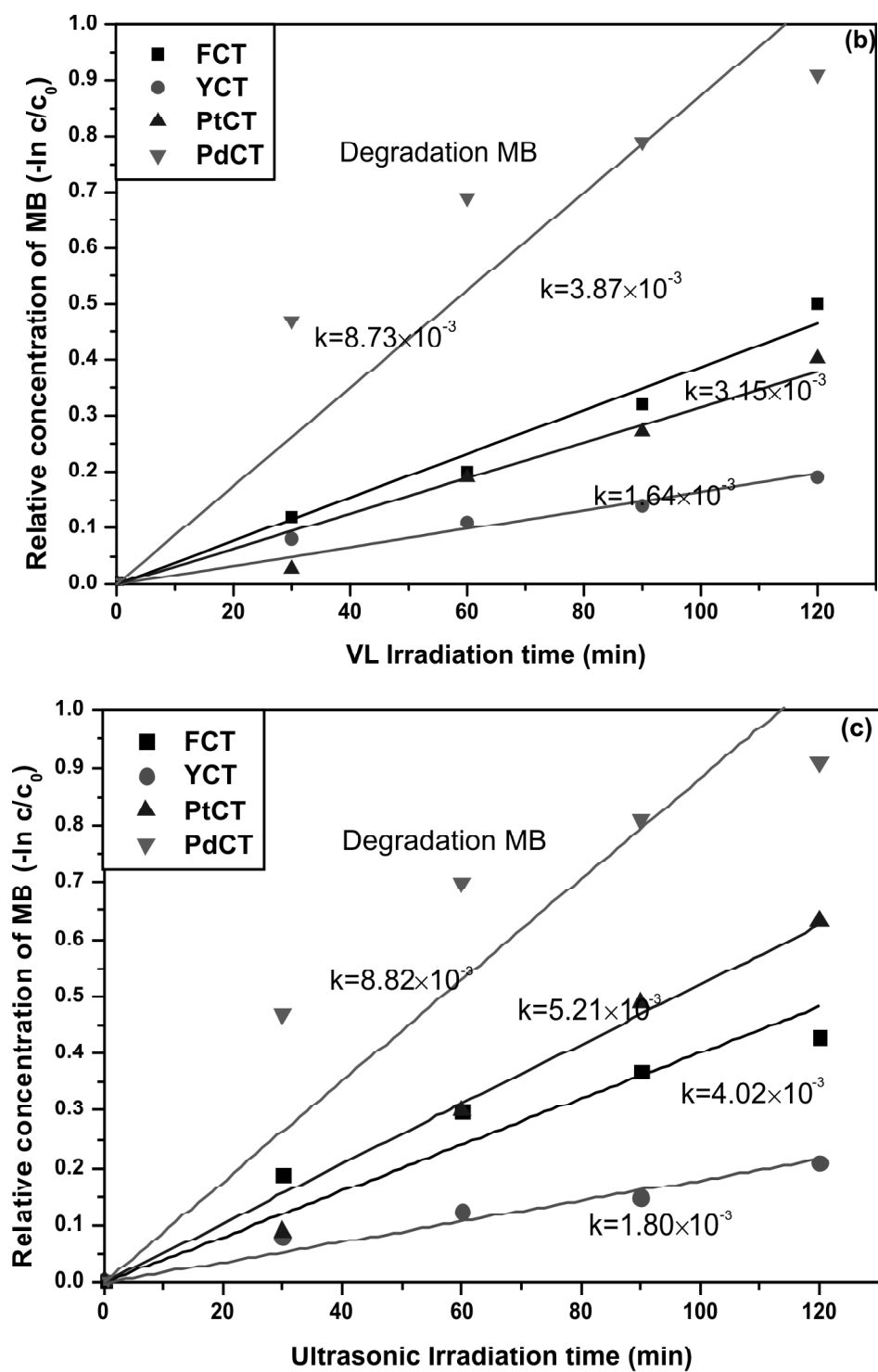
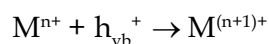
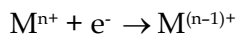
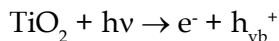


Figure 5: Different metal-fullerene/ TiO_2 degrade MB solutions in different environment.^[35]

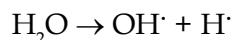
for the electron hole regeneration, and the charge trapping. The charge trapping can be demonstrated by the following equations:



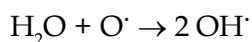
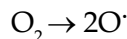
The holes can transfer to the surface of TiO₂ and react with OH· to produce active OH·. When transition metal ions replaced Ti ions of TiO₂, most of the dopant levels appeared between the valence band and the conduction band of TiO₂, which can increase the surface trapping rate of carrier and retarded the electron-hole recombination.

The most active photocatalyst was Pd-fullerene/TiO₂. It has maximum efficiency, rate constant for MB degradation. The reason for the highest activity of Fe-TiO₂ could be the lowest crystalline size, the highest surface area and the minimum band-gap energy. A decrease in crystalline size can give rise to larger surface area, which can increase the available surface active site and consequently leads to a higher adsorption of dye, electron hole generation, and interfacial charge carrier transfer rate for degradation.

Figure 6 shows a schematic illustration of hydroxyl radical formation under the ultrasonic irradiation in the presence of Fe-fullerene/TiO₂ compounds.^[36]



Oxygen is decomposed to form oxygen atom,^[37] which reacts with water to form OH radical.^[38]



The thermal energy by ultrasonic irradiation is assumed to generate positive hole in the vicinity of TiO₂ surface. The positive hole reacts with water to produce OH· radical. However, only ultrasonic irradiation to generate positive hole is limitedly.

During the ultrasonic treatment of aqueous solutions sonoluminescence, cavitation and “hot spot” were happened, leading to the dissociation of water molecules. The hydroxyl (OH) radicals were formed during the ultrasonic treatment which has high oxidative activity can degrade the toxic dyes and industrial dyestuffs.^[38] Because of sonoluminescence effect of ultrasonic irradiation, so in the ultrasonic irradiation process generated a lot of generated light. As we know that conduction band electrons (e⁻) and valence band holes (h) will be generated at the surface of TiO₂ when it is irradiated with UV light. Holes can react with surface hydroxyl ions and water to produce hydroxyl radicals (OH·), at the same time the electrons can react with adsorbed molecular oxygen yielding superoxide anion radicals (O₂^{-·}). O₂^{-·} and OH· have an excellent oxidation to degrade MB molecular. But because of the rapid recombination of photogenerated (e⁻ and h_{vb}⁺) pairs, which significantly diminishes the efficiency of TiO₂ reactions. But with the iron ion added, the iron ion leads to enhanced catalytic activity by trapping the e⁻ and

h_{vb}^+ pairs, iron doping increases the production by its capacity to act as h_{vb}^+ traps, which reduced the recombination, thus chance for the e^- and h_{vb}^+ to form oxidative radicals is improved.

In a word, we can be considered it is a promising field of using the metal treated fullerene based titania composites for the bactericidal effects in the future.

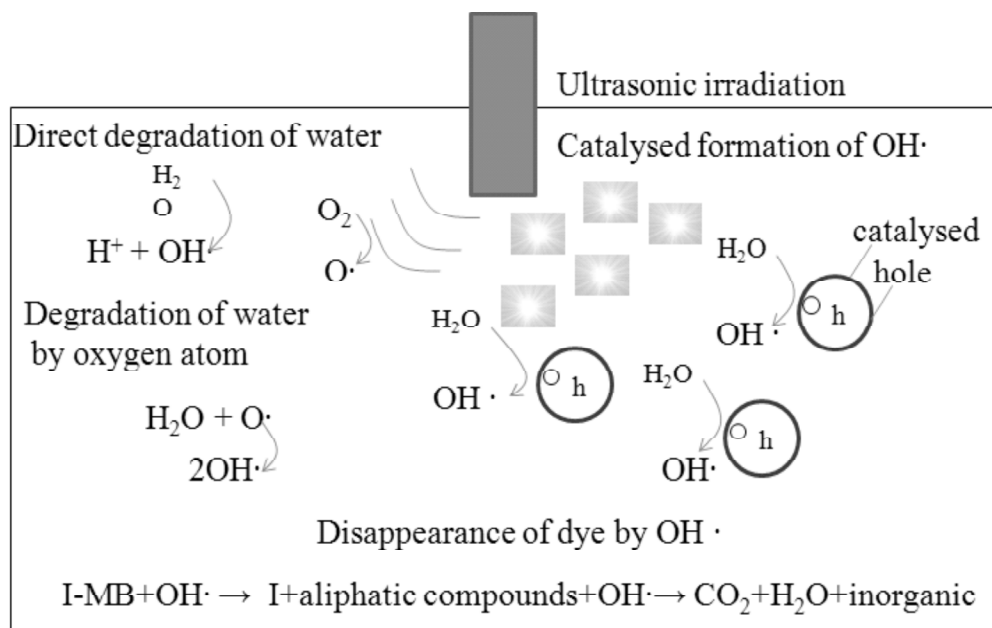


Figure 6: Schematic illustration of reaction scheme under ultrasonic irradiation with M-Fullerene/TiO₂ (h: positive hole).^[34]

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