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Synthesis and characterization of M-fullerene/TiO_2 photocatalysts designed for degradation azo dye

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ABSTRACT

Metal-fullerene/TiO_2 composites were prepared using a sol–gel method, and their photocatalytic activity was evaluated by degradation of methylene blue (MB) solutions under UV light. The surface area, surface structure, crystal phase and elemental identification of these composites were characterized by Brunauer–Emmett–Teller analysis, scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray diffraction and transmission electron microscopy, respectively. The degradation effect of MB was determined using UV/Vis spectrophotometry. Photocatalytic activity was increased because of the increase in photo-absorption effect by fullerene, and the cooperative effect of the metal introduced as a dopant.

1. Introduction

Photocatalytic processes are a promising class of advanced oxidation technologies used for environmental remediation [1,2]. TiO_2 has excellent photocatalytic properties with applications in medicine, buildings and environmental remediation [3–5]. TiO_2 has been studied intensively as a photocatalyst for the complete degradation of organic pollutants [6–8] because it is easily available, nontoxic, inexpensive and chemically stable. However, TiO_2 has some shortcomings preventing its widespread application. TiO_2 is difficult to separate from aqueous phase, and has relatively low quantum yield due to the rapid recombination of electron/hole pairs.

To develop more efficient photocatalysts, considerable effort has been made to modify TiO_2 to develop multifunctional materials and enhance the photocatalytic performance. These efforts include doping with other elements, sensitizing with dyes, and coating the surface with noble metals or other semiconductors [9,10]. The high degree of recombination between the photogenerated electrons and holes in semiconductor particles is a major limiting factor in the photodegradation process [11]. Conjugated two-dimensional π-systems 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 changes upon electron transfer [12,13]. For example, fullerene has a closed-shell configuration consisting of 30 bonding molecular orbitals with 60 π-electrons [14–17], and is suitable for efficient electron transfer reduction because of the minimal changes in structure and solvation associated with electron transfer [18,19]. However, fullerene has poor light-harvesting capability, exhibiting a low incident photo-to-photocurrent efficiency. To overcome these problems, the properties of metal-oxide-based inorganic surfaces were used for metal-doped fullerene. Doping with alkali metals, alkali-earth metals, and other elements, induces variety of phenomena, such as superconductivity, ferromagnetism, antiferromagnetism, etc., which have become attractive for optical, electronic, photovoltaic, artificial photosynthesis and solar cell applications [20–24]. The fullerene cage is expected to be charged as a result of electron transfer from the metal atom. Indeed, electron transfer plays an important role in the superconductivity of metal-intercalated fullerene materials, such as Rb_3C_{60} and K_3C_{60} [25].

Surface sol–gel processes are simple, reproducible techniques for fabricating metal oxide and metal oxide/organic nanohybrids with nanometer-precise particles, and are capable of incorporating a range of organic molecules through sequential adsorption and activation [26]. This paper reports on a novel catalyst prepared by a sol–gel process using different metallic compounds [$PdCl_2$, $H_2PtC_{l6}\cdot nH_2O$ and $Y(NO_3)_3$] to dope fullerene and improve the catalytic activity of TiO_2. This catalyst was characterized by Brunauer–Emmett–Teller (BET) analysis, scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX). The catalyst was irradiated by UV light and the catalytic activity of M-fullerene/TiO_2 particles was examined according to different UV

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irradiation times. The photocatalytic efficiencies of these composites were evaluated according to the photo-degradation of the MB solutions.

2. Experimental methods

2.1. Materials

MCPBA (m-Chloroperbenzoic acid) was purchased from Acros Organics, New Jersey, USA. Crystalline fullerene [C_{60}] powder of 99.9% purity from TCI (Tokyo Kasei Kogyo Co. Ltd., Japan) was used as the carbon matrix. Reagent-grade benzene and ethyl alcohol were purchased from Duksan Pure Chemical Co (Korea) and Daejung Chemical Co. (Korea), respectively, and used as-received unless otherwise stated. Hydrogen hexachloroplatinate (IV) hydrate ($H_2PtC_{l6}\cdot nH_2O$ n = 5.5), palladium (II) chloride ($H_2PtC_{l6}\cdot nH_2O$) and yttrium nitrate [$Y(NO_3)_3$] as the metal sources for the synthesis of the M-fullerene compounds were purchased from Kojima Chemicals Co., Ltd.

Reagent-grade titanium (IV) n-butoxide (TNB, $C_{16}H_{36}O_4Ti$) as the titanium source for the preparation of the M-fullerene/TiO_2 composites was purchased from Acros Organics (USA). Analytical grade methylene blue (MB, $C_{16}H_{18}N_3S\cdot Cl\cdot 3H_2O$) was purchased from Duksan Pure Chemical Co., Ltd.

2.2. Chemical oxidize and metal treated fullerene

MCPBA (m-Chloroperbenzoic acid, ca. 1.00 g) was suspended in 50 ml benzene, followed by the addition of fullerene [C_{60}] (ca. 100 mg). MCPBA was used to the oxidize fullerene. The mixture was heated under reflux in air and stirred for 6 h. The solvent was then dried at the boiling point of benzene (353.13 K). After completion, the dark brown precipitates were washed with ethyl alcohol and dried at 323 K, resulting in the formation of oxidized fullerene. For metal coating, Table 1 lists the nomenclature of the samples for the metallic compound solutions. The resulting mixture was heated under reflux in air and stirred at 343 K for 6 h using a magnetic stirrer in a vial. After heat treatment at 873 K, 773 K and 935 K, respectively for 1 h, the M-fullerene (Pd-fullerene, Pt-fullerene and Y-fullerene) compounds were formed.

2.3. Preparation of M-fullerene/TiO_2 composites

After washing the M-fullerene with ethanol several times, the M-fullerenes were prepared using pristine concentrations of TNB for the preparation of the M-fullerene/TiO_2 composites. M-fullerene powders were then mixed with 3 ml TNB. The solutions were then homogenized under reflux at 343 K for 5 h, while being stirred in a vial again. After stirring, the solution transformed into M-fullerene/TiO_2 gels, which were heat treated at different temperatures to produce the M-fullerene/TiO_2 composites.

2.4. Characterization of the M-fullerene/TiO_2 compounds

XRD (Shimadzu XD-D1, Japan) with Cu Kα radiation was used to examine the structural variations. The surface state and structure of the Fe-fullerene/TiO_2 composites were examined by SEM (JSM-5200 JOEL, Japan). Energy dispersive X-ray (EDX) was also used for elemental analysis of the samples. The specific surface area (BET) was determined using N_2 adsorption measurements at 77 K (Monosorb, USA). TEM (JEOL, JEM-2010, Japan) at an acceleration voltage of 200 kV was used to observe the surface state and structure of the M-fullerene/TiO_2 composites. TEM was also used to investigate the size and distribution of the titanium and metal particles deposited on the fullerene surface. The TEM specimens were prepared by placing a few drops of the sample solution onto a carbon grid.

Table 1
Nomenclatures of the samples prepared with M-fullerene/TiO_2 composites.

Preparation method	Nomenclatures
MCPBA + benzene + fullerene + 0.02 M $PdCl_2$ + TNB	Pd-fullerene/TiO_2
MCPBA + benzene + fullerene + 0.02 M $H_2PtC_{l6}\cdot nH_2O$ + TNB	Pt-fullerene/TiO_2
MCPBA + benzene + fullerene + 0.02 M $Y(NO_3)_3$ + TNB	Y-fullerene/TiO_2

2.5. Photocatalytic activities

The photocatalytic activities were evaluated by MB degradation in aqueous media under ultraviolet light irradiation. For UV irradiation, the reaction beaker was located axially and held in a UV lamp box (8 W, 365 nm). The lamp was used at a distance of 100 mm from the aqueous solution in a dark box. The initial concentration of the MB was set to 0.5×10^{-4} mol/l in all experiments. The amount of the M-fullerene/TiO_2 composite was 0.05 g per 50 ml solution. The solution was placed in a dark box for 0.5 h in order to maximize the amount of M-fullerene/TiO_2 composites particles adsorbed. After the adsorption state, the UV light irradiation was restarted to continue the degradation reaction. A glass reactor (diameter = 4 cm, height = 6 cm) was used for methylene blue degradation. The reactor was placed on a magnetic churn dasher to simulate the natural flow of a river. UV light irradiation of the reactor was performed for 10, 30, 60, 90 and 120 min. The samples were then withdrawn regularly from the reactor and the dispersed powders were removed using a centrifuge. The clean transparent solution was analyzed by UV/Vis spectroscopy. The concentration of MB in the solution was determined as a function of the irradiation time.

3. Results and discussion

3.1. Structural and morphology

Table 2 lists the BET surface areas for these three different M-fullerene/TiO_2 samples. The BET surface area of pure fullerene is 85 m^2/g, whereas the BET surface area of the M-fullerene/TiO_2 composites gradually decreased to 47 m^2/g. Pd-fullerene/TiO_2 composite has the largest BET surface area of the composites, possibly because of the higher dispersion of Pd for Pd-fullerene/TiO_2 than the other two samples, and the sintering of metal particles at higher temperatures [27]. The decrease micropore size of M-fullerene/TiO_2 might have two explanations. First, TiO_2 and/or metal particles introduced can block the micropores in the fullerene. Second, the introduction of metal on the surface or implantation of fullerene can facilitate the entry of TiO_2 particles into the micropores in the fullerenes.

Fig. 1 shows the surface characteristics of the M-fullerene/TiO_2 composites. The SEM image revealed three different M-fullerene/TiO_2 composite derivatives with the surface characteristics. The M-fullerene grain structure was clearly observed, with a large distribution on the surface of TiO_2, which is shown in Fig. 1, for the M-fullerene/TiO_2 composite. The M-fullerene units appeared to cover the TiO_2 surface. Good dispersion of small particles on the fullerene surface

Table 2
Specific BET surface areas of the M-fullerene/TiO_2 composites.

Sample	S_{BET} (m^2/g)	Kapp	More rate (C:M:TiO_2)
Fullerene	85		
Pd-fullerene/TiO_2	82.5	3.37×10^{-2}	6:7:80
Pt-fullerene/TiO_2	55.3	0.60×10^{-2}	6:5:80
Y-fullerene/TiO_2	47	0.43×10^{-2}	6:7:80
TiO_2	17.4	$0.24\times10^{-}$	