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Visible light responsive titanium dioxide–cyclodextrin–fullerene composite with reduced charge recombination and enhanced photocatalytic activity

Mohamed Mukthar Ali, Sandhya K.Y. *

Department of Chemistry, Indian Institute of Space Science and Technology, Thiruvananthapuram 695 547, Kerala , India

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ABSTRACT

Titanium dioxide (TiO_2)–fullerene (C_{60}) composite is prepared from TiO_2 and β-cylcodextrin (CD) encapsulated C_{60} using the solar light irradiation. The absorption of the composite extends to the visible light region due to the charge transfer from CD and C_{60} to TiO_2. The composite shows reduced charge recombination compared to that of the bare TiO_2 and TiO_2/CD. The rate constant values for the photodegradation reactions of methylene blue and 4-chlorophenol (4-CP) are significantly higher (~2–5 times) for the composites with 0.5 and 1.5 wt.% C_{60} compared to that of the bare TiO_2. Photocatalytic studies in the presence of scavengers reveal that the composites produce higher amount of reactive oxygen species (ROS). The enhanced photocatalytic activity of the composites is attributed to the visible light responsiveness, reduced charge recombination and increased formation of ROS. The photodegradation of 4-CP is significantly faster in the presence of the composite with 1.5 wt.% C_{60} and is attributed to the synergistic effect of higher adsorption and increased ROS formation. The ROS formation by C_{60} is possible because of the non-aggregated state of C_{60} molecules in the composite and is assigned to the method which employs CD molecules to disperse C_{60} in the composite.

1. Introduction

In recent decades, titanium dioxide (TiO_2) has been extensively investigated because of its role in dye sensitized solar cells and photocatalysis [1–3] and due to its nontoxicity, low cost, high activity, high chemical stability and superior photoelectronic properties. The efficiency of TiO_2 is, however, plagued by its wide band gap (~3.2 eV) which restricts the absorption of TiO_2 to the UV region of the solar spectra and the rapid recombination of photogenerated electrons and holes [1]. Extension of the absorption of TiO_2 to the visible region and suppression of the recombination of electron–hole pairs are of great importance to practical applications. Modifying TiO_2 semiconductor using carbon materials and surface sensitization are some of the ways to overcome the issues [4–7].

In these aspects, TiO_2–carbon composites have gained interest and widely investigated due to their enhanced photocatalytic (PC) applications. Among the allotrope of carbon, fullerene (C_{60}) is of interest because of its exceptional electronic properties and potential in photovoltaic [8] and PC applications [9,10]. C_{60} has good electron accepting properties [11] and has been investigated as electron acceptors in many TiO_2-based photochemical processes [9,12]. It was recently proposed that a direct electron transfer from the surface-complexed compound to TiO_2 conduction band (CB) can be

* Corresponding *author:* Fax: +91 4712568537.
E-mail address: sandhya@iist.ac.in (K.Y. Sandhya).
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initiated by ligand to metal charge transfer (LMCT) upon absorption of visible light, through ene-ol groups [13,14]. Following this work, Park et al. reported sensitization of TiO_2 by fullerol (C_{60}–OH) in TiO_2/C_{60}–OH [10]. However, the procedure calls for oxidation of fullerene which brings in complexity to the preparation of the TiO_2/C_{60} composite and in addition, alters the optical and electronic properties of the C_{60} molecules. TiO_2/C_{60} composites prepared by using pure C_{60} will be mostly in the form of aggregates due to the strong π–π interaction of C_{60} molecules and the resulting composite will not be uniform and will have relatively lower surface area and poor performance.

Therefore, we herein report a new method to prepare TiO_2/C_{60} composite without covalently modifying C_{60}. The method uses β-cyclodextrin (CD) to solubilize C_{60} molecules in water by forming complex of CD and C_{60} [15], hereafter referred to as C_{60}/CD. The CD molecules, on photo-irradiation, form bonds with TiO_2 creating self-assembled wires or networks [16,17]. As C_{60} molecules are enclosed by the CD molecules which bonds to TiO_2, results in the formation of a composite of TiO_2, CD, and C_{60}, hereafter referred to as $TiO_2/CD/C_{60}$. There are several advantages in using CD: enhances the PC activity, as TiO_2/CD composites are known to have higher PC activity [7], improved interfacial electron transfer processes [18,19], reduced charge recombination [7] and visible light absorption [7]. In addition, this method gives rise to uniform distribution of the C_{60} molecules in the composite because of the formation of a homogeneous solution of C_{60}/CD in water. Moreover, the original electronic and optical properties of the C_{60} molecules are retained as they are not covalently modified. It also brings the C_{60} molecules in proximity to TiO_2 nanoparticles due to the bonding of CD with TiO_2. Finally, the preparation of the composite in aqueous medium using solar light makes it a green approach. Thus prepared $TiO_2/CD/C_{60}$ composite is characterized using Fourier transform infrared (FT-IR) spectra, UV–Visible absorption (UV–Vis) spectra, solid state diffuse reflectance (DRS) spectra, thermogravimetric analysis (TGA), X-ray diffraction (XRD) pattern, scanning electron microscopy (SEM) images, high resolution transmission electron microscopy (HRTEM) images, solid state photoluminescence (PL) spectra and energy dispersive X-ray analysis (EDX) to confirm the formation and structure of the composite. Photocatalytic degradation (PCD) studies of methylene blue (MB) and 4-chlorophenol (4-CP) are conducted to evaluate the PC activity of the composites. The characterization, structure of the composites and the results of PCD studies are discussed in detail in the Section 3.

2. Experimental

2.1. Raw materials

Anatase TiO_2 nanopowder (25 nm), C_{60}, CD (97%) and sodium azide (NaN_3) were purchased from Sigma–Aldrich India Co. Ltd. CD was recrystallized before use. MB and 4-CP were purchased from Alfa Aesar Co. India Ltd and Spectrochem India respectively. Tertiary butyl alcohol (t-BuOH) was purchased from Finar Chemicals Ltd. Distilled water was used for all studies. All solvents used in this study were of analytical grade.

2.2. Preparation of C_{60}/CD composite

The preparation of C_{60}/CD composite was done by grinding C_{60} and CD in the presence of water according to the procedure described elsewhere (Patent No. 2554/CHE/2013). The product (brown powder) formed is soluble in water and yielded a yellow colored solution.

2.3. Preparation of $TiO_2/CD/C_{60}$ composite

C_{60}/CD (35 mg) was suspended in 70 ml of water (0.5 mg/ml) to form a stock solution and 5 ml of this stock solution (equivalent to 0.5 mg of C_{60}) was added to the suspension containing 99.5 mg of TiO_2 anatase in 90 ml of distilled water. This suspension was sonicated for 10 min and irradiated with sunlight for 15 h in a quartz beaker. The composite was then washed, centrifuged and dried at 70 °C in vacuum for overnight. Composite with varying concentrations of the C_{60} were prepared: $TiO_2/CD/C_{60}$(0.5%), $TiO_2/CD/C_{60}$(1.5%). Similarly composites of TiO_2 and CD were prepared by adding equivalent amount of CD instead of C_{60}/CD: TiO_2/CD(0.5%) and TiO_2/CD(1.5%).

2.4. Characterization

Universal attenuated total reflection mode of FT-IR spectroscopy was used for recording IR spectra using Perkin Elmer spectrum100 FT-IR spectrophotometer. XRD patterns were obtained using Xpert-pro diffractometer using Kα wavelength (1.54 Å) of Cu metal. TGA analyses were done using TA Q50. Solid state PL spectra were recorded in Horiba FluoroMax-4. Absorption spectra in solutions were recorded using CARY 100 Bio UV–Vis spectrophotometer and solid state DRS using Shimadzu 2600. SEM was performed on a Zeiss EVO 18 Scanning electron microscope with an acceleration voltage of 15 kV. TEM and EDX analysis were done using FEI, TECNAI S twin microscope with an accelerating voltage of 300 kV.

2.5. PCD studies

2.5.1. PCD study of MB and 4-CP

For the PCD studies of MB, 17 mg of the composite was dispersed in 15 ml of distilled water. The mixture was sonicated for 15 min to from a suspension. MB solution (10 ml, 144 μM) was added to the suspension and stirred in dark for 60 min to attain the adsorption equilibrium. For the PCD studies of 4-CP, stock solution was prepared by dissolving 10 mg of 4-CP in 1 L of distilled water. 15 mg of the catalyst was added to 15 ml of the stock solution and the mixture was sonicated for few minutes and then stirred in dark for 60 min to attain the adsorption equilibrium. Under ambient conditions, the dye suspensions were irradiated with visible light (>420 nm) using 84 W light sources. UV–Vis spectra of the supernatant solutions were recorded at 10 min interval. Absorbance values at 660 and 224 nm were used to calculate the percentage degradation and rate constant values of MB and 4-CP, respectively.