



Sensitizing of pyrene fluorescence by β -cyclodextrin-modified TiO₂ nanoparticles

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ABSTRACT

TiO₂ nanoparticles were synthesized by hydrolysis of tetraisopropyl orthotitanate in an aqueous solution of cyclodextrin. The β -cyclodextrin-modified spherical TiO₂ nanoparticles were water-dispersible and had an average particle diameter of 4.4 ± 1 nm. Pyrene fluorescence was enhanced by increasing the concentration of β -cyclodextrin-modified TiO₂ nanoparticle and the sensitization effect was triply stronger than the case of the β -cyclodextrin only. The increase in a concentration of host (β -cyclodextrin) changes its microenvironment for guest (pyrene), that is, the interaction of pyrene with apolar cavity of β -cyclodextrin increases, resulting in enhancement of fluorescence. The sensitization behavior of pyrene fluorescence in the presence of TiO₂ nanoparticles occurs from the increase in the extinction coefficient of pyrene, demonstrating the charge transfer between pyrene and metal oxide nanoparticle.

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1. Introduction

Nanostructured materials, either as such or as surface-supported architectures, are now the intense focus of fundamental and applied researches in a number of areas. Particularly, basic studies for integrating semiconductor nanoparticles into organic and inorganic compounds drive an advent of an entirely new set of functional nano-architectures with limitless applications [1–3]. The semiconductor nanoparticles are taken great research interest for many years due to the optical and electronic properties, which are largely attributed to quantum confinement or surface effect. Among the nanometer-sized semiconductors, TiO₂ is widely investigated because of its potential use in photovoltaic cells, batteries, sensing, optical emissions, photonic crystals, catalyses, photocatalyses, ion exchange, ultraviolet blockers and energy storages [4–8]. Thus, the controlled synthesis of TiO₂ nanoparticles with defined size and morphology would generate significant opportunities for applications [9–11].

β -cyclodextrin (β -CD) is a torus-shaped cyclic polysaccharide consisting of seven D-glucopyranoside units linked with 1–4 glycoside linkage and it is composed of a hydrophilic outer surface and a hydrophobic inner cavity. It is well known that β -CD molecules form a host–guest inclusion complex by the selective encapsulation of many organic and inorganic molecules [12]. Therefore they are used for variety of analytical and industrial applications, such as solubilizing agents [13], drug carriers [14] and organized ensembles for controlling chemical and photochemical reactions [15]. In

host–guest inclusion complex with fluorophores, cyclodextrin molecules offer a less polar and more rigid protective microenvironment and enhance the fluorescence of the guest molecule by shielding the excited species from the quenching and nonradioactive transition that occur in a bulk solution, while water molecules are simultaneously expelled from the cavity [16]. It was observed that the formation of host–guest inclusion complex with β -CD is accompanied by a well known photoinduced electron transfer through the formation of excimers and exciplexes [17]. A host–guest inclusion complex between donor and acceptor groups inside the cyclodextrin cavity can enhance the formation of twisted intermolecular charge transfer (TICT) and the intermolecular charge transfer in an excited state.

In the recent years semiconductor nanoparticles have been modified by cyclodextrins as electron-donating and molecular recognizing agents [18,19]. Surface absorption of β -CD to a semiconductor particle has been found to improve the charge transfer rate from the photo-excited semiconductor to the electron acceptor guest molecule in the β -CD cavity. Starukh et al. [20] studied about the fluorescence properties of pyrene- β -cyclodextrin inclusion complex in titanium–silica solution and the effect of the intermolecular electron transfer in the presence of cyclodextrin. Additionally it was found that β -CD acts as a very effective stabilizer for the preparation of colloidal metallic nanoparticles [21–24]. However, the size effect of semiconductor TiO₂ nanoparticle has never been studied on such characters.

Fluorescence is widely used in microscopic imaging, medical research, biotechnology and diagnosis [25]. The enhanced fluorescence has attracted great attention in recent years, in terms of the quantum yield and the photostability of the fluorophore

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[26,27]. It is available from numbers of reports that metal particles can enhance the fluorescence property of the fluorophores due to the near-field interaction between them [28–30]. Pyrene is a useful fluorescence probe for studying the microenvironment within the cyclodextrin cavity, since it is very sensitive to different quenching processes and microenvironmental changes.

In this paper, we investigate the photophysical property of the synthesized cyclodextrin-modified TiO₂ nanoparticles in an aqueous medium, where interfacial electron transfer carries from cyclodextrin-modified TiO₂ nanoparticle to the guest (pyrene) molecule inside the host CD cavity. The surface-modified TiO₂ nanoparticle is able to enhance the excited state of pyrene molecule in β-CD via interfacial electron transfer between the fluorophore and metal oxide semiconductor. The transmission electron microscopic (TEM) and energy dispersive X-ray (EDX) examination is performed to confirm the formation of surface-modified TiO₂ nanoparticles. In addition the β-CD-modified TiO₂ nanoparticles were characterized by Fourier transform-infrared (FT-IR) absorption spectroscopy. The fluorescence and ultraviolet–visible (UV–vis) absorption spectroscopy is used to interpret the mechanism of charge transfer between the pyrene molecules and the cyclodextrin-modified TiO₂ nanoparticles. The efficient sensitization effect by β-CD-modified TiO₂ nanoparticle discussed here should give us future aim to utilize it as a material of sensitizer.

2. Experimental

2.1. Reagents

Tetraisopropyl orthotitanate, pyrene, and isopropanol were purchased from Wako chemicals. β-CD was purchased from Junsei Chemical Ltd. All reagents were of analytical grade and used without further purification. Ultrapure (Millipore Milli-Q) water was utilized throughout all experiments.

2.2. Measurements

UV–vis absorption spectra were collected with a Shimadzu Bio-Spac-1600 spectrometer using quartz cells (10 mm path). Fluorescence was measured with a HITACHI F-3010 fluorometer with a 10 mm path cell. The microscopic observation was performed on a Hitachi H-7000 transmission electron microscope (TEM) equipped with a CCD camera attachment, operating at 100 kV. Samples for TEM were prepared by casting a droplet of the solution on a copper grid, which was coated with a thin carbon film. EDX spectrum was taken from TECNAI F20 EDX analyzer where a sample was cast on a copper substrate. FT-IR spectra were recorded with a Thermo scientific Nicolet 6700 spectrometer using KBr pellet method.

2.3. Synthesis of β-cyclodextrin-modified TiO₂ nanoparticles

TiO₂ nanoparticles were prepared by the hydrolysis of [(CH₃)₂CHO]₄Ti in aqueous β-cyclodextrin solutions. Liquid [(CH₃)₂CHO]₄Ti (3.4 × 10⁻⁵ mol) in 1-propanol (5 cm³) cooled at 0 °C was slowly added, under vigorous stirring, to an aqueous β-CD solution (10 cm³) which was maintained at 0 °C. The pH (10) of the β-CD solutions was adjusted by adding NaOH prior to the synthesis of TiO₂ nanoparticles. The mole ratio of β-CD and [(CH₃)₂CHO]₄Ti was 1:1. The dialysis of the reaction solutions by water (1000 cm³) in a dialysis membrane of molecular weight cut-off 1000 (MWCO-1000) was repeated for two days in order to remove the unreacted chemicals.

2.4. Procedure of pyrene encapsulation

A 2 × 10⁻⁴ M pyrene solution and a 3 × 10⁻⁴ M β-CD solution were prepared in ethanol and water, respectively. The mother aqueous solution of synthesized β-CD-modified TiO₂ nanoparticles was diluted to be a β-CD concentration of 3 × 10⁻⁴ M. The pyrene solution (1 cm³) was added to the different volumes (1–5 cm³) of a β-CD or a β-CD-modified TiO₂ nanoparticle solution and then adjusted to be total volume of 6 cm³ by adding water. The mixtures were stirred and then allowed to equilibrate for overnight.

3. Results and discussion

3.1. Characterization of β-CD-modified TiO₂ nanoparticles

The morphology of the synthesized TiO₂ particles was observed by TEM. As seen in Fig. 1, the TiO₂ particles were a sphere and fairly small. Histogram of size distribution of particles (300 samples) prepared with β-CD is shown in a supporting information (Fig. S1). The average diameter is 4.4 ± 1.0 nm, that is, the particle size is almost uniform with a narrow size distribution. Then the solution of the β-CD-modified TiO₂ nanoparticle was almost transparent (water-soluble) and very stable owing to too small size and enough protection by β-CD. Similar water-dispersible TiO₂ nanoparticles have been prepared using water-soluble dendrimers in place of β-CD [10,11].

The UV–vis absorption spectra of aqueous solutions of the β-CD-modified TiO₂ nanoparticle and β-CD are shown in supporting information (Fig. S2). While an absorption band of the β-CD was very weak, an absorption spectrum of the β-CD-modified TiO₂ nanoparticles showed strong absorbance below 330 nm. This increase of absorbance is due to the existence of TiO₂ nanoparticles. Then the band gap can be determined from the optical absorption spectrum where the absorbance of β-CD-modified TiO₂ nanoparticles were plotted against band gap (eV = 1240/wavelength) [31]. Inset of Fig. S2 indicates the band gap of 3.45 eV for the β-CD-modified TiO₂ nanoparticle.

The band gap can be calculated from particle size using the relationship as below [32].

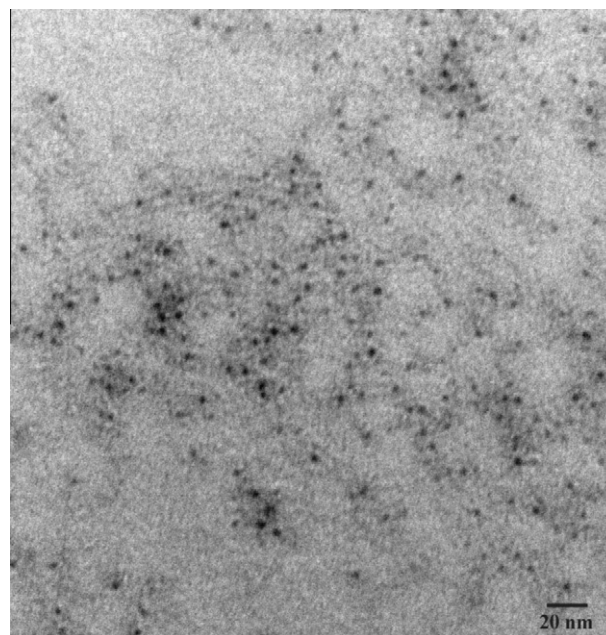


Fig. 1. A TEM picture of β-cyclodextrin-modified TiO₂ nanoparticles.

$$\Delta E = (E_g^2 + 4\lambda)^{1/2} = \left[E_g^2 + 2h^2 E_g \left(\frac{\pi}{R} \right)^2 \right]^{1/2} \quad (1)$$

where ΔE is the calculated band gap of the β -CD-modified TiO_2 nanoparticles, E_g is the band gap of the bulk TiO_2 , λ is the eigenvalue, R is the radius of the nanoparticles (evaluated from the TEM image), and $m^* = 1.2 m_e$, h is the reduced Planck constant, that is, the Planck constant divided by 2π . The band gap calculated (3.4 ± 0.1 eV) was higher than that (3.2 eV) of bulk anatase TiO_2 [31] but it was very close to the value obtained from the optical absorption spectrum (Fig. S2). The increase in band gap of particle TiO_2 from bulk TiO_2 is due to the size effect of the synthesized β -CD-modified TiO_2 nanoparticles (<5 nm).

An EDX spectrum of the β -CD-modified TiO_2 nanoparticles is shown in Fig. S3. The C and O peaks arise with Ti peaks, indicating the presence of the organic molecules and TiO_2 . The Cu peaks come from the copper substrate. The FT-IR spectra of the β -CD-modified TiO_2 nanoparticles and β -CD are shown in Fig. S4. The FT-IR spectrum of the β -CD-modified TiO_2 nanoparticles was found to be fairly similar to that of β -CD, that is, bands at 3378, 1640, 1360, 1160, 1080 and 1030 cm^{-1} assigned to the O–H stretching, O–H bending, O–H deformation and C–O–C stretching vibration modes were observed commonly in both spectra. Only one additional band of the Ti–O–Ti stretching mode occurred at 708 cm^{-1} in the spectrum of the β -CD-modified TiO_2 nanoparticles, different from that of β -CD. These results from EDX and IR spectra suggest that during the hydrolysis reaction in the aqueous solution the spherical TiO_2 nanoparticles are formed and stabilized by the β -CD molecules, maybe, by hydrogen-bonding of the hydrophilic hydroxyl groups of β -CD on TiO_2 nanoparticles.

3.2. Photophysical properties of β -CD-pyrene inclusion complex on TiO_2 nanoparticles

Formation of inclusion complex between pyrene and β -CD was examined by UV–vis absorption spectra. Fig. 2 shows absorption spectra of pyrene (3.3×10^{-5} M) in aqueous solutions containing various concentrations of β -CD. The absorption intensity slightly increased with increasing concentration of β -CD. This phenomenon relates to the fact that the electronic properties of the guest molecule, pyrene, are perturbed by host molecule, β -CD, resulting in the variation on absorption spectra of guest molecules [33]. This means that the pyrene is kept in more hydrophobic microenvironment of the β -CD by the formation of inclusion complex.

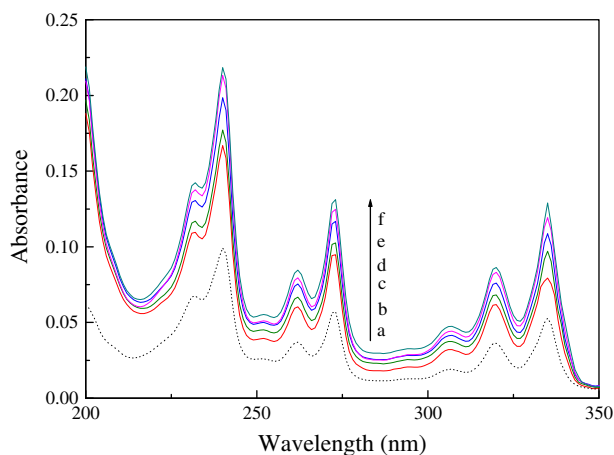
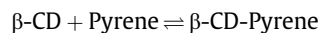
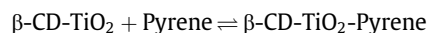


Fig. 2. UV–vis absorption spectra of pyrene (3.3×10^{-5} M) in aqueous solutions of β -cyclodextrin. Concentration of β -cyclodextrin: (a) 0.0 mM, (b) 0.05 mM, (c) 0.10 mM, (d) 0.15 mM, (e) 0.20 mM, (f) 0.25 mM.

Similar examination was carried out even for β -CD-modified TiO_2 nanoparticle. Fig. 3 exhibits the absorption spectra of pyrene (3.3×10^{-5} M) in aqueous solutions containing various concentrations of β -CD-modified TiO_2 nanoparticle. Upon the addition of β -CD-modified TiO_2 nanoparticle (β -CD- TiO_2), the absorption intensity of pyrene increased, although the absorbance below 330 nm increased with increasing nanoparticle concentration. Then it can be assumed that the following association reaction occurs:



or



Figs. 4 and 5 illustrate the fluorescence emission spectra (excited at 350 nm) of pyrene in aqueous solutions containing various concentrations of β -CD and β -CD-modified TiO_2 nanoparticle, respectively. The fluorescence intensity was enhanced upon the successive addition of β -CD and β -CD-modified TiO_2 nanoparticle to a solution of pyrene (3.3×10^{-5} M). The factor involved in the enhancement is considered to be the suppression of radiationless deactivation due to the property change of microenvironment, the restricted available space and the quenching by host molecule. In the β -CD-pyrene inclusion complex the observed emission enhancement of the hydrophobic pyrene originates in the protection from the quenching of the pyrene emission by water molecule owing to apolar cyclodextrin cavity.

It was also revealed from the comparison between Figs. 4 and 5 that the emission intensity of β -CD-pyrene inclusion complex increased triply in the presence of TiO_2 nanoparticles. Upon the binding to the β -CD-modified TiO_2 nanoparticles, the observed enhanced fluorescence intensity of pyrene reflects the suppression of the nonradiative decay process due to the improved charge transfer at the β -CD-pyrene inclusion complex/semiconductor interface. Namely, the marked increasing in the fluorescence intensity comes from the TICT between TiO_2 semiconductive nanoparticles and pyrene molecules encapsulated in β -CD. It could be attributed to the electron transfer from pyrene molecule in CD to the TiO_2 semiconductor nanoparticles (<5 nm). Similar qualitative aspect of fluorescence enhancement has been recently discussed for a β -CD-modified CdSe/ZnS quantum dot system [34], although they did not examine concentration dependency of quantum dots. In most cases, the photoinduced charge transfer between the adsorbed molecule and the TiO_2 surface resulted in a quenching of

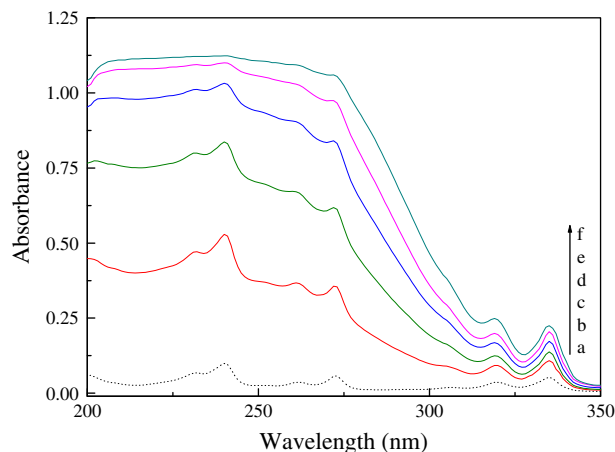


Fig. 3. UV–vis absorption spectra of pyrene (3.3×10^{-5} M) in aqueous solutions of β -cyclodextrin-modified TiO_2 nanoparticle. Concentration of β -cyclodextrin-modified TiO_2 nanoparticle: (a) 0.0 mM, (b) 0.05 mM, (c) 0.10 mM, (d) 0.15 mM, (e) 0.20 mM, (f) 0.25 mM.

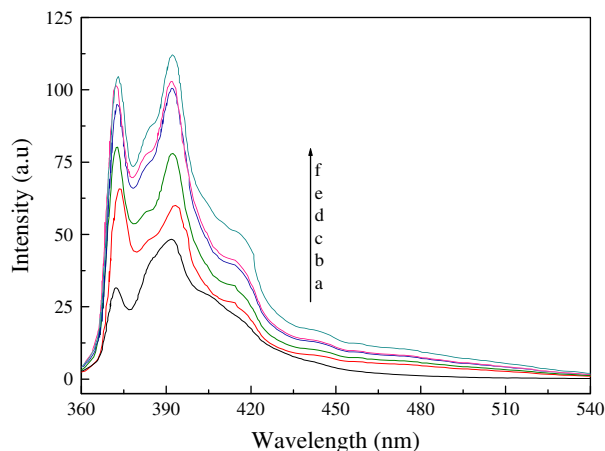


Fig. 4. Fluorescence spectra of pyrene (3.3×10^{-5} M) in aqueous solutions of β -cyclodextrin (excited at 350 nm). Concentration of β -cyclodextrin: (a) 0.0 mM, (b) 0.05 mM, (c) 0.10 mM, (d) 0.15 mM, (e) 0.20 mM, (f) 0.25 mM.

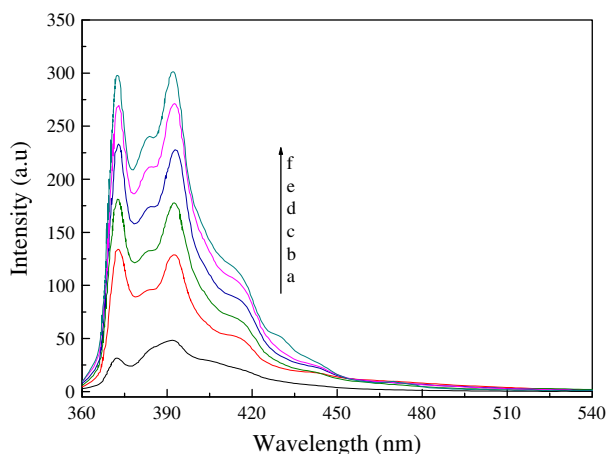


Fig. 5. Fluorescence spectra of pyrene (3.3×10^{-5} M) in aqueous solutions of β -cyclodextrin-modified TiO_2 nanoparticle (excited at 350 nm). Concentration of β -cyclodextrin-modified TiO_2 nanoparticle: (a) 0.0 mM, (b) 0.05 mM, (c) 0.10 mM, (d) 0.15 mM, (e) 0.20 mM, (f) 0.25 mM.

the fluorescence of fluorophore molecule. However, in the present system it should be assumed that the TiO_2 surface was modified by CD molecules and the distance between the TiO_2 surface and pyrene encapsulated in CD is long enough to prevent the quenching on the excited state of pyrene from the TiO_2 . Similar kind of enhancement behavior on fluorescence has been reported for another nanostructural material [35].

3.3. Charge transfer between pyrene and β -cyclodextrin-modified TiO_2 nanoparticles

The extinction coefficient (ϵ and ϵ') and apparent association constant (K_{app} and K'_{app}) of β -CD-Pyrene and β -CD- TiO_2 -Pyrene, respectively, can be calculated from the UV-vis absorption and fluorescence data using the following equation based on the 1:1 (CD:pyrene) inclusion model [36]:

$$\frac{[\text{Py}]}{X} = \frac{1}{\epsilon} + \frac{1}{K_{\text{app}}\epsilon[\beta\text{-CD}]} \quad (2)$$

or

$$\frac{[\text{Py}]}{X'} = \frac{1}{\epsilon'} + \frac{1}{K'_{\text{app}}\epsilon'[\beta\text{-CD-TiO}_2]} \quad (3)$$

($X = A$ or I and $X' = A'$ or I') where $[\text{Py}]$, $[\beta\text{-CD}]$ and $[\beta\text{-CD-TiO}_2]$ are the concentrations of pyrene, β -CD and β -CD-modified TiO_2 nanoparticles added, respectively, and A or I (A' or I') are the absorbance or emission intensity of β -CD-Pyrene (β -CD- TiO_2 -Pyrene) at a given wavelength. In the present case, an absorption band at 335 nm is chosen as a given wavelength, because the superposition of TiO_2 absorption is less. From the emission spectra (excited at 350 nm) a band at 373 nm (first vibronic fluorescence band) is a given wavelength. The symmetry forbidden 0–0 band (I_1) at 373 nm is enhanced as the concentration of TiO_2 nanoparticles changes, as seen in Fig. 5.

Using absorption data, plots of $[\text{Py}]/A$ against $1/[\beta\text{-CD}]$ and $[\text{Py}]/A'$ against $1/[\beta\text{-CD-TiO}_2]$ are shown in Fig. 6, where absorbance values were used after background correction. The linear relations indicate that the data follows the equation by Benesi and Hildebrand for 1:1 (CD:pyrene) inclusion complex. From the plots, extinction coefficients ϵ and ϵ' were calculated to be 4290 and $8370 \text{ cm}^{-1} \text{ M}^{-1}$, respectively, for CD-Pyrene and CD- TiO_2 -Pyrene. Then the association constant K_{app} and K'_{app} were $2.4 \times 10^4 \text{ M}^{-1}$ and $1.2 \times 10^4 \text{ M}^{-1}$, respectively. Similarly plots $[\text{Py}]/I$ against $1/[\beta\text{-CD}]$ and $[\text{Py}]/I'$ against $1/[\beta\text{-CD-TiO}_2]$ from the fluorescence data are shown in Fig. 7. The linear relations again indicate that a 1:1 (CD:pyrene) inclusion complex is formed. According to Eqs. (2) and (3), the calculated emission coefficients ϵ and ϵ' were 3.63×10^6 and $11.7 \times 10^6 \text{ cm}^{-1} \text{ M}^{-1}$ and the apparent association constants were calculated to be $2.3 \times 10^4 \text{ M}^{-1}$ and $1.0 \times 10^4 \text{ M}^{-1}$ for CD-Pyrene and CD- TiO_2 -Pyrene, respectively.

The association constants obtained from fluorescence spectra are same order as values from the absorption spectra in the present work and values reported for anthracene-9-carboxylic acid/colloidal TiO_2 system [37] and over all equilibrium constant for the pyrene- β -CD complex [38]. It is noticed that the association constants evaluated from fluorescence data are more acceptable than those from UV-vis absorption data, because the analytical error by correction of background spectra as carried out on absorption spectra is not necessary to take into consideration on fluorescence spectra. The large values of association constants, which were obtained from plots in Figs. 6 and 7, support the strong association of pyrene with the β -CD and β -CD-modified TiO_2 nanoparticles. This large association constant of pyrene is an essential factor for making the heterogeneous charge-transfer complex between the semiconductor and pyrene.

It should be noted that the association constant of β -CD-pyrene (1:1) inclusion complex decreased at the immobilization of β -CD

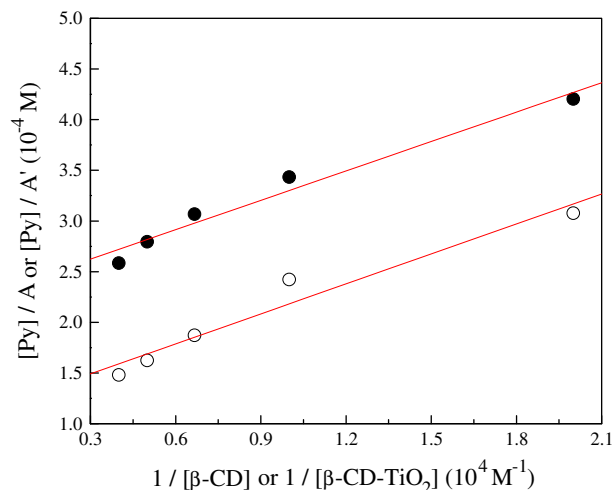


Fig. 6. Plots of $[\text{Py}]/A$ and $[\text{Py}]/A'$ against concentration of β -CD (\bullet) and β -CD- TiO_2 (\circ), respectively.

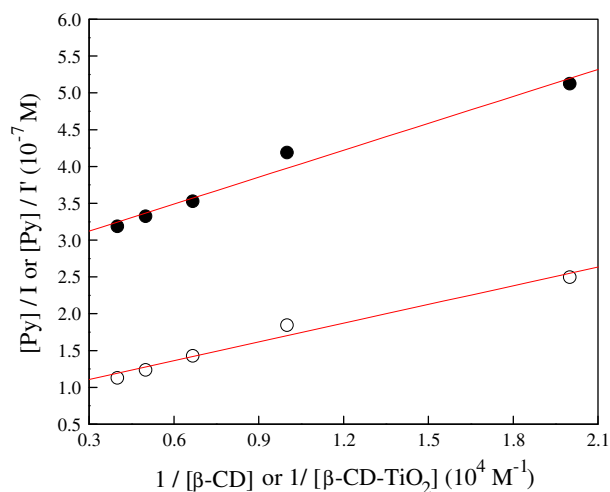


Fig. 7. Plots of $[Py]/I$ and $[Py]/I'$ against concentration of β -CD (●) and β -CD- TiO_2 (○), respectively.

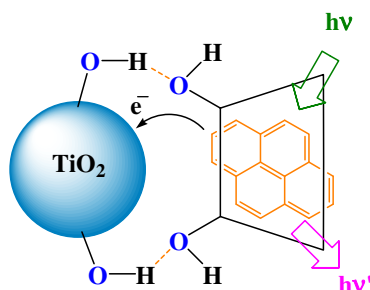


Fig. 8. Proposed mechanism of interfacial charge transfer between TiO_2 semiconductor and pyrene- β -CD complex to stabilization of excited state.

on TiO_2 nanoparticle. The reason is that the outer rim hydroxyl groups of β -CD are concentrated on TiO_2 nanoparticles because of the interaction between metal oxide and hydroxyl group, which changes the feature of the β -CD cavity and diminishes the binding of pyrene to β -CD. Meanwhile extinction coefficients from both absorption and fluorescence spectra are larger for β -CD- TiO_2 -Pyrene than for β -CD-Pyrene. The outer rim hydroxyl groups of cyclodextrin molecules, which became more concentrated on semiconductor metal oxide, resulted in concentrated charges around the CD-pyrene inclusion complex.

These results support that the cyclodextrin on TiO_2 nanoparticle acts not only as molecular recognizing agent but also as an electron donor for energy transfer from the nanoparticle to the guest molecule for improving photocatalysis and for generating sensitizing effect, as illustrated in Fig. 8.

4. Conclusions

TiO_2 has been extensively investigated in the field of dye-sensitized solar cells, sensors, and photocatalyses. To improve the photophysical property of TiO_2 involves a charge transfer from a surface modifier into the conduction band of TiO_2 , and the efficient methodology for such improvement is required now. Then in this work the nanocrystalline TiO_2 semiconductor was designed by highly-effective binding with β -CD for charge transfer. β -CD-modified water-dispersible TiO_2 nanoparticles were synthesized by a single pot hydrolysis of titanate in an aqueous solution of β -CD.

The β -CD-modified TiO_2 nanoparticles with narrow size distribution had high band gap energy and UV-vis absorption below 330 nm.

On the investigation of the fluorescence property of a pyrene molecule in an inclusion complex with β -CD, it was observed that the fluorescence intensity of pyrene in an aqueous solution increased with adding cyclodextrin and in the presence of TiO_2 nanoparticle. The investigation suggests that the β -CD molecule offering a unique microenvironment to pyrene becomes a binding site for pyrene- TiO_2 interaction and promotes the charge injection from the excited pyrene molecule to the TiO_2 nanoparticle. Finally, the triply sensitizing of pyrene fluorescence by β -CD-modified TiO_2 nanoparticle indicates that this nanoparticle is a promising material for improving catalysis, sensing molecules and so on. Such unique properties let us to be prospective the applications of β -CD-modified TiO_2 nanoparticle as a promised sensitizing material for improving technology in solar cell, fuel cell and other devices.

Appendix A. Supplementary material

Supporting Information Available. A size histogram of β -cyclodextrin-modified TiO_2 nanoparticle, FT-IR and UV-vis absorption spectra of β -cyclodextrin-modified TiO_2 nanoparticle and β -cyclodextrin (Inset: optical absorption spectra of the β -cyclodextrin-modified TiO_2 nanoparticle) and an EDX spectrum of cyclodextrin-modified TiO_2 nanoparticles are provided. This information is available free of charge via the internet at www.sciencedirect.com. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jcis.2010.08.055](https://doi.org/10.1016/j.jcis.2010.08.055).

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