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Synthesis, isolation, and redispersion of resorcinarene-capped anatase TiO$_2$ nanoparticles in nonaqueous solvents

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Abstract

C-undodecylcalix[4]-resorcinarene (C$_{11}$-resorcinarene)-capped anatase TiO$_2$ nanoparticles have been synthesized and could be isolated and redispersed in different nonaqueous solvents. The adsorption of C$_{11}$-resorcinarene onto the surface of TiO$_2$ nanoparticles led the shifting of the onset wavelength of the optical absorption in the visible range along with a broad band centered at 422 nm corresponding to ligand-to-metal charge transfer transition within the surface titanium(IV)–C$_{11}$-resorcinarene complex. The interaction of TiO$_2$ nanoparticle with C$_{11}$-resorcinarenes was investigated by photoluminescence (PL). Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy study revealed that the C$_{11}$-resorcenarene molecules adsorbed chemically onto the surfaces of TiO$_2$ nanoparticles. The average particle diameter of bare anatase TiO$_2$ and C$_{11}$-resorcinarene-capped TiO$_2$ was determined using transmission electron microscopy (TEM) and was found to be equal to ca. 5 nm.
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1. Introduction

The anatase TiO$_2$, which is one of the three different crystalline polymorphs of TiO$_2$: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic), has been studied extensively because of its potential applications mainly in the photoelectric conversion in solar cells [1–9] and photocatalysis [10–14]. It has been pointed out that the anatase TiO$_2$ can prove to be the most efficient among its polymorphs if it exhibits the unique ability to absorb visible light significantly. Unfortunately, however, anatase TiO$_2$ is a poor visible light absorber as it requires large band gap energy (3.2 eV) for the excitation of electrons from the filled valence band to the vacant conduction band. Therefore, a number of different approaches have been devoted for the enhancement of the photo-response and improvement of the photo-activity of TiO$_2$ by: (a) doping transition metals or nonmetals into TiO$_2$ [14–17]; (b) reducing TiO$_2$ using hydrogen plasma [18]; and (c) adsorbing metal complexes [19–23] or organic dyes [24–35] onto the surfaces of TiO$_2$. More or less,

all these attempts have enhanced the visible light absorption ability of TiO$_2$. Consistent findings have revealed that the dye-sensitized TiO$_2$ has attracted a great degree of attention due to its potential applications in the dye-sensitized solar cell, which is known as a class of hybrid materials used in photovoltaic devices [36,37].

N-methylphenazinium ion was known to be the first used dye for the sensitization of TiO$_2$ which shifted the optical absorption to the 500 nm region [38]. This dye-sensitized TiO$_2$ was used for solar energy conversion in photoelectrochemical cells; the conversion efficiency of such a device was very low and the stability of the dye was in question, though. The research on dye-sensitized TiO$_2$ has therefore received more attention since Grätzel et al. [19] reported a photochemical solar cell using nanoparticles TiO$_2$ by a more efficient and stable dye, *cis*-dithiocyanato-bis(4,4′-dicarboxy-2,2′-bipyridine) ruthenium(II) complex, which exhibited 7–10% conversion efficiency under solar conditions. Few years later, Grätzel et al. [20] reported another new dye, trithiocyanato (4,9,14-tricarboxy-2,2′-6,6′-terpyridyl) ruthenium(II), which displayed the efficiency of about 11%. Thus, it remains to be an intriguing topic of research and new dye-sensitized TiO$_2$ nanoparticles materials are in high demand since then.

However, there are very few approaches of surface modification of TiO$_2$ nanoparticles by organic dyes having long hydrophobic tails, which enable TiO$_2$ particles to disperse in non-aqueous organic solvents, reported in literature. For instances, Ghosh and Ramakrishnan [26] reported dodecylbenzenesulfonate-capped TiO$_2$ nanoparticles; Wang et al. [25] reported dodecylamine-capped TiO$_2$ particles; Weller et al. [34] reported oleic acid-capped TiO$_2$ particles. The binding nature of all these dyes is in monodentate fashion. The multidentate macrocycle C-alkylcalix[4]-resorcinarene, which has four hydrophobic tails and eight hydroxyl groups on its own skeleton, can be an effective surface modifier for nanoparticles. C-alkylcalix[4]-resorcinarenes exhibit four conformers [39,40]. Among these, the crown conformer is the most thermodynamically stable isomer. It has a cylindrical structural conformation; all four substituents at the methylene bridges linking the resorcinol moieties are tethered downward from the upper rim, while hydroxyl groups point upward, above its cavity. In 1997 Atwood and McGillivray [41] reported the structure of resorcinarene as shown in Scheme 1 in the solid state and suggested its expanded possibilities for molecular recognition in solution. It has been widely used as a molecular recognition [42]. However, its nanoparticle recognition property has not been explored widely, although it has the similar potentiality as it is for molecular recognizer. Recently, C$_{11}$-resorcinarene has been employed as a capping and dispersant agent for gold nanoparticles in organic solution [43]. In our previous paper [43], we explored its use in the phase transfer of gold nanoparticles from aqueous solution to organic solution without using any other additional agent. Resorcinarene is advantageous over conventional small and single chain modifiers in several regards: (i) its adsorption onto the nanoparticle surface can be greatly stabilized by its cooperative multidentated nature of interactions; (ii) it may be reduced the entropy cost of dissolution for having lower surfactant/particle ratio; (iii) it may increase the solubility of nanoparticles in nonpolar solvents for having greater mobility of the pendant hydrocarbon tails. In this report we present a simple method for the synthesis of dispersions of C-undodecylcalix[4]-resorcinarene (C$_{11}$-resorcinarene)-capped TiO$_2$ nanoparticles in 1-propanol, with the particularity that the particles can be dispersed into other nonaqueous solvents through a dry state.

2. Experimental

2.1. Materials and instruments

Titanium(IV) tetraisopropoxide {Ti[OCH(CH$_3$)$_2$]$_4$; 284.26} (Aldrich, 97%, Milwaukee, WI, USA), resorcinol (C$_6$H$_6$O$_2$; 110), ethanol absolute, isopropanol, 1-propanol and hydrochloric acid (Riedel-de Haën, Seelze, Germany) and nitric acid (Merck, Darmstadt, Germany) were purchased from the indicated sources and were used as received without further purification.

UV–vis absorption spectra were recorded on a Hitachi U-3200 spectrophotometer using quartz cell with a path length of 1 cm. Photoluminescence (PL) spectra at room temperature were obtained using a Hitachi F-4010 fluorescence spec-

R = -CH$_2$(CH$_2$)$_9$CH$_3$
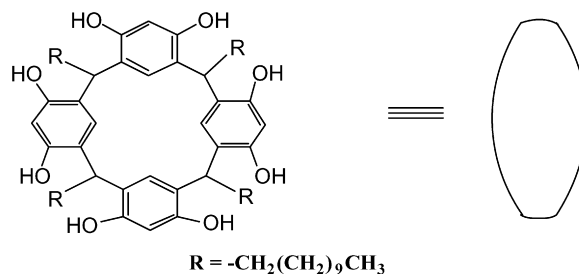
Scheme 1. C-undodecylcalix[4]-resorcinarene.

trophotometer. ^{1}H NMR spectra were recorded at 400 MHz on a Bruker AC-400 spectrometer. TEM photographs were taken on Hitachi H-7100 transmission electron microscopes at acceleration voltage of 75 kV. The samples for TEM measurements were prepared by placing a drop of proper solution of bare and C$_{11}$-resorcinarene-capped TiO$_2$ nanoparticles onto a copper microgrid and dried at room temperature.

2.2. Preparation of C$_{11}$-resorcinarene

C$_{11}$-resorcinarene was prepared following the method described in our previous report [43].

2.3. Preparation of TiO$_2$ nanoparticles

An aqueous solution of TiO$_2$ nanoparticles was prepared via the hydrolysis of Ti^{IV} tetraisopropoxide in water under controlled pH conditions, as reported earlier [28]. A transparent solution of TiO$_2$ nanoparticles was obtained by adding dropwise a 2.5 ml aliquot of Ti[OCH(CH$_3$)$_2$]$_4$ dissolved in 47.5 ml isopropyl alcohol to 450 ml of pure water at 2 °C adjusted to pH 1.5 with HNO$_3$ and continuously stirred for 12 h or longer until a transparent solution obtained. Solution can be stored over 3 months at low temperature (4 °C) without coagulation. A 50 ml of the aqueous TiO$_2$ nanoparticles solution was concentrated to 1 ml at 50 °C (using vacuum rorary-evaporator) which was either subjected to react with C$_{11}$-resorcinarene or used to take out the TEM image for TiO$_2$ particles.

2.4. Synthesis of C$_{11}$-resorcinarene-capped TiO$_2$ nanoparticles

C$_{11}$-resorcinarene (210 mg, 0.19 mM) was dissolved in 50 ml of 1-propanol. A 50 ml of as-prepared TiO$_2$ nanoparticles solution was concentrated to 1 ml at 50 °C using vacuum rorary-evaporator and was then added into the solution of C$_{11}$-resorcinarene, leading to the formation of an orange-yellow color solution immediately. The reaction mixture was stirred for 3 h at room temperature. The solution was driven off using vacuum rotary-evaporator at 50 °C leaving an orange-red color residue which was washed thoroughly with water and dried. The residue was then redispersed in dichloromethane. The UV–vis spectra and TEM photographs of orange-yellow solution in 1-propanol and orange-red solution in dichloromethane were recorded. The residuals C$_{11}$-resorcinarene could be filtered off from the methanolic solution by distillation of dichlo-

romethane solution followed by redispersion of residue in methanol. The methanolic solution was evaporated and gave an orange-red color residue, which was then dried in vacuum. ^1H NMR spectrum of the isolated residue was recorded in $CDCl_3$.

3. Results and discussion

UV–vis spectroscopy was studied to characterize the optical absorptions of the nanoparticles solutions. The onset wavelength (λ_{OS}) of the optical absorption and the corresponding bandgap energy (E_g) of TiO_2 are $\lambda_{OS} = 385$ nm and $E_g = 3.2$ eV for anatase [44] and $\lambda_{OS} = 415$ nm and $E_g = 3.0$ eV for rutile [45]. UV–vis absorption spectra along with a photograph (inset) of the solutions of C_{11}-resorcinarene in 1-propanol (a), C_{11}-resorcinarene in 1-propanol upon addition of TiO_2 nanoparticles (b), and C_{11}-resorcinarene-capped TiO_2 nanoparticles collected from the reaction mixture b by distilling off the solvent at $50\,^\circ C$ and redispersed in dichloromethane (c) are shown in Fig. 1. Obviously, C_{11}-resorcinarene has no absorption band in the region 300–600 nm (Fig. 1a). However, C_{11}-resorcinarene-capped TiO_2 nanoparticles show a broad absorption band centered at 422 nm (Figs. 1b and 1c). Figs. 2a and 2b represent the UV–vis absorption spectra of uncapped TiO_2 nanoparticles in water and C_{11}-resorcinarene-capped TiO_2 nanoparticles in comparatively high concentrated solution in dichloromethane, respectively. To determine the onset wavelength of the optical absorption of C_{11}-resorcinarene-capped TiO_2 nanoparticles, the UV–vis spectrum (Fig. 2b) was recorded. The onset wavelength of the optical absorption for uncapped TiO_2 appears at 366 nm or 3.39 eV, which is blue-shifted compared to the bulk anatase TiO_2, indicating the formation of nanoparticles solution. The spectrum of C_{11}-resorcinarene-capped TiO_2 nanoparticles (Fig. 2b) shows the onset wavelength of the optical absorption at 663 nm or

1.87 eV. In comparison with the bare TiO_2 (3.39 eV), the onset wavelength of C_{11}-resorcinarene-capped TiO_2 shifts by 1.52 eV to the red, revealing that the surface modification of TiO_2 has been occurred by the C_{11}-resorcinarenes. Apart from the red-shift in the absorption edge, it has been seen that the UV–vis spectrum (Fig. 2b) taken at higher concentration of C_{11}-resorcinarene-capped TiO_2 nanoparticles solution rises as steeply as bare TiO_2 nanoparticles solution toward higher energies, indicating that the optical absorption properties for C_{11}-resorcinarene-capped TiO_2 semiconductor nanoparticles are parallel to the absorption properties characteristic of the band structure in semiconductor TiO_2 nanoparticles. The optical absorption red-shift induced by surface modification of TiO_2 with several monodentate organic dyes was observed by several authors: Zou et al. [27] with stearic acid, Ghosh et al. [26] with sodium dodecylbenzenesulfonate-, and Wang et al. [25] with dodecylamine-capped TiO_2 particles. The authors attributed the absorption red shift to an intraband surface states that formed by surfactant molecules chemically bound on the TiO_2 surface. They demonstrated that the interfacial interaction between titania and surfactants could lead to formation of a dipole layer of oxygen vacancies and surfactants; the dipole layer might become the trap state center of an exciton, which could enhance the exciton binding energy more significantly, and induce the red shift of the absorption band edge of the dye sensitized TiO_2. In a different approach, Rajh et al. [30–32] have reported the surface modification of nanocrystalline anatase TiO_2 particles with *ortho*-substituted hydroxylated enediols ligands (e.g., catechol, dopamine, alizarin, etc.), which as well improves the optical response in the visible region. The chelation of surface Ti-atoms with the electron donating bidentate ligands in these systems changes the electron properties of nanoparticles. Authors attributed the red shift in the absorption edge in the modified semiconductor nanoparticles to the excitation of localized electrons from the surface modifier into the conduction band continuum states of the semiconductor particles. They pointed out that the binding of surface
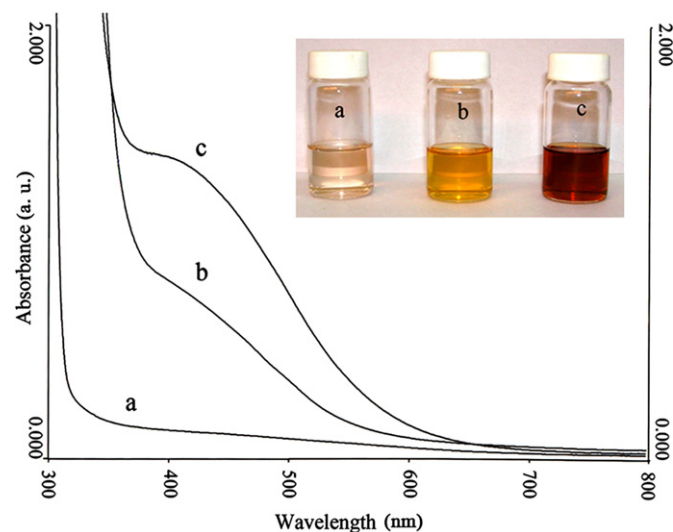

Fig. 1. UV–vis spectra of (a) C_{11}-resorcinarene, (b) C_{11}-resorcinarene-capped TiO_2 NPs in 1-propanol, and (c) C_{11}-resorcinarene-capped TiO_2 NPs in dichloromethane. Inset is the photograph of corresponding solutions of a, b, and c.
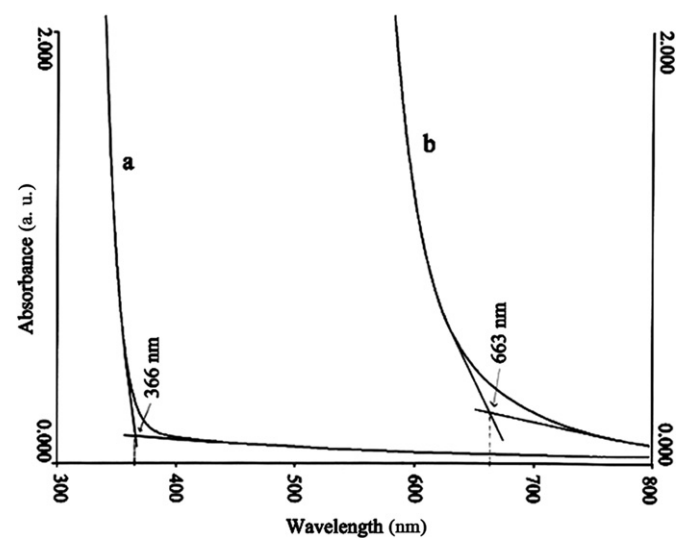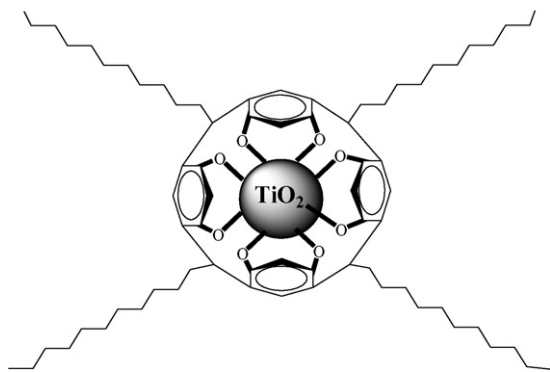

Fig. 2. UV–vis spectra of (a) as-prepared TiO_2 nanoparticles in aqueous solution and (b) C_{11}-resorcinarene-capped TiO_2 nanoparticles in dichloromethane.

Scheme 2. Schematic representation of a C_{11}-resorcinarene-TiO$_2$ complex consisting of a TiO$_2$ core and a C_{11}-resorcinarene ligand.

Fig. 3. Excitation spectrum of C_{11}-resorcinarene in 1-propanol upon emission at 648 nm.

modifiers was exclusively characteristic of small particle colloids and was stabilized by ligand adsorption-induced surface restructuring of the nanoparticle surface. C_{11}-resorcinarene, which is a multidentate macrocyclic ligand containing four resorcinol units linked through methylene bridges along with long hydrocarbon chains, can form multiple O$_2$Ti–O-resorcinarene bonding. TEM images (discussed later) show that the bare TiO$_2$ particles have an average diameter of about ca. 5 nm whereas C_{11}-resorcinarene has the surface area of the concave headgroups of diameter about ca. 1 nm. It is therefore, expected that one C_{11}-resoecinarene moiety could cover 1 nm surface area of a TiO$_2$ particle upon adsorption. A schematic representation of C_{11}-resorcinarene complex consisting of a TiO$_2$ core and a C_{11}-resorcinarene ligand is shown in Scheme 2. The multiple O$_2$Ti–O–C_{11}-resorcinarene bonding can also be inferred from the photoluminescence of C_{11}-resorcinarene and proton-NMR of C_{11}-resorcinarene-capped TiO$_2$ studies. The shift in the band edge to the red, which is similar to that of *ortho*-substituted hydroxylated bidentate aromatic enediols modifiers, in the present investigation can therefore, be attributed to a consequence of adsorption-induce restructuring of the TiO$_2$ nanoparticle surface by C_{11}-resorcinarene. C_{11}-resorcinarene-capped TiO$_2$ nanoparticles shows an absorption band centered at 422 nm, similar as observed by Rajh et al. [32] in case of alizarin-modified TiO$_2$ nanoparticles, suggesting excitation to a localized state rather than excitation to a continuum. Huber et al. [24] investigated the mechanism of electron injection from alizarin into TiO$_2$ with ultrfast optical spectroscopy and concluded that surface states play an important role in the electron transfer mechanism. Due to the presence of long hydrophobic tails in the skeleton of C_{11}-resocinarene, modification can provide the dispersibility and stability of TiO$_2$ particles in the non-aqueous solvents. Nevertheless, the C_{11}-resorcinarene-capped TiO$_2$ particles are extremely stable in organic solvents such as dichloromethane, chloroform etc, because no time dependent changes in the UV–vis spectra or precipitation were observed even a month after dispersing nanoparticles into the organic solvents.

Excitation spectrum of C_{11}-resorcinarene in 1-propanol upon emission at 648 nm shows four bands including a strong band at 308 nm (Fig. 3). The bands in the region of 250–350 nm can be attributed to the transitions in the aromatic groups;
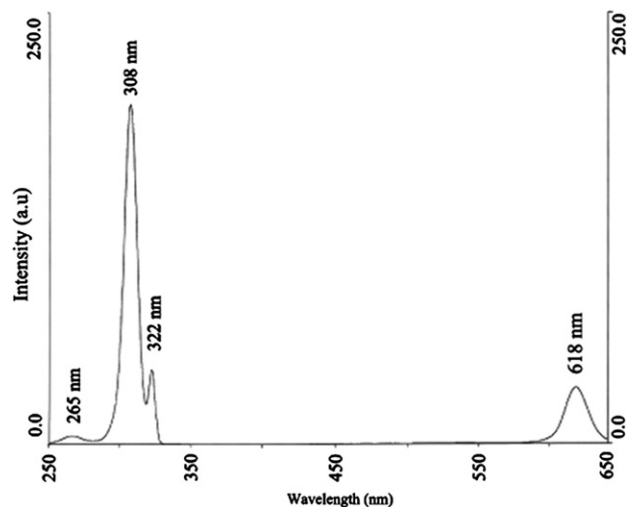
the band at 618 nm can be attributed to the formation of intramolecular hydrogen bonding between the hydroxyl groups of resorcinol rings as a result of the essential redistribution of electron density takes place, causing the delocalization of π-electrons through H-bridges [46]. Thus, the effect of bonding of C_{11}-resorcinarene to TiO$_2$ nanoparticles was studied on photoluminescence upon excitation at 308 nm. In order to investigate the interaction of TiO$_2$ nanoparticle with C_{11}-resorcinarenes, five sets of reaction mixtures were prepared. Each set contained 10 ml of C_{11}-resorcinarene solution (2 mM) in 1-propanol, but the added microliter volume of aqueous solution of as-prepared TiO$_2$ nanoparticles was varied from set to set. Reaction mixtures were stirred for 2 h and aged for 4 h. Photoluminescence (PL) spectra of all sets were taken at room temperature. Fig. 4 shows the PL spectra of C_{11}-resorcinarene solutions in the absence and presence of as-prepared TiO$_2$ nanoparticles in 1-propanol, by using 308 nm for excitation wavelength. Evaluating the spectra, it could be seen that the presence of nanoparticles induced changes on the spectra. The shapes of the PL spectra are very similar: the maximum intensity was obtained at 327 nm in cases of both C_{11}-resorcinarene and C_{11}-resorcinarene in presence of TiO$_2$ particles solutions. While there were no major changes in the wavelength, the change in intensity was significant. The PL intensity of pure C_{11}-resorcinarene was significantly reduced in presence of TiO$_2$ nanoparticles, indicating effective charge transfer from the C_{11}-resorcinarene moiety to the conduction band of TiO$_2$ through chelation. The interaction of C_1-resorcinarene with metal ions showed similar trend in PL spectra [47,48].

The proton NMR spectra of C_{11}-resorcinarene and C_{11}-resorcinarene-capped TiO$_2$ particles are given in Figs. 5a and 5b. The phenolic-OH groups of C_{11}-resorcinarene (Fig. 5a) are separated at $\delta = 9.62$ and 9.29, respectively, because half of the OH groups are subjected to intramolecular hydrogen bonding to stabilize the cyclic structure [49]. The signals of two hydrogen atoms of benzene rings originated from resorcin are well separated and appeared at $\delta = 7.19$ and 6.09, respectively,
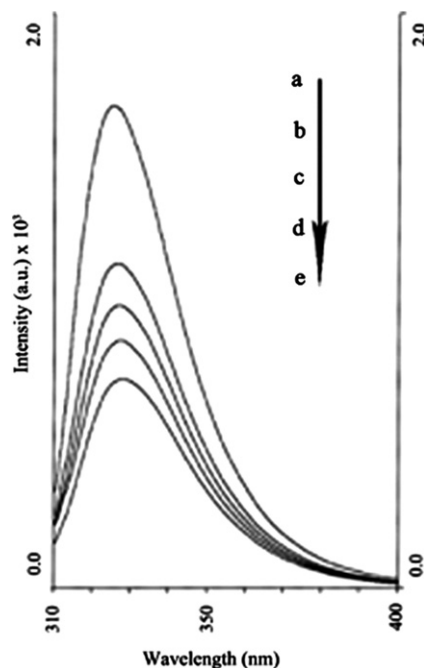
Fig. 4. PL spectra of (a) C_{11}-resorcinarene and C_{11}-resorcinarene in presence of (b) 50, (c) 100, (d) 150, and (e) 200 μl as-prepared aqueous TiO_2 nanoparticles solution in 1-propanol.

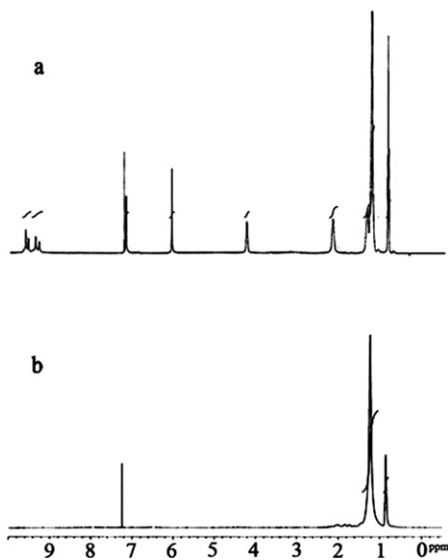Fig. 5. ^{1}H NMR spectra of (a) C_{11}-resorcinarene and (b) C_{11}-resorcinarene-capped TiO_2 nanoparticles in $CDCl_3$.

indicating that the molecule has C_{4v} symmetry. A comparison of the spectra of C_{11}-resorcinarene and C_{11}-resorcinarene-capped TiO_2 nanoparticles reveal that the proton resonances of hydroxyl groups, resorcinarene rings, methylene bridges and alkyl chains from resorcinarene [δ (ppm): 9.62–9.29 (ArOH), 7.19–6.09 (ArH), 4.29 (ArCRHAr), 2.21–1.26 (–CH_2–) and 0.87 (–CH_3)] are broaden after adsorption of C_{11}-resorcinarene onto the surfaces of TiO_2 nanoparticles. In fact, the proton signals from resorcin rings are completely missing in the spectrum of C_{11}-resorcinarene-capped particles. The result is due to both the discontinuity in the diamagnetic susceptibility of
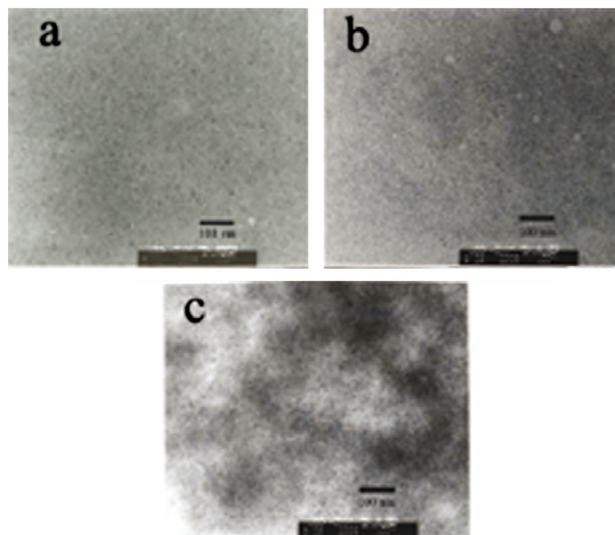

Fig. 6. Transmission electron micrograph of (a) bare TiO_2 nanoparticles in water, (b) C_{11}-resorcinarene-capped TiO_2 in 1-propanol, and (c) C_{11}-resorcinarene-capped TiO_2 in dichloromethane.

the TiO_2-hydrocarbon interface and the residual dipolar interactions in the layer due to spatial constraints, which confirms that C_{11}-resorcinarene is chemically bound to the particle surface [50–52]. The completely absence of the resonance of hydroxyl protons of C_{11}-resorcinarene in C_{11}-resorcinarene-capped TiO_2 complex indicates the presence of multiple O_2Ti–O–C_{11}-resorcinarene bonding. However, the resonances assigned to the C_2–C_{11} methylene remain largely unchanged, revealing that the bound ligands extend into the solvent with a relatively high degree of mobility.

TEM images of bare TiO_2 nanoparticles in water and C_{11}-resorcinarene-capped TiO_2 nanoparticles in 1-propanol and in dichloromethane are shown in Figs. 6a–6c, respectively. These were obtained by placing a drop of the corresponding solutions on the carbon-coated copper grid and allowing them to dry at ambient temperature. The average particle diameter of the bare TiO_2 in water and C_{11}-resorcinarene-capped TiO_2 in 1-propanol and dichloromethane was found to be equal to ca. 5 nm. TEM images show that the nature of dispersion of bare TiO_2 particles in water and C_{11}-resorcinarene-capped TiO_2 in 1-propanol and dichloromethane are same, revealing that C_{11}-resorcinarene could stabilize and disperse TiO_2 particles in nonaqueous solvents.

4. Conclusions

Anatase TiO_2 is a poor visible light absorber which goes against its applicability to be an effective material in conversion of photoelectric in solar cells. However, such limitation can be overcome if its surface modification is made. The multidentate macrocycle C-alkylcalix[4]-resorcinarene, which has four hydrophobic tails and eight hydroxyl groups on its own skeleton, can be an effective surface modifier for TiO_2 nanoparticles. Surface modification of anatase TiO_2 nanoparticles has been made by C_{11}-resorcinarene. We successfully synthesized C_{11}-resorcinarene-capped TiO_2 nanoparticles that could be iso-

lated and redispersed in different nonaqueous solvents, following a very simple innovative route. TEM images show that the TiO$_2$ particles are well dispersed in nonaqueous solvents such as 1-propanol and dichloromethane. Multidentate macrocycle C$_{11}$-resorcinarene adsorbed chemically onto the surface of TiO$_2$ and induced shifting of the onset wavelength of the optical absorption of TiO$_2$ nanoparticles into the visible region. The effective charge transfer from the C$_{11}$-resorcinarene moiety to the conduction band of TiO$_2$ through chelation was studied by photoluminescence. ^{1}H NMR study evidences the formation of multiple O$_2$Ti–O-resorcinarene bonding. We hope C$_{11}$-resorcinarene-capped TiO$_2$ would be one among the effective dye-sensitized semiconductor materials.

Acknowledgment

References

[1] B. O'Regan, M. Grätzel, Nature 353 (1991) 737.
[2] L. Kavan, B. O'Regan, A. Kay, M. Grätzel, J. Electroanal. Chem. 346 (1993) 293.
[3] M.S. Zhang, Z. Yin, Q. Chen, X.J. Wu, X.L. Ji, Ferroelectrics 168 (1995) 131.
[4] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, M. Grätzel, Nature 395 (1998) 583.
[5] W.H. Ma, Z. Lu, M.S. Zhang, Appl. Phys. A 66 (1998) 621.
[6] A. Hagfeldt, M. Grätzel, Acc. Chem. Res. 33 (2000) 269.
[7] N.G. Park, J.V.D. Lagemaat, A.J. Frank, J. Phys. Chem. B 104 (2000) 8989.
[8] S. Nakade, M. Matsuda, S. Kambe, Y. Saito, T. Kitamura, T. Sakata, Y. Wada, H. Mori, S. Yanagida, J. Phys. Chem. B 106 (2002) 10004.
[9] M. Thelakkat, C. Schmitz, H.W. Schmidt, Adv. Mater. 14 (2002) 577.
[10] J.C. Yu, J. Yu, W. Ho, L. Zhang, Chem. Commun. (2001) 1942.
[11] Z.B. Zhang, C.C. Wang, R. Zakaria, J.Y. Ying, J. Phys. Chem. B 102 (1998) 1087.
[12] C.A. Melenders, A. Narayanaswamy, V.A. Maroni, R.W. Siegel, J. Mater. Res. 4 (1989) 1246.
[13] M. Anpo, T. Shima, S. Kodama, Y. Kubokawa, J. Phys. Chem. 91 (1987) 4305.
[14] W. Choi, A. Termin, M.R. Hoffmann, J. Phys. Chem. 98 (1994) 13669.
[15] A.K. Ghosh, H.P. Maruska, J. Electrochem. Soc. 124 (1977) 1516.
[16] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269.
[17] S.M. Prokes, J.L. Gole, X. Chen, C. Burda, W.E. Carlos, Adv. Funct. Mater. 15 (2005) 161.
[18] T. Ihara, M. Miyoshi, M. Ando, S. Sugihara, Y. Iriyama, J. Mater. Sci. 36 (2001) 4201.
[19] M.K. Nazeeruddin, A. Kay, R. Humphry-Baker, E. Muller, P. Liska, N. Vanchopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.
[20] M.K. Nazeeruddin, P. Pechy, M. Grätzel, J. Chem. Soc. Chem. Commun. (1997) 1705.
[21] K. Kalyanasundaram, M. Grätzel, Coord. Chem. Rev. 177 (1998) 347.
[22] S.M. Zakeeruddin, M.K. Nazeeruddin, P. Pechy, F.P. Rotzinger, R. Humphry-Baker, K. Kalyanasundaram, M. Grätzel, V. Shklover, T. Haibach, Inorg. Chem. 36 (1997) 5937.
[23] A.F. Nogueira, L.F.O. Furtado, A.L.B. Formiga, M.N.K. Araki, H.E. Toma, Inorg. Chem. 43 (2004) 396.
[24] R. Hubber, S. Spörlein, J.E. Moser, M. Grätzel, J. Walhtveitl, J. Phys. Chem. B 104 (2000) 8995.
[25] Y. Wang, S. Zhang, X. Wu, Nanotechnology 15 (2004) 1162.
[26] G. Ramakrishna, H.N. Ghosh, Langmuir 19 (2003) 505.
[27] B. Zou, L. Xiao, T. Li, Appl. Phys. Lett. 59 (1991) 1826.
[28] G. Ramakrishna, H.N. Ghosh, J. Phys. Chem. B 105 (2001) 7000.
[29] J. Moser, S. Punchihewa, P.P. Infelta, M. Grätzel, Langmuir 7 (1991) 3012.
[30] T. Rajh, J.M. Nedeljkovic, L.X. Chen, O. Poluektov, M.C. Thurnauer, J. Phys. Chem. B 103 (1999) 3515.
[31] T. Rajh, O. Poluektov, A.A. Dubinski, G. Wiederrecht, M.C. Thurnauer, A.D. Trifunac, Chem. Phys. Lett. 344 (2001) 31.
[32] T. Rajh, L.X. Chen, K. Lukas, T. Liu, M.C. Thurnauer, D.M. Tiede, J. Phys. Chem. B 106 (2002) 10543.
[33] W.J.E. Beek, R.A.J. Janseen, Adv. Funct. Mater. 12 (2002) 519.
[34] P.D. Cozzoli, A. Kornowski, H. Weller, J. Am. Chem. Soc. 125 (2003) 1453.
[35] Y. Nakanishi, T. Imae, J. Colloid Interface Sci. 297 (2006) 122.
[36] M. Grätzel, Prog. Photovoltaics 8 (2000) 171.
[37] A. Hagfeldt, M. Grätzel, Acc. Chem. Res. 33 (2000) 269.
[38] S. Chen, S.K. Deb, H. Witzke, U.S. patent 4,080,488, March 21, 1978.
[39] L. Abis, E. Dalcanale, A.D. Vosel, S. Spera, J. Org. Chem. 53 (1988) 5475.
[40] A.G.S. Hoegberg, J. Am. Chem. Soc. 102 (1980) 6046.
[41] L.R. MacGillivray, J.L. Atwood, Nature 389 (1997) 469.
[42] N. Tbeur, T. Rhlalou, M. Hlaibi, D. Langevin, M. Metayer, J.F. Verchere, Carbohydr. Res. 329 (2000) 409, and references therein.
[43] T.K. Misra, J. Chen, C.Y. Liu, J. Colloid Interface Sci. 297 (2006) 584, and references therein.
[44] C. Kormann, D.W. Bahnemann, M.R. Hoffmann, J. Phys. Chem. 92 (1994) 5196.
[45] K. Kandori, K. Kon-No, A. Kitahara, J. Colloid Interface Sci. 122 (1998) 78.
[46] S.V. Shevchuk, N.V. Rusakova, A.M. Turianskaya, Y.V. Korovin, N.A. Nazarenko, A.I. Gren, J. Fluorescence 8 (1998) 225.
[47] S. Kunsagi-Mate, L. Nagy, G. Nagy, I. Bitter, L. Kollar, J. Phys. Chem. B 107 (2003) 4727.
[48] S.V. Shevchuk, N.V. Rusakova, A.M. Turianskaya, Y.V. Korovin, N.A. Nazarenko, A.I. Gren, J. Fluorescence 8 (1998) 225.
[49] Y. Aoyama, Y. Tanaka, S. Sugahara, J. Am. Chem. Soc. 111 (1989) 5397.
[50] R.H. Terrill, T.A. Postlethwaite, C.H. Chen, C.D. Poon, A. Terzis, et al., J. Am. Chem. Soc. 117 (1995) 12537.
[51] A. Badia, S. Sing, L. Demers, L. Cuccia, G.R. Brown, R.B. Lennox, Chem. Eur. J. 2 (1996) 359.
[52] B.A. Korgel, S. Fullam, S. Connolly, D. Fitzmaurice, J. Phys. Chem. B 102 (1998) 8379.