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BRIEF COMMUNICATION

Efficient carbon-doped nanostructured TiO_2 (anatase) film for photoelectrochemical solar cells

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Abstract In this paper, we have demonstrated that carbon-doped nanostructured TiO_2 (CD ns-TiO_2) films could be prepared simply and cheaply with oxalic acid and tetrabutylammonium bromide ($Bu_4N{\cdot}Br$) as the carbon sources. The surface morphology of the films was a multiple-porous network structure.The average size of nanoparticle was about 40 nm. Carbon doped into substitutional sites of TiO_2 has also proven to be indispensable for band-gap narrowing and photovoltaic effect. Carbon doping lowered the band gap of n-TiO_2 to 1.98, 1.64, and 1.26 eV. The CD ns-TiO_2 film was first used as photoanode for solar cells, exhibiting high photocurrent densities (l.34 mA/cm^2) and yielding an overall conversion efficiency (η) of 4.42 %.

Keywords Carbon-doped · Titanium dioxide · Solar cells · Photovoltaic effect · Sol–gel process · Nanocomposites · Energy conversion

Introduction

Photoelectrochemical solar cells are the most ambitious targets in the utilization of solar energy field (Grätzel 2001, 2003, 2004; O'Regan and Grätzel 1991; Chen et. al. 2006). Among the new materials being developed for solar cells, photocatalytic and other applications, titanium dioxide (TiO_2) remains one of the most promising materials because of its high efficiency, low cost, chemical inertness, eco-friendly nature and photostability (Fujishima and Honda 1972; Neumann et al. 2005; Kisch et al. 1998). However, the widespread use of TiO_2 is hindered by its low utilization of solar energy in the visible region (about 3–5%) because of the wide band gap (3.0 eV for rutile and 3.2 eV for anatase crystalline phase). Therefore, many efforts were concentrated on narrowing the optical band gap of titania. In dye-sensitized solar cells, this is being implemented successfully by anchoring low band gap ruthenium dye on to the surface of TiO_2. But the ruthenium dyes are expensive and unstable in aqueous solutions (Peter et al. 2003).

Narrowing of the band gap has been reported in polycrystalline powders and films of TiO_2 doped with anion impurities such as nitrogen (Asahi et al. 2001; Morikawa et al. 2001), carbon (De Vos et al. 2002; Khan et al. 2002; Sakthivel and Kisch 2003; Irie et al. 2003; Bard and co-workers 2006; Milani and co-workers 2005; Kisch and co-workers 2001) and sulfur (Ohno et al. 2003, 2004). In particular, carbon-doped

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TiO_2 was indicated as one of the best in terms of band gap narrowing. There are mainly several methods for preparing the carbon-doped TiO_2, such as direct oxidation of the Ti metal in the flame of a burner, oxidizing commercial TiC powders, the wet process synthesis, etc. Khan et al. (2002) reported incorporation of carbon during n-TiO_2 (rutile) synthesis by flame oxidation of Ti metal sheet lowered the band gap of n-TiO_2 to 2.32 eV (535 nm) and thereby exhibited water-splitting efficiency under xenon lamp illumination, but there is still disagreement about its solar-to-hydrogen conversion efficiency of 8.35 % (Fujishima 2003; Grätzel and co-workers 2003; Lackner 2003). Sakthivel and Kisch (2003) reported the wet process synthesis of carbon-doped TiO_2 (anatase) by hydrolysis of $TiCl_4$ with tetrabutylammonium hydroxide, and the samples (band gap of 3.02 eV) containing 2.98% carbon possessed the maximum band-gap narrowing of 0.14 eV. Irie et al. (2003) reported that the carbon-doped anatase TiO_2 powders (the percentage of carbon was 0.32 %) could be obtained by oxidizing commercial TiC powders. Recently, Bard and co-workers (2006) reported that novel carbon-doped TiO_2 nanotube arrays (band gap of 2.22 eV, the percentage of carbon was 8–42%) with high aspect ratios for efficient solar water splitting were prepared by controlling the anodizing conditions and heating with CO at 600 °C. Milani and co-workers (2005) obtained carbon-doped nanostructured TiO_2 films (rutile, the percentage of carbon was 17%) by cluster beam deposition with a band gap of 2.06 eV, but this method required high temperature.

The wet process synthesis of carbon-doped TiO_2 has received significant attention owing to its low cost, ease to scale up and eco-friendly nature (Kisch and co-workers 2004; Cong et al. 2006; Reddy et al. 2005; Khan and co-workers 2006a, b). Tetrabutylammonium hydroxide ($C_{16}H_{36}NOH$) (Kisch and co-workers 2004; Cong et al. 2006; Reddy et al. 2005) and glucose ($C_6H_{12}O_6$) (Khan and co-workers 2006a, b) were used as the carbon sources in the wet process synthesis. In either case, the percentage of carbon in carbon-doped TiO_2 was no more than 11.2% (Khan and co-workers 2006a, b). Although these carbon-doped TiO_2 samples synthesized in the presence of either of the two carbon sources show the shift of optical response from UV to near infrared region, the tetrabutylammonium hydroxide ($C_{16}H_{36}NOH$) and glucose ($C_6H_{12}O_6$) have large size, which are difficult to diffuse. Compared to glucose ($C_6H_{12}O_6$) and tetrabutylammonium ions ($C_{16}H_{36}N^+$), oxalic acid ($C_2H_2O_4$) will be easier diffusion due to its smaller size. However, there is little report on preparing carbon-doped TiO_2 film in the presence of oxalic acid ($C_2H_2O_4$) and using as photoanode for photoelectrochemical solar cells.

Recently, our group found that nanostructured TiO_2 (ns-TiO_2) films prepared using titanium ethanolate ($Ti(OEt)_4$) ethanol solution (containing carbon) as precursors by sol–gel process showed excellent photovoltaic activity to absorb visible light. The precursors of $Ti(OEt)_4$ ethanol solution were electrosynthesized firstly in the presence of oxalic acid and tetrabutylammonium bromide ($Bu_4N{\cdot}Br$) in our laboratory (Zhou et al., 2002). The gel of ns-TiO_2 films coated on the fluorine-doped SnO_2 (FTO) conducting glass was calcined at 450 °C for 30 min in air. Subsequently, the successful incorporation of the carbon into the ns-TiO_2 host was confirmed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscope (SEM), and UV-Visible spectra. The synthesized carbon-doped nanostructured TiO_2 (CD ns-TiO_2) films (anatase) absorbs well into the visible light to near infrared region up to 800 nm and have narrower band gap energy of 1.98 (628 nm), 1.64 (758 nm) and 1.26 eV (958 nm). The doping concentration of carbon in the CD ns-TiO_2 was 41% (as determined from the XPS peaks). We investigated the photoelectrochemical behavior of the CD ns-TiO_2 film photoanode for solar cells, it was found that the CD ns-TiO_2 film photoanode exhibited photocurrent densities (1.34 mA/cm^2) and an overall conversion efficiency (η) of 4.42 % under visible light illumination at 11 mW/cm^2.

Experimental

All reagents were analytical pure, 1,2-propanediol carbonate, $Bu_4N{\cdot}Br$, oxalic acid and Iodine were purchased from ShangHai Chemical Company, and lithium iodide was obtained from Alfa. The fluorine-doped SnO_2 (FTO) conducting glass was placed in deionized water and sonicated for 30 min, then washed thoroughly with deionized water and ethanol, respectively, then dried at room temperature. The precursors of $Ti(OEt)_4$ and TiO_2 sols were prepared as described in our previously works (Chu et al. 2005), the TiO_2 sols were coated on treated conducting glass, after calcining at 450 °C in air for 30 min and cooling to room temperature, a transparent CD ns-TiO_2 film electrode was obtained. The undopant ns-TiO_2 film was prepared in the same way.

XRD spectra were collected on a Philips X' Pert-pro X-ray diffractometer (Cu Kα). UV-visible absorption was collected with a U-4100 spectrophotometer (Hitachi, Kyoto Japan), UV-visible absorption of films on FTO were measured against the FTO substrate as a blank. SEM was collected using a FE-SEM (JSM-6700F, JEOL). XPS spectra were obtained by a VG ESCALAB MK II.

The current-voltage (I–V) characteristics were measured using LK 2005 microcomputer electroanalysis system. Appropriate cut-off filters were used. A 150 W xenon lamp was used as the light source, the incident light intensity calibrated by using a photometer. The photocurrent density versus measured potential for FTO/CD ns-TiO_2 photoanode characteristics were carried out using electrochemical workstation with a three-electrode system. The CD ns-TiO_2 film electrode, platinum foil, and an aqueous SCE served as the working, counter, and reference electrodes, respectively. The electrolyte solution consisted of 0.3 M LiI and 0.03 M I_2 in 1,2-propanediol carbonate. The current-voltage characteristics of the cell were measured two-electrode system under 11 mW/cm^2. The CD ns-TiO_2 film electrode served as photoanode, the cathode was obtained by electroplated FTO conducting glass in the solution of H_2PtCl_6. All experiments were carried out at room temperature.

Results and discussion

Figure 1 gives XRD pattern of CD ns-TiO_2 powders. XRD results demonstrated that the CD ns-TiO_2 nanoparticles were of homogeneous anatase structure with low crystallinity, and the average grain sizes calculated from Scherrer equation (crystallite size or grain size, d = $0.9\lambda/\beta_{1/2}$ cosθ, where λ is the characteristic X-ray wavelength applied (0.154056 nm), $\beta_{1/2}$ is the half width of the peak at the 2θ value) were found to be about 12 nm.

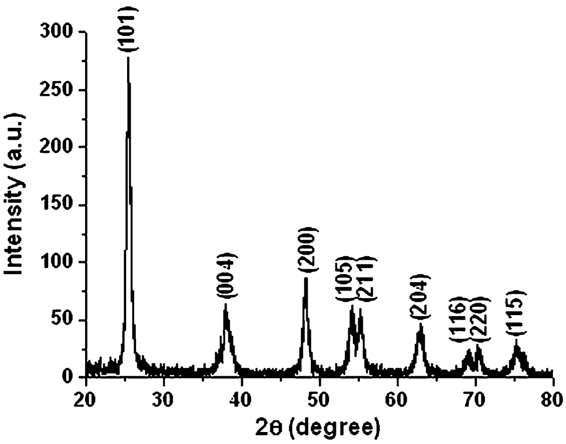

Fig. 1 XRD pattern of CD ns-TiO_2 powders

Figure 2 shows SEM image of CD ns-TiO_2 film. The surface morphology of films was a multiple-porous network structure. The average size of nanoparticle was 40 nm. The pore diameter was about 80 nm.

For further analysis of the chemical structure of the CD ns-TiO_2 films, we have examined three areas of the XPS spectra (Fig. 3): the C 1s region near 280 eV, Ti 2p the region near 460 eV and the O 1s region.

XPS measurements of the C 1s binding energy indicated the complete absence of carbon in the sample, peaks at binding energies at 284.6, 286.3 and 288.5 eV were found. The two features of 288.5, 286.3 eV at higher binding energies were attributed to

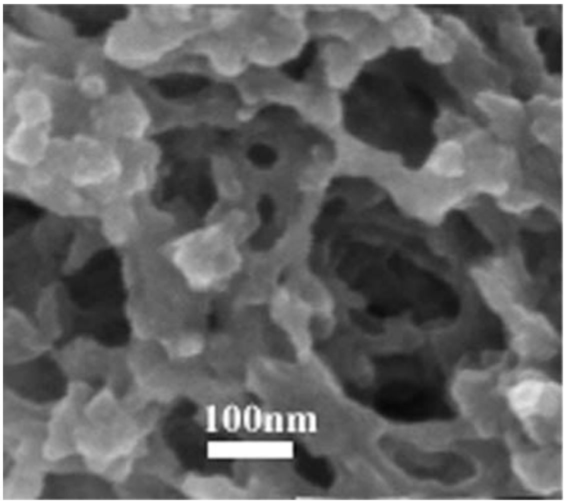

Fig. 2 SEM image of the surface morphology of CD ns-TiO_2 film

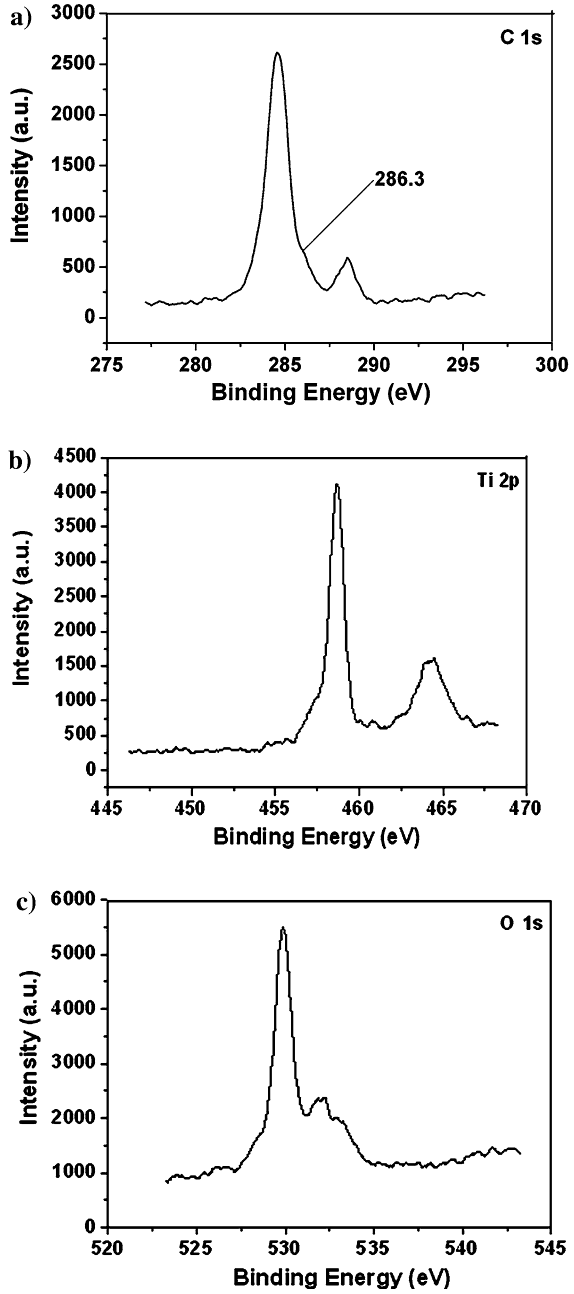

Fig. 3 XPS spectra for the (**a**) C 1s and (**b**) Ti 2p and (**c**) O 1s of the CD ns-TiO_2 films

the C–O binding, the carbon peak at 284.6 eV was assigned to the C remained in the precursor organic compound. No appreciable signal related to carbide (281.5 eV) was observed, showing that the amount of Ti-bonded carbon was very low.

When scanning the Ti 2p XPS regions, three peak structures at binding energies at 464.4, 458.6, and 457.3 eV. The first value arises from the $2p_{1/2}$ peaks. Compared to the classic paper of Saha and Tompkins (1992), we suggest that the Ti $2p_{3/2}$ XPS peak at 458.6 eV is consistent with the formation of a crystalline TiO_2 sample. The carbon incorporation shifts the XPS spectrum to a lower binding energy (a peak is observed at 457.3 eV) because of surface strain and lattice distortion induced by the incorporation of the carbon.

The O 1s core levels of CD ns-TiO_2 films revealed four peak structures at binding energies at 533.2, 531.7, 529.8, and 528.4 eV in the CD ns-TiO_2 films. The peaks appeared after the air calcinations at the binding energy of 533.2 and 531.7 eV were assigned to O–H bonds, the peak at 529.8 eV ascribes to Ti–O bond, the peak at 528.4 eV further testified that incorporation shifted the XPS spectra to a lower binding energy, although it can not be seen in the XRD pattern.

We found that the doping concentration of carbon in the CD ns-TiO_2 lattice was estimated to be 41% as determined from the XPS peaks. This suggested that further increase of the doped amount content in the CD ns-TiO_2 films were realized by using oxalic acid and tetrabutylammonium bromide as carbon sources by sol–gel process. This may be attributed to easier diffusion of oxalic acid ($C_2H_2O_4$) due to its smaller size compared to glucose ($C_6H_{12}O_6$) and tetrabutylammonium ions ($C_{16}H_{36}N^+$). And the photoresponse in visible region can be enhanced by increasing the doped carbon content (Bard and co-workers 2006; Milani and co-workers 2005; Khan and co-workers 2006a, b).

The UV-visible absorption measurements are used to evaluate the nanostructured TiO_2 (ns-TiO_2) and CD ns-TiO_2 films. Figure 4 shows the optical absorbance spectra of ns-TiO_2 and CD ns-TiO_2 films. Compared with ns-TiO_2, it reveals that the new powerful absorption at 400–800 nm is related to the high carbon content. The CD ns-TiO_2 films show two optical absorption thresholds at 628 and 758 nm in the visible range, which corresponds to a band gap energy of 1.98 (628 nm) and 1.64 eV (758 nm). Particularly, there is a wide absorption peak in the CD ns-TiO_2 films at 605 nm and extends to near infrared region. It is clear that an optical absorption threshold lies in at about 980 nm in the infrared region, which corresponds to a band gap energy of 1.26 eV. Nie and Sohlberg (2004) showed that

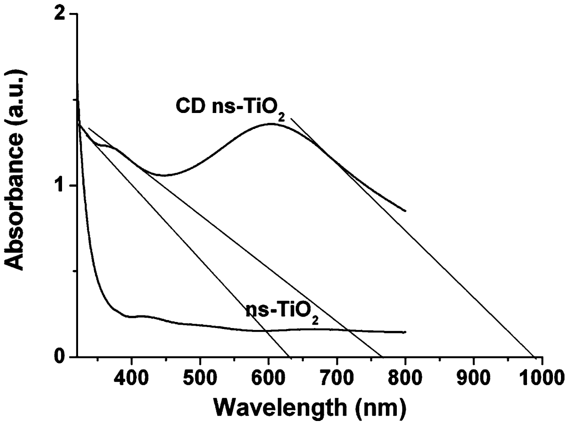

Fig. 4 UV-Visible spectra of FTO/ ns-TiO$_2$ and FTO/ CD ns-TiO$_2$ films

carbon-doping gives rise to two band gaps by theoretical calculation, which was confirmed by experiments (Khan et al. 2002; Khan and co-workers 2006a, b). The finding of three band gaps can be attributed to the higher carbon content in the CD ns-TiO$_2$ films. It is evident that the amazing photoresponse observed from the CD ns-TiO$_2$ films was attributed to the band gap lowering and the formation of the intragap band (Kamisaka et al. 2005; Gole and Stout, 2004).

Figure 5 shows a comparison of the photocurrent density versus applied potential curves of the FTO/ CD ns-TiO$_2$ photoanode in the dark and under visible illumination. The observed dark current densities were found to be negligible. The increased photocurrent generation at anodic potentials shows that the CD ns-TiO$_2$ film possesses n-type semiconducting behavior, which delivers a maximum photocurrent of 1.34 mA/cm^2 under anodic bias 0.3 V (versus SCE). The CD ns-TiO$_2$ film structure also shows a steeper increase in the photocurrent with applied potential. With nanoporous network structure, e$^-$h$^+$ pairs induced by photon absorption split more readily, and also produced a high photoanodic response probably because of an increased light penetration depth and better scattering within a regular pore structure.

Figure 6 presents a photocurrent density-voltage curve of CD ns-TiO$_2$ solar cell. The photovoltaic characteristics are analyzed using equations 1 and 2,

$$FF = \frac{W_{\max}}{V_{\mathrm{oc}} \times I_{\mathrm{sc}}} = \frac{V_{\max} \times I_{\max}}{V_{\mathrm{oc}} \times I_{\mathrm{sc}}} \tag{1}$$

$$\eta(\%) = \frac{V_{\mathrm{oc}} \times I_{\mathrm{sc}} \times FF}{I} \times 100 \tag{2}$$

Where the fill factor (*FF*) is the maximum power delivered to an external load, calculated from the short-circuit current density (I_{sc}) and the open-circuit voltage (V_{oc}). The overall conversion efficiency (η) is normalized by the intensity of the incident light (I).

The open circuit voltage (V_{oc}), short-circuit photocurrent (I_{sc}) and the fill factor (*FF*) of the cell were 0.50 V, 0.256 mA/cm^2 and 0.47, respectively. The η obtained from the cell system was 4.42 %. The results

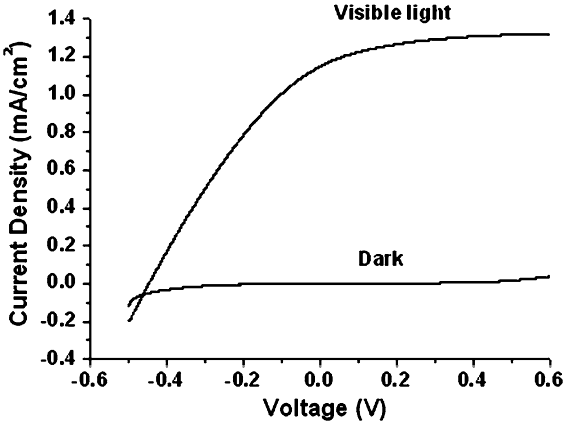

Fig. 5 Variation of photocurrent density versus measured potential for FTO/CD ns-TiO$_2$ photoanode in the dark and under visible illumination (cell active area: 0.56 cm^2)

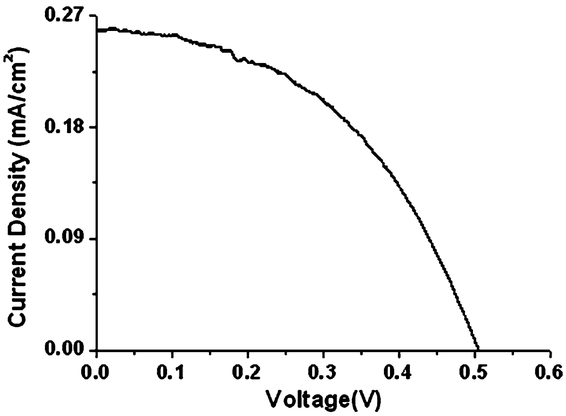

Fig. 6 Current density-voltage curve of CD ns-TiO$_2$ solar cell under 11 mW/cm^2 visible illumination (cell active area: 0.56 cm^2)

indicated that incorporation of carbon into nanoporous space of TiO_2 was very successful.

Conclusions

In conclusion, we have demonstrated that CD ns-TiO_2 films with three optical band gap of 1.98, 1.64, and 1.26 eV and 41% carbon content can be obtained with oxalic acid and $Bu_4N{\cdot}Br$ as the carbon sources by the sol–gel process. The evidence for the presence of carbon states within CD ns-TiO_2 film is demonstrated by UV-Visible spectra and XPS. The CD ns-TiO_2 films have revealed a superior harvesting light capability and improvement photovoltaic activity under visible light. Carbon doped into substitutional sites of TiO_2 has also proven to be indispensable for band gap narrowing and photovoltaic effect. The CD ns-TiO_2 film was firstly used as photoanode for solar cells, exhibiting photocurrent densities (1.34 mA/cm^2) and yielding an overall conversion efficiency (η) of 4.42 %.

This investigation shows that our method of narrowing the band gap has low cost, simple processing, excellent reproducibility, easy large-scale production and extensive application in the field of solar energy conversion and photocatalysis. However the influence of calcination temperature for nanostructure and doping concentration of carbon are not disscussed, we will study these aspects for next steps.

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References

Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y (2001) Visible light photocatalysis in nitrogen-doped titanium oxides. Science 293:269–271

Barborini E, Conti AM, Kholmanov I, Piseri P, Podesta A, Milani P, Cepek C, Sakho O, Macovez R, Sancrotti M (2005) Nanostructured TiO_2 films with 2 eV optical gap. Adv Mater 17:1842–1846

Chen CY, Wu SJ, Wu CJ, Chen JG, Ho KC (2006) A ruthenium complex with superhigh light-harvesting capacity for dye-sensitized solar cells. Angew Chem Int Ed 45:5822–5825

Chu DB, Feng DX, Zhang JH, Lin HS, Hu WL, Tian ZW (2005) Novel system of direct methanol fuel cell anode catalysts: nanoTiO_2-CNT-PtNi complex catalysts. Acta Chim Sinica 63:2027–2031

Cong Y, Chen F, Zhang J, Anpo M (2006) Carbon and nitrogen-codoped TiO_2 with high visible light photocatalytic activity. Chem Lett 35:800–801

De Vos DE, Dams M, Sels BF, Jacobs PA (2002) Ordered mesoporous and microporous molecular sieves functionalized with transition metal complexes as catalysts for selective organic transformations. Chem Rev 102:3615–3640

Fujishima A (2003) Comment on ''efficient photochemical water splitting by a chemically modified n-TiO_2'' (I). Science 301:1673a

Fujishima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. Nature 238:37–38

Grätzel M (2001) Photoelectrochemical cells. Nature 414:338–344

Grätzel M (2003) Dye-sensitized solar cells. J Photochem Photobiol C 4:145–153

Grätzel M (2004) Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells. J Photochem Photobiol A 164:3–14

Gole JL, Stout JD, Burda C, Lou Y, Chen X (2004) Highly efficient formation of visible light tunable $TiO_{2-x}N_x$ photocatalysts and their transformation at the nanoscale. J Phys Chem B 108:1230–1240

Hägglund C, Grätzel M, Kasemo B (2003) Comment on ''efficient photochemical water splitting by a chemically modified n-TiO_2'' (II). Science 301:1673b

Irie H, Watanabe Y, Hashimoto K (2003) Carbon-doped anatase TiO_2 powders as a visible-light sensitive photocatalyst. Chem Lett 32:772–773

Kamisaka H, Adchi T, Yamashita K (2005) Theoretical study of the structure and optical properties of carbon-doped rutile and anatase titanium oxides. J Chem Phys 123:084704

Khan SUM, Al-Shahry M, Ingler Jr WB (2002) Efficient photochemical water splitting by a chemically modified n-TiO_2. Science 297:2243–2245

Kisch H, Zang L, Lange C, Maier Wf, Antonius C, Meissner D (1998) Modified, amorphous titania-A hybrid semiconductor for detoxification and current generation by visible light. Angew Chem Int Ed 37:3034–3036

Lackner KS (2003) Comment on ''efficient photochemical water splitting by a chemically modified n-TiO_2'' (III). Science 301:1673c

Lettmann C, Hildenbrand K, Kisch H, Macyk W, Maier WF (2001) Visible light photodegradation of 4-chlorophenol with a coke-containing titanium dioxide photocatalyst. Appl Catal B 32:215–227

Morikawa T, Asahi R, Ohwaki T, Aoki K, Taga Y (2001) Band-gap narrowing of titanium dioxide by nitrogen doping. Jpn J Appl Phys 40:L561–L563

Neumann B, Bogdanoff P, Tributsch H, Sakthivel S, Kisch H (2005) Electrochemical mass spectroscopic and surface photovoltage studies of catalytic water photooxidation by undoped and carbon-doped titania. J Phys Chem B 109:16579–16586

Nie X, Sohlberg K (2004) Materials Research Society Proceedings on Materials and Techanology for Hydrogen Economy, vol 801, p 205

O'Regan B, Grätzel M (1991) A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. Nature 353:737–740

Ohno T, Mitsui T, Matsumura M (2003) Photocatalytic activity of S-doped TiO_2 photocatalyst under visible light. Chem Lett 32:364–365

Ohno T, Akiyoshi M, Umebayashi T, Asai K, Mitsui T, Matsumura M (2004) Preparation of S-doped TiO_2 photocatalysts and their photocatalytic activities under visible light. Appl Catal B 265:115–121

Park JH, Kim S, Bard AJ (2006) Novel carbon-doped TiO_2 nanotube arrays with high aspect ratios for efficient solar water splitting. Nano lett 6:24–28

Peter LM, Wijayantha KGU, Reily DJ, Waggett JP (2003) Band-edge tuning in self-assembled layers of Bi_2S_3 nanoparticles used to photosensitize nanocrystalline TiO_2. J Phys Chem B 107:8378–8381

Reddy KM, Baruwati B, Jayalakshmi M, Rao MM, Manorama SV (2005) S-, N- and C-doped titanium dioxide nanoparticles: synthesis, characterization and redox charge transfer study. J Solid State Chem 178:3352–3358

Saha NC, Tompkins HG (1992) Titanium nitride oxidation chemistry: An x-ray photoelectron spectroscopy study. J Appl Phys 72:3072–3079

Sakthivel S, Kisch H (2003) Daylight photocatalysis by carbon-modified titanium dioxide. Angew Chem Int Ed 42:4908–4911

Sakthivel S, Janezarek M, Kisch H (2004) Visible light activity and photoelectrochemical properties of nitrogen-doped TiO_2. J Phys Chem B 108:19384–19387

Xu CK, Killmeyer R, Gray ML, Khan SUM (2006a) Photocatalytic effect of carbon-modified n-TiO_2 nanoparticles under visible light illumination. Appl Catal B 64:312–317

Xu CK, Killmeyer R, Gray ML, Khan SUM (2006b) Enhanced carbon doping of n-TiO_2 thin films for photoelectrochemical water splitting. Electrochem Commun 8:1650–1654

Zhou XF, Chu DB, Lin CJ (2002) Anodic dissolution of spongy titanium in ethanol solution for preparation of nano-sized TiO_2 powder. Electrochim Acta 47:2769–2773