Enhanced photosensitization of nanocrystalline TiO₂ film with a sulfonic sensitizer by surface protonation

Yan-Jie Ren,[a] He Tian[b] and Sheng-Min Cai*[a]

[a] College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.
E-mail: caism@pku.edu.cn; Fax: +86-10-62751708
[b] Institute of Fine Chemicals, East China University of Science & Technology,
Shanghai 200237, China

The interaction between an azo sensitizer containing an –SO₃⁻ anchoring group, 4-amino-5-hydroxy-6-azobenzene-1,7-naphthyl disulfonic sodium (**K**), and nanocrystalline TiO₂ film was studied using IR microscopy, and was attributed to physical adsorption due to the negligible peak shift of **K**. Photoelectrochemical experiments were carried out to characterize the interface charge transfer. Maximum incident photon-to-current conversion efficiency (IPCE) was greatly increased from 7.7 to 43.7% by HCl pretreatment of TiO₂ film. This strong photosensitization enhancement was assigned to surface protonation of the TiO₂ film, which enables **K** anions to be closely attracted to the TiO₂ nanocrystalline surface by electrostatic forces, thus facilitating interface charge transfer. An overall energy conversion efficiency of ~2% was achieved for the sandwich-type photoelectrochemical cell constructed with **K** sensitized protonated TiO₂ film, while this value was 0.37% for the untreated TiO₂ film. Surface protonation provides a general solution to improving the photosensitization of TiO₂ film with dyes containing SO₃⁻ anchoring groups.

Surface modification of wide band gap semiconductors with sensitizers is a well-established procedure to alter their photophysical and photochemical properties.[1–3] In the sensitized systems, molecules attached to the semiconductor surface inject electrons into the conduction band of the semiconductor after being excited, thus extending the photoreponse of the semiconductor into the visible region. Research on such sensitized systems has greatly advanced since the development of nanocrystalline TiO₂ film and highly efficient Ru complex sensitizers by Grätzel and co-workers.[4,5] Dye-sensitized nanocrystalline TiO₂ photoelectrochemical cells have shown promising prospects in practical applications and also have stimulated enormous interest in fundamental research.[6–10] Nanocrystalline TiO₂ films provide huge interior surfaces for sensitizer attachment, which ensures high light harvesting efficiency. Interface charge transfer is another key step controlling overall energy conversion efficiency. The rate of this process is critically dependent on the degree of electronic coupling between the donor sensitizer orbital and the acceptor TiO₂ orbital,[11] which is obviously related to the way of sensitizer adsorption. Satisfactory performance has been achieved by attaching suitable anchoring groups on the sensitizer molecule.

The usual anchoring group employed is –COOH. Through a number of Raman and IR spectroscopic studies of sensitizer–TiO₂ systems, it was concluded that sensitizers functionalized with carboxylate groups anchor to the TiO₂ film through an ester-like bond with the surface –OH groups.[12–14] Recently, sensitizers with –SO₃⁻ as the anchoring group were also reported for photoelectric conversion.[15,16] A better understanding of the interaction between these sensitizers and the TiO₂ surface is obviously very important since it is closely related to sensitization efficiency, as mentioned above. However, to the best of our knowledge, no studies have been made in this regard.

Azo derivatives are cheap and stable dyes that have found wide applications in the textile industry.[17] In the present study, an azo dye containing a –SO₃⁻ group, 4-amino-5-hydroxy-6-azobenzene-1,7-naphthyl disulfonic sodium (**K**), and having suitable absorption and redox properties was chosen to sensitize the nanocrystalline TiO₂ film. The nature of the interaction between sensitizer and TiO₂ was investigated using IR microscopy. The results show **K** is physisorbed onto the TiO₂ nanocrystalline surface. The surface of as-prepared TiO₂ is hydroxylated.[18] Surface –OH groups may repel the –SO₃⁻ containing **K** from intimate contact, which is unfavorable for efficient interface charge transfer. If the TiO₂ surface is positively charged, will electrostatic forces attract **K** closer to the TiO₂ surface, and will interface charge transfer be facilitated? We found that after surface protonation of a TiO₂ film by soaking in HCl solution, photoresponse was greatly enhanced as expected.† An overall energy conversion efficiency of about 2% was achieved in the improved case.

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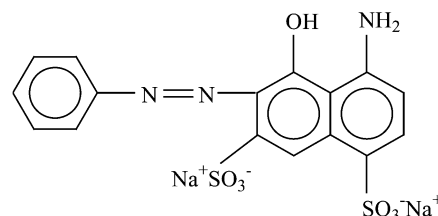
† During the publication process for this work, a paper was published (Z. S. Wang, Y. Liu, G. Yu, C. Xu, J. Zhang and D. Zhu, *J. Phys. Chem. B*, 2001, **105**, 9422) reporting separate work on the photocurrent enhancement of a series of hemicyanine dyes containing the SO₃⁻ group with acid treatment.

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Experimental

Materials

ITO conducting glass (indium doped SnO_2, sheet resistance 20 Ω cm^{-2}, transmission $>85\%$ in the visible) was purchased from Shenzhen Weiguang Conducting Glass Company of China. **K** dye was synthesized and purified. Its structure was confirmed by ^1H NMR.[17] LiI and carbowax were purchased from Aldrich. All the other solvents and chemicals were at least reagent grade (Beijing Chemical Company, China) and used without further purification. Propylene carbonate (PC) was dried with molecular sieves and then distilled before use.

Preparation of K coated nanocrystalline TiO_2 film

Preparation of TiO_2 nanocrystalline film has been described elsewhere.[19] TiO_2 nanoparticles were synthesized by autoclaving the hydrolysis product of tetrabutyl titanate at 230 °C for 12 h. The TiO_2 particles were redispersed under ultrasonication with addition of carbowax (40% of TiO_2 weight). After evaporation, a viscous TiO_2 paste was obtained. ITO conducting glass was used as the substrate for depositing the TiO_2 film. To control the thickness of the film and to mask electric contact strips, two edges of the ITO glass plate were covered with adhesive tape. TiO_2 paste was spread uniformly on the substrate by sliding a glass rod along the tape spacer. After drying, the sample was heated in air for 30 min at 450 °C, then was soaked in 0.3 mM **K** solution in MeCN for 3 h. Excess dye was removed by rinsing with MeCN. For surface protonation, the TiO_2 film was soaked in an HCl solution of pH 2 for 3 h, then dried under a hot air flow before soaking in the **K** solution. The TiO_2 film thickness was measured to be 6 μm using an ALPHA-step 500 profilometer.

Micro IR and UV-Vis characterization

Pure **K** and trace amounts of sample scratched from **K** coated nanocrystalline TiO_2 film were subject to micro FTIR characterization using a MAGNA-IR 750 spectrometer series II combined with a Nic-Plan® IR microscope (Nicolet). UV-Vis absorption spectra of **K** solution in MeCN and **K** coated TiO_2 film were measured using a Cary 1 E UV-Vis spectrometer (Varian); MeCN and bare ITO glass were used as references, respectively.

Electrochemical and photoelectrochemical experiments

Cyclic voltammetry (CV) of **K** was performed on a CHI650A electrochemical workstation (CH Instruments). A conventional three-electrode cell composed of Pt wire working electrode, Pt plate counter electrode and saturated calomel reference electrode (SCE) was used. $NaClO_4$ (0.5 M) in deionized water served as supporting electrolyte.

Photoelectrochemical experiments were carried out to characterize interface charge transfer between **K** and TiO_2. Sandwich-type cells were constructed with platinized ITO glass as counter electrode and 0.3 M $LiI/0.03$ M I_2 PC solution as electrolyte. A 150 W xenon lamp with a high intensity grating monochromator served as light source. Light intensities were measured with an EG&G light gauge radiometer/photometer (Gamma Scientific). In current–voltage measurements, a 10 cm water filter and a 350 nm cut-off filter were placed in the beam, and the 15% transmission loss in ITO glass was corrected. The current–voltage curves were obtained at a scan rate of 5 mV s^{-1} in a two-electrode arrangement, which is identical to loading a variable resistor.[19]

Results and discussion

Absorption and redox properties

Fig. 1 shows the absorption spectra of **K** solution in MeCN and **K** coated TiO_2 film. **K** has a characteristic π–π* electronic transition absorption band around 500 nm. This strong, broad absorption in the visible region is essential for high light harvesting efficiency. By comparing spectra a and b in Fig. 1, it can be seen that the absorption of **K** in solution and on TiO_2 film is similar and the two peaks are almost at the same wavelength, suggesting that **K** has been adsorbed onto the TiO_2 film without aggregation.

Besides the absorption behavior, the availability of a suitable energy level is another key factor for efficient sensitization, which ensures that electron injection from the excited **K** molecule into the TiO_2 conduction band is thermodynamically possible. CV results on **K** give the redox potential of **K** as 0.58 V *vs.* SCE. Combining electrochemical and absorption spectroscopic data, the redox potential of excited state **K** is estimated to be -1.26 V *vs.* SCE (about -3.58 eV in vacuum level), about 0.36 eV above the conduction band edge (about -0.90 V *vs.* SCE, -3.94 eV in vacuum level) of a nanocrystalline TiO_2 film in aprotic solvent with no less than 0.1 M Li^+ ion.[20] It can be seen that **K** has the proper absorption behavior and energy level to sensitize nanocrystalline TiO_2 film.
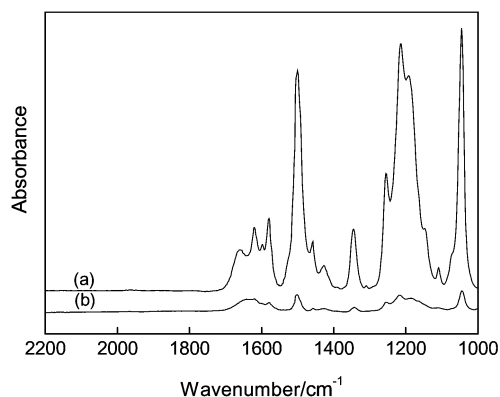
Nature of interaction between K and TiO_2

Microscope IR was measured between 4000 and 650 cm^{-1}. Strong absorption of TiO_2 below 1000 cm^{-1} and broad absorption of –OH groups above 3400 cm^{-1} were seen for uncoated and **K** coated TiO_2 film samples. Z. Wang *et al.*[15] recently applied a series of hemicyanine derivatives containing the SO_3^- group to sensitize TiO_2 nanocrystalline films. They found that the presence of SO_3^- was essential for successful adsorption, as hemicyanines without SO_3^- were hardly adsorbed on TiO_2 films. Thus, only the $-SO_3^-$ anchoring group is of concern for scrutinizing the nature of the adsorption.

A restricted region of the IR spectra of pure **K** and **K** adsorbed onto TiO_2 nanocrystalline film is shown in Fig. 2. The strong absorption peaks of spectrum a at 1214 and 1255 cm^{-1} are attributed to the symmetric and asymmetric stretching modes of S=O. For **K** adsorbed on TiO_2 film, the corresponding peaks are at 1217 and 1254 cm^{-1}. Upon adsorption of a sensitizer with a –COOH group, a 20 cm^{-1} peak shift to higher frequency of the C=O stretching mode was observed compared to free sensitizer, which is believed to arise from chemical adsorption of the sensitizers onto the oxide particles *via* formation of an ester-like bond between the
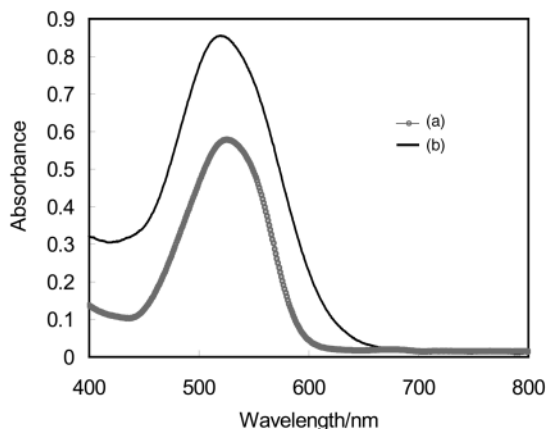
Fig. 1 Absorption spectra of (a) **K** solution in MeCN and (b) **K** coated nanocrystalline TiO_2 film.

Fig. 2 FTIR spectra of (a) pure **K** and (b) **K** coated nanocrystalline TiO$_2$ film.

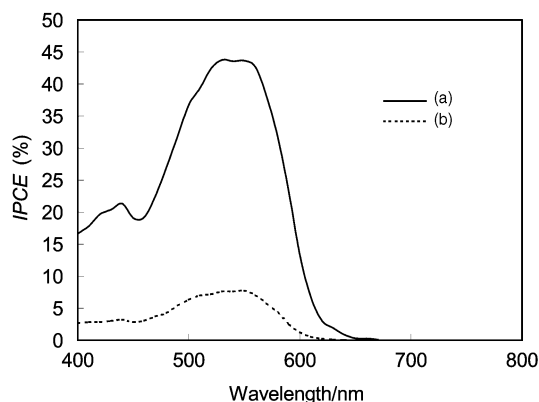**Fig. 4** Absorption spectra of **K** coated TiO$_2$ film pretreated with HCl (a) and without pretreatment (b).

carboxylic acid groups and the hydroxyl moieties on the TiO$_2$ surface.[12] In our case the minor S=O absoption peak shifts imply that there is no chemical interaction between adsorbed **K** molecules and TiO$_2$. The relatively small electronegativity of S rules out the possibility of an H-bond between **K** and TiO$_2$, although this is found to be possible for –COOH and an oxide surface by molecular modelling calculations.[13] **K** molecules may be physically adsorbed onto the TiO$_2$ nanocrystalline surface through a solvent layer[21] or electrostatic forces.

K adsorbed onto a TiO$_2$ film is easily washed off with water, contrasting with sensitizers having –COOH as anchoring group, while **K** in aqueous solution was not adsorbed at all. These facts show that the interaction between **K** and TiO$_2$ is weak and support the physisorption nature of the interaction.

Photosensitization

TiO$_2$ is a wide band gap n-type semiconductor only responsive to UV light. The short-circuit photocurrent produced by photosensitization in the visible region of **K** coated, untreated and pretreated, TiO$_2$ film was measured. The action spectra are shown in Fig. 3, where the incident photon-to-current efficiency (IPCE) determined from the short-circuit photocurrent is plotted as a function of wavelength. In both cases the photocurrent extends to the visible region and follows the same profile as the absorption spectrum of **K** in solution. For the pretreated film the IPCE was increased more than fivefold over the whole region compared with the untreated film. The maximum IPCEs of the **K** sensitized, HCl pretreated and untreated, TiO$_2$ films are 43.7 and 7.7%, respectively.

To clarify this large enhancement of the photosensitization, the UV-Vis absorption character of the **K** coated TiO$_2$, with
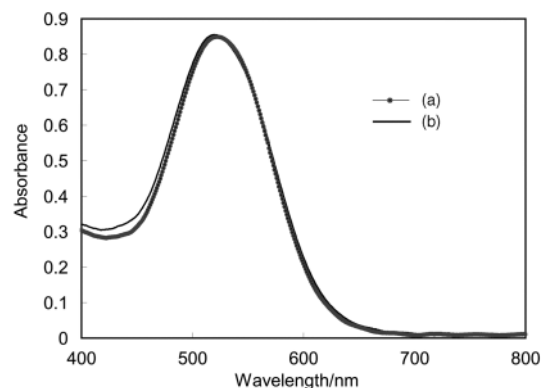
and without HCl pretreatment, was first investigated. As shown in Fig. 4, there is little difference between the two absorption spectra, indicating that the HCl pretreatment process does not affect the arrangement of **K** molecules on the TiO$_2$ nanocrystalline surface. This is understandable since **K** molecules do not tend to aggregate when adsorbed on TiO$_2$ nanoparticle, as concluded from Fig. 1. At the same time, TiO$_2$ is so stable and well crystallined after autoclaving that HCl of pH 2 will not change the surface morphology. So the enhancement of photosensitization cannot be rationalized in terms of the absorption itself.

HCl pretreatment has another influence on the TiO$_2$ film. TiO$_2$ band edge positions or the flat band potential are known to be dependent on the pH value of the contact solution.[20,22,23] Adsorption of protons is associated with a downward energy shift of the band edges, and thus will increase the driving force for electron injection from excited **K** into the TiO$_2$ conduction band. But this cannot be the decisive factor for the great photosensitization enhancement. As discussed above, the energy difference between the excited **K** and the conduction band of TiO$_2$ already provides a driving force for interface charge transfer. Our experiments also show that HCl pretreatment of TiO$_2$ film does not induce any notable increase in IPCE when sensitized with the well-known Ru dye [*cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II)] having –COOH as anchoring group.

Due to the physisorption nature of **K** on TiO$_2$ film, there is no interlocking bridge present between **K** and TiO$_2$ such as the ester-like bond present in –COOH containing sensitizer-TiO$_2$ systems. Surface –OH groups of TiO$_2$ nanocrystalline may prevent intimate contact between **K** and TiO$_2$, and thus retard efficient charge transfer. However, protons are easily adsorbed by TiO$_2$ nanocrystalline during soaking of the film in HCl aqueous solution. In the dye-coating process, that is dipping of the TiO$_2$ film in **K** solution, ionized **K** anions will be electrostatically bound to the positively charged TiO$_2$ nanocrystalline surface. The electrostatic interaction attracts **K** anions close to the protonated TiO$_2$ surface, consequently favoring efficient charge injection.

Fig. 5 shows current-voltage curves of photoelectrochemical cells constructed with **K** sensitized protonated and untreated nanocrystalline TiO$_2$ films under white light illumination of 27.2 mW cm^{-2}. Short-circuit current and open-circuit voltage for the cell constructed with the untreated TiO$_2$ nanocrystalline film are 0.39 mA cm^{-2} and 0.44 V, respectively (see Fig. 5). For the cell constructed with the protonated TiO$_2$ nanocrystalline film, the corresponding values are 2.03 mA cm^{-2} and 0.45 V. Both cells have the same fill factor of 0.6, giving overall energy conversion efficiencies of 0.37 and 1.96%. Both the short-circuit current and overall energy conversion efficiency are enhanced more than fivefold in magnitude by HCl

Fig. 3 Action spectra of **K** sensitized nanocrystalline TiO$_2$ film pretreated with HCl (a) and without pretreatment (b).

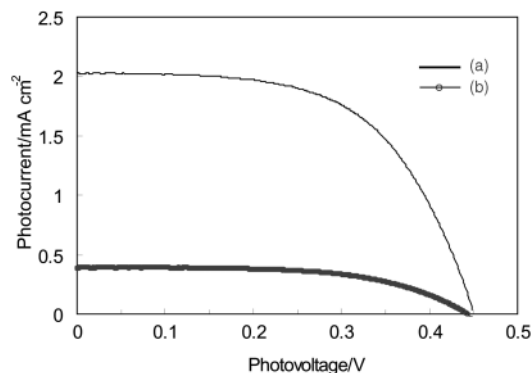**Fig. 5** Current–voltage curves of the photoelectrochemical cells constructed with **K** sensitized TiO_2 film pretreated with HCl (a) and without pretreatment (b).

pretreatment, which is attributed to the improved interface charge transfer resulting from close contact between sensitizer **K** molecules and the TiO_2 nanocrystalline film.

Conclusion

Interaction between an azo sensitizer containing $-SO_3^-$ as anchoring group, 4-amino-5-hydroxy-6-azobenzene-1,7-naphthyl disulfonic sodium (**K**) and nanocrystalline TiO_2 film is found to be physical adsorption through a micro IR investigation. A significant maximum IPCE increase from 7.7 to 43.7% was achieved by soaking the TiO_2 film in an HCl solution of pH 2 before dye-coating, which is attributed to the fact that surface protonation of the TiO_2 film enables **K** anions to be closely attracted to the TiO_2 surface by electrostatic forces, thus facilitating interface charge transfer. An overall energy conversion efficiency of $\sim 2\%$ was achieved for the sandwich-type photoelectrochemical cell constructed with **K** sensitized protonated TiO_2 film, contrasting with a value of 0.37% for the untreated TiO_2 film. Surface protonation provides a general solution to improving sensitization efficiency of nanocrystalline TiO_2 films with dyes containing $-SO_3^-$ anchoring groups.

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