

# ESR Signal of Superoxide Radical Anion Adsorbed on TiO<sub>2</sub> Generated at Room Temperature

Junhua Yu, Jingrong Chen, Chao Li, Xuesong Wang,\* Baowen Zhang,<sup>\*,†</sup> and Huiying Ding

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, P. R. China

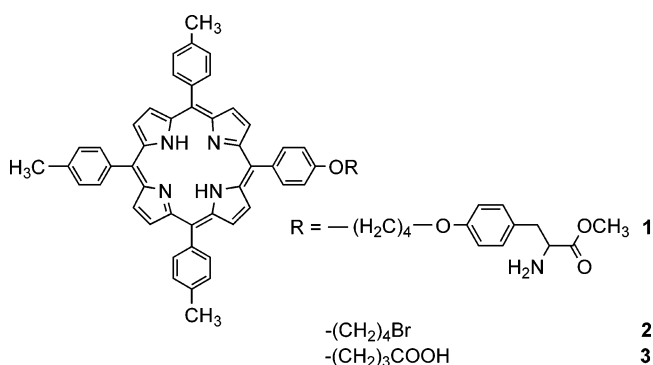
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The electron spin resonance spectrum of superoxide anion radical adsorbed on the surface of colloidal TiO<sub>2</sub> was detected directly at room temperature for the first time. This signal was generated partially by porphyrin-sensitized titanium dioxide, i.e., the reduction of adsorbed oxygen on the TiO<sub>2</sub> nanocluster surface by the just injected electron from the excited porphyrin.

TiO<sub>2</sub> has been widely used in photocatalytic degradation of pollutants,<sup>1</sup> in which interfacial electron transfer (ET) between solute and TiO<sub>2</sub> plays the most important role in degradation mechanism of pollutants and the colloidal TiO<sub>2</sub> is usually applied as a model for studying such processes at the liquid–semiconductor interface.<sup>2</sup> The initial process for heterogeneous photocatalysis of organic and inorganic compounds by semiconductors is the generation of electron–hole pairs in the semiconductor particles by UV light, and the resulting highly active species react with the adsorbed molecules.<sup>3</sup> Surface sensitization of TiO<sub>2</sub> can increase the efficiency of the excitation process and expand the excitation wavelength to the visible range through excitation of the sensitizer followed by ET to the semiconductor. The electrons in turn can be transferred to the acceptor molecules adsorbed on the surface such as oxygen. The activated oxygen, superoxide radical anion (O<sub>2</sub><sup>•−</sup>), is the primary oxidizing agents in this case and reacts with other pollutants.<sup>4</sup> O<sub>2</sub><sup>•−</sup> is deemed to be stable even at room temperature, and several methods, such as a luminal chemiluminescent probe<sup>5</sup> or the complex formation between 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and O<sub>2</sub><sup>•−</sup>,<sup>6</sup> have been applied to detect it. Whereas O<sub>2</sub><sup>•−</sup> is detected indirectly by the methods mentioned above, ESR spectroscopy is an especially suitable technique for the detection of photogenerated radicals, which act as intermediates in the photocatalytic processes. The ESR signal of O<sub>2</sub><sup>•−</sup> adsorbed on the TiO<sub>2</sub> surface (TiO<sub>2</sub>–O<sub>2</sub><sup>•−</sup>) has been detected at 77 or 4.2 K, with the line-shape characteristic of an orthorhombic *g* tensor (*g*<sub>1</sub> = 2.025, *g*<sub>2</sub> = 2.009, *g*<sub>3</sub> = 2.003).<sup>7</sup> Interestingly, no such ESR spectra recorded at room temperature were reported to the best of our knowledge. Though some authors note that O<sub>2</sub><sup>•−</sup> is stable because the ESR signal of TiO<sub>2</sub>–O<sub>2</sub><sup>•−</sup> can still be detected after the sample containing TiO<sub>2</sub>–O<sub>2</sub><sup>•−</sup> was warmed to room temperature,<sup>8</sup> all the spectra were measured at very low temperature. Here we used porphyrin-capped TiO<sub>2</sub> nanoclusters in neutral ethanol solution to investigate the interfacial ET process and *directly* observed the ESR signal of O<sub>2</sub><sup>•−</sup> at room temperature under the irradiation of pulsed laser at 532 nm.

One porphyrin used is anisyltritylporphyrin (ATTP) terminated with tyrosine methyl ester and the others terminated with bromo group and carboxyl, respectively (Chart 1). The neutral ethanol solution of TiO<sub>2</sub> is prepared by neutralization of the acid ethanol solution of TiO<sub>2</sub> with solid KOH.<sup>9</sup>

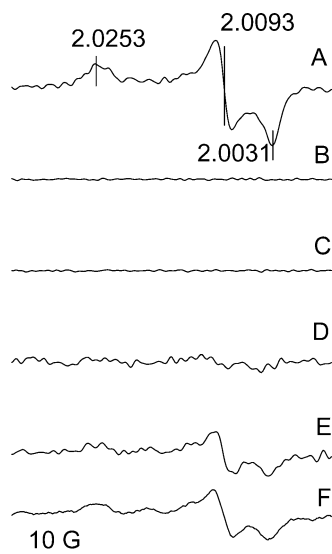
CHART 1



Irradiation of aerated ethanol solution of **1** with 4 g L<sup>−1</sup> TiO<sub>2</sub> by pulsed laser (10 Hz, 5 mJ/pulse) at 532 nm results in the ESR signal shown in Figure 1A. In the absence of light (not shown), TiO<sub>2</sub> (Figure 1B), and porphyrin (Figure 1C), respectively, no ESR signal is detected in above solution. When the sample was degassed by bubbling with N<sub>2</sub> for 10 min, the intensity of the ESR signal decreased almost to baseline level (Figure 1D), suggesting that oxygen is also indispensable to generating the signal. This signal is identical with a signal observed following oxygen photoadsorption on hydrated anatase surfaces at 77 K<sup>7</sup> and can be attributed to the TiO<sub>2</sub>–O<sub>2</sub><sup>•−</sup>. To verify its existence, superoxide dismutase (SOD, 40 μg mL<sup>−1</sup>) was added into the above solution, and the ESR signal is strongly restricted. Similar ESR spectra were also observed by the UV irradiation of oxygen-adsorbed TiO<sub>2</sub> at 77 K or the mixture of H<sub>2</sub>O<sub>2</sub> and colloidal TiO<sub>2</sub> at 77 K,<sup>10,11</sup> but none of them was obtained at room temperature.

We previously reported the ET between **1** and TiO<sub>2</sub> nanoclusters in neutral ethanol solution enhanced by the bridge of tyrosine methyl ester.<sup>9</sup> Injection of electron from excited ATTP into the conduction band becomes more efficient because the consequent cationic porphyrin radical can be reduced exoergically by the nearby tyrosine. Since the trapped electrons are believed to react with preadsorbed molecular oxygen to produce superoxide radical anion,<sup>12</sup> and the ESR signal can be ascribed to the reduction of adsorbed oxygen on the TiO<sub>2</sub> nanocluster surface by the just injected electron from **1** (Scheme 1). It was estimated that TiO<sub>2</sub>–O<sub>2</sub><sup>•−</sup> could be generated from the reaction of trapped holes produced by band gap excitation with UV light and surface hydroxy groups by three consecutive steps, i.e.,

<sup>†</sup> E-mail: g203@ipc.ac.cn.



**Figure 1.** (A) ESR spectrum at room temperature generated from the irradiation of an aerated ethanol solution containing **1** ( $2 \times 10^{-4}$  mol  $L^{-1}$ ) and  $TiO_2$  ( $4 \text{ g } L^{-1}$ ) with pulsed laser at 532 nm; the *g* tensors are obtained by using DPPH ( $g = 2.0036$ ) for frequency calibration. (B) Same as spectrum A but in the absence of  $TiO_2$ . (C) Same as A but in the absence of **1**. (D) Same as A but bubbled with  $N_2$  for 20 min. (E) Same as A but **1** was substituted by **2**. (F) Same as A but **1** was substituted by **3**. Instrumental settings for all EPR measurements: microwave power, 10 mW; modulation amplitude, 2.0 G; scan width, 300 G; receiver gain,  $1 \times 10^5$ .

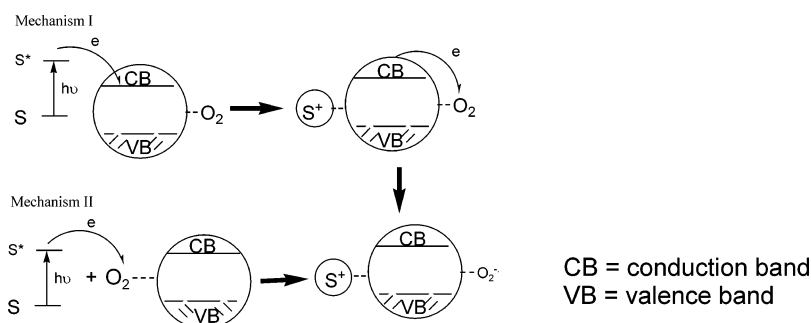
reaction of holes with surface hydroxyl groups produced hydroxyl radicals which immediately dimerized to form peroxide; peroxide then trapped a further hole to form  $O_2^{\cdot-}$ .<sup>7</sup> In our experiments, no UV light was used, and thus no holes were generated; therefore, the above mechanism is more reasonable (mechanism I). Kevan<sup>2</sup> et al. showed that the efficiencies of charge separation are comparable either by ET from electron donor to acceptor via colloidal semiconductor particles as relay, or by UV-photoinduced electron–hole pair generation and subsequent trapping by acceptor and donor molecules. A similar investigation was also carried out by Kamat et al.:<sup>13</sup> ca. 6% of the injected electron from excited anthracene-9-carboxylic acid to colloidal  $TiO_2$  could be transferred to the acceptor; the low efficiency was ascribed to the fast recombination between the injected electron and anthracene cation. All these experiments show that the mechanism I is feasible.

ESR signals can also be generated via direct ET from excited porphyrin to molecular oxygen either free or bound to  $TiO_2$  surface (mechanism II). Compounds **2** and **3**, which is relatively inert to the neutral  $TiO_2$  because of the small driving force for electron injection from the triplet ATTP moiety to  $TiO_2$ ,<sup>9,14</sup> and the lack of enhancement effect exerted by tyrosine as in **1**, were used as reference sensitizers to detect the ESR signal generated

by mechanism II. For the reasons mentioned above, **2** and **3** produce  $O_2^{\cdot-}$  predominantly through the mechanism II. The results show that the ESR signal of  $TiO_2-O_2^{\cdot-}$  generated from **2** and **3** are significantly lower (Figure 1, parts E and F, respectively). Another experiment shows that the signal intensity generated from a solution of **1** doubles during the concentration of  $TiO_2$  increasing from 1 (3300 au) to 4  $g L^{-1}$  (6100 au), while that of **2** changes only a little (from 1500 to 1800 au, see Supporting Information). The increase of  $TiO_2$  concentration supplies more surface adsorption sites, which would accordingly raise the ESR signal intensity because of the enrichment of adsorbed oxygen as well as porphyrin. The little signal change of **2** means the generation of ESR signal from **2** is not as strongly dependent on the adsorption sites because of its poor adsorption ability on the surface of  $TiO_2$  and the increment is mainly contributed from the increasing adsorbed molecular oxygen. This in turn suggests that **1** adsorbs on the surface of  $TiO_2$  more stronger than **2** and may generate the ESR signal through the relay of  $TiO_2$ . For compound **1**, it is possible to react with the adsorbed molecular oxygen around its absorption site, leading to the higher ESR signal. Thus, compound **3**, which is considered to adsorb on the surface of  $TiO_2$  well with carboxyl as attaching group, is applied to investigate its ESR signal generation. The adsorption of porphyrins onto titanium dioxide particles was testified by using a solid thin film made from neutral ethanol solution of  $TiO_2$ , which showed that the absorption ability of **1** lay between **2** and **3** (see Supporting Information). As shown in Figure 1, the signal is similar to that of **2**, indicating that the difference in direct ET from the excited porphyrin to the molecular oxygen around the adsorption site is not significant, and the role of electron relay of  $TiO_2$  is confirmed further.

Direct ET from excited porphyrin to dissolving molecular oxygen can also generate superoxide anion radical (see Supporting Information). Using DMPO as spin-trapping agent, the aerated ethanol solution of **1** ( $2 \times 10^{-4}$  mol  $L^{-1}$ ) exhibits a typical ESR signal of the adduct of superoxide anion radical with DMPO ( $DMPO-O_2^{\cdot-}$ ). We now cannot distinguish the fate of the dissolved  $O_2^{\cdot-}$ . However, the generation of  $DMPO-O_2^{\cdot-}$  shows that the ESR signal intensity in the presence of  $TiO_2$  is more than twice as strong as that without  $TiO_2$ . In the presence of  $TiO_2$ ,  $O_2^{\cdot-}$  generated from the direct reduction of dissolved oxygen by excited porphyrin cannot exceed in number that generated in the absence of  $TiO_2$ , because the interfacial ET between **1** and  $TiO_2$  will quench the dissolved  $O_2^{\cdot-}$  generation in this way. Therefore, the doubled ESR signal intensity in the presence of  $TiO_2$  means there is another fruitful process for the generation of superoxide anion; i.e.,  $O_2^{\cdot-}$  can be generated from the reduction of  $O_2$  adsorbed on the  $TiO_2$  surface by the electron in conduction band of  $TiO_2$  injected from the excited porphyrin, supporting the mechanism shown in Scheme 1.

## SCHEME 1



The reason we can obtain the ESR signal at room temperature may be due to the relatively long lifetime of the photoinduced species compared to the electron–hole pair. Upon band-gap excitation of semiconductor, the generated electron–hole pairs are prone to recombination when without strong scavengers,<sup>15</sup> while in our experiments, the recombination between oxidized porphyrin and injected electron, or between oxidized porphyrin and  $\text{O}_2^{\cdot-}$ , would be slow and allow the accumulation of  $\text{O}_2^{\cdot-}$  on  $\text{TiO}_2$  surface to the ESR detection limitation.

In summary, the ESR spectrum of the superoxide radical anion generated by dye-sensitized  $\text{TiO}_2$  was reported at room temperature for the first time.

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**Supporting Information Available:** Text and figures showing the adsorption of **1**, **2**, and **3** on the surface of  $\text{TiO}_2$ , the comparison of ESR signal of  $\text{TiO}_2\text{--O}_2^{\cdot-}$  to the concentration of colloidal  $\text{TiO}_2$ , and the relationship between the concentration of  $\text{TiO}_2$  and the ESR signal intensity and text discussing the certification of ESR signal of  $\text{DMPO--O}_2^{\cdot-}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) (a) Fujishima, A.; Honda, K. *Nature (London)* **1972**, 238, 37–38. (b) Grela, M. A.; Coronel, M. E. J.; Colussi, A. J. *J. Phys. Chem.* **1996**, 100, 16940–16946. (c) Hirakawa, T.; Kominami, H.; Ohtani, B.; Nosaka, Y. *J. Phys. Chem. B* **2001**, 105, 6993–6999. (d) Yu, J. C.; Lin, J.; Lo, D.; Lam, S. K. *Langmuir* **2000**, 16, 7304–7308.
- (2) (a) Kurshev, V.; Kevan, L. *Langmuir* **1997**, 13, 225–228. (b) Martini, I.; Hodak, J. H.; Hartland, G. V. *J. Phys. Chem. B* **1998**, 102, 607–614.
- (3) (a) Serpone, N.; Pelizzetti, E.; Hidaka, H. In *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier: London, 1993; pp 225–250. (b) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, 95, 69–96.
- (4) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, 95, 735–758.
- (5) (a) Hirakawa, T.; Nakaoka, Y.; Nishino, J.; Nosaka, Y. *J. Phys. Chem. B* **1999**, 103, 4399–4403. (b) Ishibashi, K.-I.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Phys. Chem. B* **2000**, 104, 4934–4938. (c) Hirakawa, T.; Kominami, H.; Ohtani, B.; Nosaka, Y. *J. Phys. Chem. B* **2001**, 105, 6993–6999.
- (6) (a) Finkelstein, E.; Rosen, G. M.; Rauckman, E. J. *Arch. Biochem. Biophys.* **1980**, 200, 1–16. (b) Ben-Hur, E.; Carmichael, A. Riesz, P.; Rosenthal, I. *Int. J. Radiat. Biol.* **1985**, 48, 837–846.
- (7) Howe, R. F.; Grätzel, M. *J. Phys. Chem.* **1987**, 91, 3906–3909.
- (8) Attwood, A. L.; Murphy, D. M.; Edwards, J. L.; Egerton, T. A.; Harrison, R. W. *Res. Chem. Intermed.* **2003**, 29, 449–465.
- (9) Yu, J.; Chen, J.; Wang, X.; Zhang, B.; Cao, Y. *Chem. Commun.* **2003**, 1856–1857.
- (10) Howe, R. F.; Grätzel, M. *J. Phys. Chem.* **1985**, 89, 4495–4499.
- (11) Coronado, J. M.; Maira, A. J.; Martínez-Arias, A.; Conesa, J. C.; Soria, J. *J. Photochem. Photobiol. A: Chem.* **2002**, 150, 213–221.
- (12) Draper, R. B.; Fox, M. A. *Langmuir* **1990**, 6, 1396–1402.
- (13) Kamat, P. V. *J. Phys. Chem.* **1989**, 93, 859–864.
- (14) Kalyanasundaram, K.; Vlachopoulos, N.; Krishnan, V.; Monnier, A.; Grätzel, M. *J. Phys. Chem.* **1987**, 91, 2343–2347.
- (15) Bahnemann, D. W.; Hilgendorff, M.; Memming, R. *J. Phys. Chem. B* **1997**, 101, 4265–4275. (b) Rothenberger, G.; Moser, J.; Grätzel, M.; Serpone, N.; Sharma, D. K. *J. Am. Chem. Soc.* **1985**, 107, 8054–8059.