Organic dye-sensitized TiO_2 for the redox conversion of water pollutants under visible light[†]

Yiseul Park,^a Su-Hyun Lee,^b Sang Ook Kang^b and Wonyong Choi*^a

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Titania nanoparticles sensitized with metal-free organic dye exhibit high visible-light activities for the redox conversion of water pollutants in a wider pH range in comparison with TiO_2 sensitized with ruthenium bipyridyl complexes.

Dye-sensitized TiO₂ has been frequently investigated to utilize solar light for chemical conversion. In particular, ruthenium bipyridyl derivatives have been extensively studied as an efficient sensitizer of TiO₂ for visible light photocatalysis (e.g., the degradation of water pollutants, production of hydrogen).¹⁻³ However, Ru-based dyes are not environmentally and economically acceptable because ruthenium is an expensive and toxic element. Therefore, metal-free organic dye sensitizers with low production costs, higher visible light absorption, high stability, and facile molecular design have attracted attention.4-7 Although organic dye-sensitized TiO₂ has been successfully applied for dye-sensitized solar cells, its applications in environmental photocatalysis are few.^{8,9} Organic dyes for sensitized-TiO₂ photocatalysts should have (1) strong visible light absorption, (2) suitable energetics for electron injection and regeneration, and (3) high affinity for the TiO_2 surface and stability in water over a wide pH range. In this study, we designed and synthesized an organic dye with such characteristics and tested its performance as a sensitizer of TiO₂ for the redox conversion of water pollutants. The organic dye-sensitized TiO₂ demonstrated superior performance in comparison with the common Ru-dye sensitized TiO₂.

The synthesized organic dye was ((*E*)-3-(5-(5-(4-(bis(4-((2-(2-methoxy)ethoxy)methyl)phenyl)phenyl)phenyl)phenyl)phenyl)phenyl)-thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid) and its molecular structure is shown in Fig. 1 (refer to ESI for synthetic



Fig. 1 Molecular structures of OD and RuL₃.

Table 1 $\,$ Spectroscopic and electrochemical parameters of OD and RuL_3

Dye	$\lambda_{\max}{}^a/nm$	$\frac{\varepsilon_{\max}^{a}}{M^{-1}}$ cm ⁻¹	$\Delta E^b/{ m V}$	$E^{0}(\mathrm{dye/dye^{\bullet}}^{+})/\mathrm{V_{NHE}}$	$E^{0}(\mathrm{dye}^{*}/\mathrm{dye}^{\bullet}^{+})/\mathrm{V_{NHE}}$
OD	445	24 500	2.45	1.35	-1.0
RuL_3^c	465	19 500	2.20	1.39	-0.81
^a UV-v	is absor	ption spectr	a in ESI	. ^b HOMO–LUM	10 gap. ^c ref. 12.

method[†]). The dye molecule consists of a diphenylaminophenyl-2,2'-bithiophene (donor part where HOMO electron density is localized), a cyanoacrylic acid (acceptor part where LUMO electron density is localized), and ethylene-oxide chains (hydrophilic part that increases the solubility).

 $Ru^{II}(4,4-bpy(COOH)_2)_3$ was also prepared according to the previous studies^{1,2} and compared as a reference sensitizer of TiO₂ (see ESI†). The organic and Ru-dye sensitizers will be referred as OD and RuL₃, respectively throughout the communication. They are compared for their spectroscopic and electrochemical parameters in Table 1. The optical absorption and energy levels of OD are similar to those of RuL₃.

OD was dissolved in an acetonitrile–*tert*-butyl alcohol mixture (1:1) and RuL₃ in water (pH 3). The dissolved dyes were adsorbed on the surfaces of TiO₂ particles (Degussa P25; size 20–30 nm) and the dye-adsorbed TiO₂ was recovered from the slurry by filtration. The dye loading was 10 µmol dye/(gTiO₂). Comparison of the λ_{max} absorption of the dye solution before and after the adsorption on TiO₂ confirmed that the adsorption of the dye was almost quantitative. Dyes adsorbed on TiO₂ remained stable without desorption in aqueous suspension. The visible-light activities of the dye-sensitized TiO₂ catalyst were tested for the oxidation of 4-chlorophenol (4-CP) and arsenite (As^{III} to As^V (less toxic form)) and the reduction of chromate (Cr^{VI} to Cr^{III} (less toxic form)) in water.¹⁰

Fig. 2 shows the time profiles of the photocatalytic removal of 4-CP, As^{III} (the production of As^V monitored) and Cr^{VI} in aqueous suspensions of OD/TiO₂, RuL₃/TiO₂ and bare TiO₂ under visible light illumination. OD/TiO₂ exhibited higher or comparable photocatalytic activities in comparison with RuL₃/TiO₂ for all cases. The apparent photonic efficiencies [(substrates removed)/(incident photons) × 100] determined for the photocatalytic conversion under visible light are 0.6, 0.09, and 1.3% for 4-CP, As^{III}, and Cr^{VI}, respectively (see ESI†). OD/SiO₂ was also prepared as a control sample since the excited OD cannot inject the electron into SiO₂. OD/SiO₂ showed a negligible photoactivity for 4-CP degradation (Fig. 2a), which implies that the photoactivity of OD/TiO₂

^a School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 790-784,

South Korea. E-mail: wchoi@postech.edu; Fax: +82-54-279-8299 ^b Department of Materials Chemistry, Sejong Campus, Korea

University, Chung-Nam, 339-700, South Korea

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Fig. 2 Visible light-induced oxidation of (a) 4-CP and (b) As^{III} and (c) reduction of Cr^{VI} in aqueous suspensions of OD/TiO₂, RuL₃/TiO₂ and bare TiO₂. The concentration at time zero indicates the equilibrium concentration after adsorption on the catalyst surface. Experimental conditions: $[4-CP]_0 = [As^{III}]_0 = 100 \ \mu\text{M}$, $[Cr^{VI}]_0 = 200 \ \mu\text{M}$, $[catalyst] = 1 \ g \ L^{-1}$, pH_i = 4.5 (a), 3 (b, c), dye loading 10 μ mol/(gTiO₂), $\lambda > 420 \ \text{nm}$, air-equilibrated.

should be based on the photoinduced electron transfer from OD to TiO_2 .

The general action of dye-sensitized TiO₂ photocatalysts is initiated by the electron injection from an excited dye to the TiO₂ conduction band (CB) (eqn (1)) and completed through the subsequent electron transfer reactions.^{1,2} The substrates (S, S') may be converted upon direct electron transfer (eqn (2), (3)) or indirectly transformed through the reaction with reactive oxygen species (eqn (4)) (*e.g.*, superoxide).

$$Dye-TiO_2 + h\nu(visible) \rightarrow Dye^{\bullet +} -TiO_2(e_{cb})$$
(1)

$$e_{cb}^{-} + S \rightarrow S_{red}$$
 (2)

$$Dye^{+} - TiO_2 + S' \rightarrow Dye - TiO_2 + S'_{ox}$$
 (3)

$$\mathbf{e_{cb}}^{-} + \mathbf{O}_2 \to \mathbf{O}_2^{\bullet -} \tag{4}$$

The dye should be regenerated to be catalytic after the electron injection. To reduce 200 μ M of Cr^{VI} to Cr^{III} (Fig. 1b), 600 μ M of OD is needed, provided that the dye is a one-electron donor. Since the total concentration of OD contained in the suspension is only 10 μ M, the dye should be recycled and the corresponding turnover number is 60. As for the oxidation of 100 μ M 4-CP, the turnover number is 10 on the basis of one-electron oxidation. The main electron donor that reduces the oxidized dye should be either the substrate to be oxidized (eqn (3)) or water molecule (eqn (5)) (E^0 (O₂/H₂O) = 1.05 V_{NHE} at pH 3 *vs.* E^0 (dye/dye⁺) = 1.35 V_{NHE}).

$$Dye^{-+}-TiO_2 + 0.5H_2O \rightarrow Dye-TiO_2 + H^+ + 0.25O_2$$
 (5)

The *in situ* generation of O_2 through eqn (5) was monitored using an oxygen electrode in the deaerated suspension of OD/TiO₂ under visible light. An alternative electron acceptor, $S_2O_8^{2-}$ (10 mM), was added in excess to inhibit both the back electron transfer in eqn (1) and the immediate consumption of O₂ through eqn (4). About 0.1 ppm of dissolved oxygen was



Fig. 3 The effect of oxygen and ferric ion (alternative electron acceptor) on the conversion of 4-CP and Cr^{VI} in an OD/TiO₂ system. Experimental conditions: [4-CP]₀ = 100 μ M, [Cr^{VI}]₀ = 200 μ M, [Fe³⁺] = 1 mM, [TBA] = 0.1 M, [catalyst] = 1 g L⁻¹, pH_i = 3, dye loading 10 μ mol/(gTiO₂), λ > 420 nm, air-equilibrated or continuous N₂ purged.

generated after 30 min irradiation while the dark control test showed no production of O_2 .

In the overall photocatalysis, the role of O_2 is essential as an electron acceptor (eqn (4)). Fig. 3 shows that the photocatalytic oxidation of 4-CP on OD/TiO₂ is negligible in the absence of O₂ (N₂-saturated) since the injected electron recombines with the dye cation (dye^{\bullet^+}) in the absence of suitable electron acceptors. The addition of an alternative electron acceptor (Fe^{3+}) markedly enhanced the removal rate, which demonstrated the importance of electron acceptors. The addition of tert-butyl alcohol (TBA: OH radical scavenger) had little influence on the removal rate. This implies that the degradation of 4-CP is mainly mediated by direct electron transfer (eqn (3)), not by the OH radical. On the other hand, Cr^{VI} reduction was significantly retarded in the presence of the electron acceptor (Fe^{3+}) because of the competition for electrons between Cr^{VI} and Fe^{3+} (eqn (2)). This confirms that Cr^{VI} reduction proceeds by accepting electrons from the dye-sensitized TiO₂.

The visible light-induced electron transfer on OD/TiO₂ was directly monitored by collecting photocurrents in the aqueous catalyst suspension as shown in Fig. 4. The redox couple of Fe^{3+}/Fe^{2+} serves as an electron shuttle that transfers electrons from TiO₂ to a Pt collector electrode immersed in the illuminated catalyst suspension.¹¹ The appearance of photocurrents under visible light indicates that electrons are injected from the adsorbed sensitizers to TiO₂. OD/TiO₂ generated higher photocurrent than RuL₃/TiO₂, which is



Fig. 4 Photocurrent $(I_{\rm ph})$ collected *via* ${\rm Fe}^{3+}/{\rm Fe}^{2+}$ redox couple in suspensions of dye/TiO₂ catalysts. Experimental conditions: $[{\rm Fe}^{3+}] = 1 \text{ mM}$, [acetate] = 0.2 M (electron donor), [catalyst] = 1 g L⁻¹, dye loading 10 µmol/(gTiO₂), pH_i = 2, applied potential = 0.7 V_{Ag/AgCl}, Ag/AgCl (RE), graphite rod (CE), Pt (WE), $\lambda > 420 \text{ nm}$, continuous N₂ purged.



Fig. 5 pH-dependent photoactivities of OD/TiO_2 and RuL_3/TiO_2 for the degradation of 4-CP. The experimental conditions were the same as for Fig. 2a.



Fig. 6 DRUVS of dye/TiO_2 coated electrode before and after (a) basic solution treatment (pH 10, 2 h) and (b) visible light irradiation (1 h).

consistent with the higher photocatalytic activity of OD/TiO_2 and the higher absorption of visible light of OD (see Table 1).

The most marked difference between the OD/TiO₂ and RuL₃/TiO₂ systems is the pH dependence of the photoactivity as shown in Fig. 5. The visible light activity of RuL₃/TiO₂ is maintained only in the acidic region because the adsorption of RuL₃ on TiO₂ is limited only in the acidic pH region.² On the other hand, the photoactivity of OD/TiO₂ remained constant over a wide pH range, which indicates that the binding of OD onto the TiO₂ surface is little affected by pH.

The stability of the dyes (OD or RuL₃) adsorbed on TiO₂ was monitored by measuring the diffuse reflectance UV-vis spectra (DRUVS) of dye/TiO₂ electrodes under different conditions. A TiO₂-coated electrode was immersed into a solution of dye over 12 h for adsorption of dye. Then the dye/TiO₂ electrode was immersed in a basic solution (pH 10) for 2 h and dried at room temperature. Although RuL₃ was markedly desorbed in the basic conditions, the desorption of OD was minimal (Fig. 6a). The photostability of OD under visible light irradiation is also much higher than RuL₃ (Fig. 6b). The superior stability of OD/TiO₂ over RuL₃/TiO₂ should be related with the property of the chemical anchoring bonding between the dye and the surface.

Both OD and RuL_3 should be anchored onto the surface through the carboxylate linkage. However, the binding of RuL_3 should be sensitively affected by the pH-dependent

surface charge on TiO₂ because RuL₃ is negatively charged. Above pH_{zpc} \approx 6 of TiO₂, the negative surface charge on TiO₂ electrostatically repels the anionic sensitizer (deprotonated RuL₃; pK_a < 3)¹² with inhibition of its adsorption. The electrostatic repulsion among the adsorbed sensitizers may undermine the stability of RuL₃/TiO₂ as well. On the other hand, OD adsorbed on TiO₂ is little affected by the TiO₂ surface charge. The sensitizer molecule consists of the carboxylate group that binds to the surface, the chromophoric aromatic portion, and the hydrophilic ethylene-oxide group that increases the compatibility of the dye at the water/TiO₂ interface. The hydrogen bonding between the cyano group (or the ethylene-oxide group) and the surface hydroxyl group add to the OD/TiO₂ binding strength.^{13,14}

In summary, we have prepared metal-free organic dye-sensitized TiO_2 and compared it with the popular Ru-complex sensitized TiO_2 system for its visible light photocatalytic activity. The synthesized OD is similar in comparison with RuL₃ as a sensitizer and has a higher visible light absorptivity. OD/TiO₂ showed better or comparable activities for a wider pH range and higher stability in water. The proposed OD/TiO₂ can serve as a model of a green photocatalyst working under visible light.

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References

- 1 E. Bae and W. Choi, Environ. Sci. Technol., 2003, 37, 147-152.
- 2 E. Bae, W. Choi, J. Park, H. S. Shin, S. B. Kim and J. S. Lee, J. Phys. Chem. B, 2004, 108, 14093–14101.
- 3 S. Ardo and G. J. Meyer, Chem. Soc. Rev., 2009, 38, 115–164.
- 4 S. Kim, J. K. Lee, S. O. Kang, J. Ko, J.-H. Yum, S. Fantacci, F. D. Angelis, D. D. Censo, M. K. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2006, **128**, 16701–16707.
- 5 N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki and K. Hara, J. Am. Chem. Soc., 2006, **128**, 14256–14257.
- 6 S.-L. Li, K.-J. Jiang, K.-F. Shao and L.-M. Yang, Chem. Commun., 2006, 2792–2794.
- 7 R. Li, X. Lv, D. Shi, D. Zhou, Y. Cheng, G. Zhang and P. Wang, J. Phys. Chem. C, 2009, 113, 7469–7479.
- 8 J. P. Ghosh, C. H. Langford and G. Achari, J. Phys. Chem. A, 2008, 112, 10310–10314.
- 9 R. Abe, K. Shinmei, K. Hara and B. Ohtani, *Chem. Commun.*, 2009, 3577–3579.
- 10 J. Ryu and W. Choi, Environ. Sci. Technol., 2008, 42, 294-300.
- 11 H. Park and W. Choi, J. Phys. Chem. B, 2003, 107, 3885-3890.
- 12 H. Park, E. Bae, J.-J. Lee, J. Park and W. Choi, J. Phys. Chem. B, 2006, 110, 8740–8749.
- 13 Y. Hao, X. Yang, J. Cong, H. Tian, A. Hagfeldt and L. Sun, *Chem. Commun.*, 2009, 4031–4033.
- 14 Y. Ooyama, Y. Shimada, Y. Kagawa, Y. Yamada, I. Imae, K. Komaguchi and Y. Harima, *Tetrahedron Lett.*, 2007, 48, 9167–9170.