

Design of All-Inorganic Molecular-Based Photocatalysts Sensitive to Visible Light: Ti(IV)–O–Ce(III) Bimetallic Assemblies on Mesoporous Silica

Ryuhei Nakamura,[†] Akihiro Okamoto,[†] Hitoshi Osawa,[‡] Hiroshi Irie,[†] and Kazuhito Hashimoto^{*,†,§}

Department of Applied Chemistry, School of Engineering, the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, Japan Synchrotron Radiation Research Institute, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan, and Exploratory Research for Advanced Technology (ERATO), JST

Received May 22, 2007; E-mail: hashimoto@light.t.u-tokyo.ac.jp

Photocatalytic systems working under visible light have been studied extensively from the viewpoints of energy conversion¹ and environmental accountability.² Recently, it was discovered that substitutional doping with anion elements such as N, S, and C to semiconductor photocatalysts, such as TiO₂, leads to extension of the photoactive region to visible light.³ A considerable number of materials have been developed on the basis of this strategy. However, the present achievements are not enough compared to the performance demanded by the practical application, and the preparation of more efficient visible-light photocatalysts is anticipated. The main obstacle toward this is the fact that design and control of properties of semiconductor photocatalysts is strictly limited in flexibility, since the doping needs to be made under highly reactive conditions. Furthermore, the serious problems of attendant formation of effective charge-carrier recombination centers have also remained unsolved yet. These have now been recognized as inherent drawbacks of semiconductor photocatalysts toward the effective utilization of visible-light photons.

The inventive work for this end has been recently reported by Frei et al.⁴ They demonstrated the use of metal-to-metal charge transfer (MMCT) of hetero-bimetallic assemblies as a new class of visible-light absorbing chromophores.^{4a} The anchored Zr(IV)–O–Cu(I) assembly on the pore of mesoporous silica showed the photochemical splitting of CO₂ to CO by photoexcitation of the Zr(IV)/Cu(I) MMCT band at 355 nm.^{4b} The use of oxo-bridged hetero-bimetallic assembly as a photoinduced redox center is a promising strategy for developing the visible-light photocatalysts because the molecular design and fine control of oxidation/reduction potential as well as absorption wavelength of photocatalysts are readily made if the proper combination of two metal ions are selected according to their redox potential. More importantly, such design and control can be realized without using organic functionalities. Thus these allow developing molecular-based inorganic photocatalysts with high durability and high degree of flexibility in their photo and electronic properties.

Herein we report the first photocatalysis driven by the visible-light induced MMCT for hetero-bimetallic Ti(IV)–O–Ce(III) assemblies on the pore of mesoporous silica, MCM-41 (Figure 1A). The combination of Ti(IV) and Ce(III) ion as constituting elements ($E^0(\text{Ce}^{4+}/\text{Ce}^{3+}) = 1.72 \text{ V}$, $E^0(\text{TiO}_2/\text{Ti}^{3+}) = -0.67 \text{ V}$) was selected to drive the photocatalytic oxidative decomposition of organic compounds under visible-light irradiation. The bimetallic Ti/Ce assembly exhibited the intense MMCT absorption up to 540 nm and its visible-light activity was remarkably higher than the one of the most active photocatalyst, nitrogen-doped TiO₂^{3a}.

The synthesis of Ti(IV)–O–Ce(III) assemblies on the pore of MCM-41 was made by applying the nucleophilic character of titanol

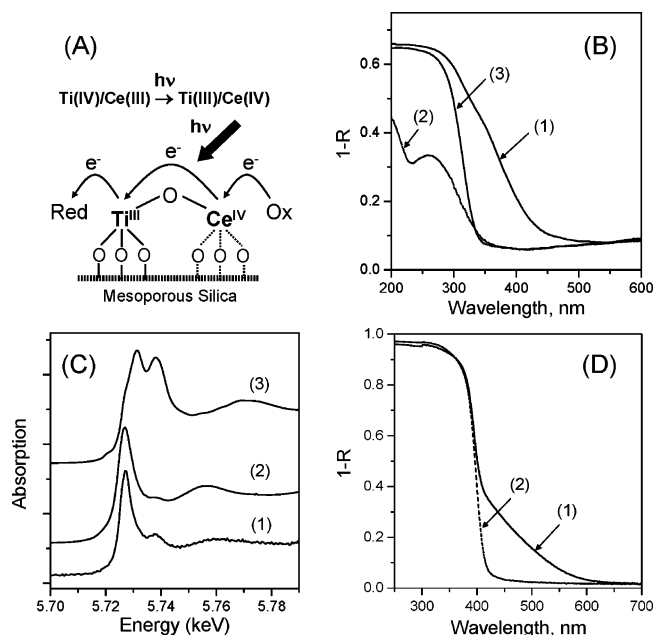


Figure 1. (A) Schematic illustration of anchored Ti(IV)/Ce(III) bimetallic assembly on the pore of MCM-41 and its photocatalysis driven by the photoinduced MMCT. (B) Diffuse reflectance UV-vis spectra of dehydrated (1) Ti/Ce-MCM-41, (2) mononuclear Ce(III)-MCM-41, and (3) Ti(IV)-MCM-41 wafer. (C) Ce L_{III}-edge XANES spectra of (1) Ti/Ce-MCM-41, (2) Ce(NO₃)₃·6H₂O, and (3) CeO₂. (D) Diffuse reflectance UV-vis spectra of dehydrated (1) Ce-TiO₂ (rutile) and (2) TiO₂ (rutile) wafer.

groups of (OH)Ti(OSi)₃ sites. Namely, isolated (OH)Ti(OSi)₃ sites were first synthesized on the pore surface of MCM-41 using the TiCp₂Cl₂ precursor method⁵ (Ti/Si = 0.03). Subsequently, dehydrated Ti-MCM-41 crystalline was added to a dry acetonitrile solution of Ce(III)NO₃ and stirred at 55 °C for 18 h. The pale yellow crystallites thus obtained were filtered, washed, and dried under dynamic vacuum at 40 °C.

The UV-vis diffuse reflectance spectrum of Ti/Ce-MCM-41 exhibits the intense absorption extending from the UV to 540 nm, as can be seen from Figure 1B, trace 1. Since neither the Ce(III) nor the Ti(IV) ion possesses the 4f → 5d transition or LMCT band in this spectral region, trace 2 and 3 in Figure 1B, respectively, the visible absorption is attributed to the MMCT of Ti/Ce assemblies, that is, Ti(IV)/Ce(III) → Ti(III)/Ce(IV). The Ce L_{III}-edge XANES spectrum for Ti/Ce-MCM-41 is shown in Figure 1C, trace 1. The spectral shape and position of Ti/Ce-MCM-41 agreed well with that of Ce(III)NO₃ (Figure 1C, trace 2), confirming that the valency of Ce ion is trivalent and also excluding the possibility of formation of CeO₂ clusters. Since Ce(III) but not Ce(IV) can act as an electron donating element in Ti/Ce MMCT chromophores, these results strongly support the aforementioned assignment. No MMCT band was observed when Ce(III) grafting was undertaken at room

[†] University of Tokyo.

[‡] Japan Synchrotron Radiation Research Institute.

[§] Exploratory Research for Advanced Technology, JST.

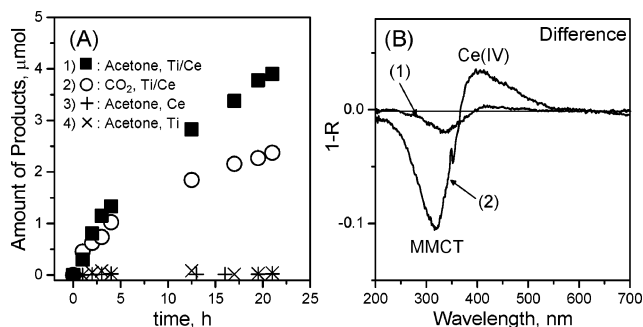


Figure 2. (A) The time course of amount of (1) acetone and (2) CO₂ from 10 mg of Ti/Ce–MCM-41 wafer under 460 nm-light illumination ($I = 27 \text{ mW cm}^{-2}$) in the presence of 2-propanol (10 Torr) and O₂ (750 Torr). Acetone generation from (3) Ce–MCM-41 and (4) Ti–MCM-41 wafer under the same photochemical conditions as those for Ti/Ce–MCM-41. (B) Difference UV–vis spectra after 460 nm-illumination for 2 h for Ti/Ce–MCM-41 in the presence of (1) 2-propanol and O₂ and (2) O₂ only.

temperature. This is an indication that the mild heating at 55 °C is needed to facilitate anchoring of Ce(III) ions to titanol groups.

As expected, grafting of Ce(III) ions onto nanocrystalline TiO₂ (rutile) powder⁶ also led to the change in color of crystalline from white to intense yellow, and its absorption band was now extended to 620 nm (Figure 1D, trace 1). Red shift of the absorption band compared to the Ti/Ce–MCM-41 (Figure 1B, trace 1) is characteristic to MMCT since the absorption energy of MMCT is dominated by the difference in energy between the HOMO of acceptor and LUMO of donor elements.⁷ The conduction-band bottom of rutile-TiO₂ lies at 0.6 eV more positive than the LUMO⁵ of isolated TiO₄ species so that the corresponding shift in energy can be regarded as a conclusive evidence for formation of Ti(IV)/Ce(III) MMCT chromospheres for bimetallic Ti/Ce assemblies.

To prove the abilities to drive photocatalysis by photoexcitation of the Ti/Ce MMCT band, we made the photooxidation reaction of 2-propanol in the presence of O₂ for pressed wafers of Ti/Ce–MCM-41 under monochromatic light irradiation at $\lambda = 460 \text{ nm}$.⁶ Products analyses were made by transmission FTIR and GC. As shown in Figure 2A, trace 1 and 2, light irradiation led to formation of acetone and CO₂. They were increased in amount with time, and turnover number was reached to 8 after 45 h of irradiation. No products were formed for the mononuclear Ce(III)– and Ti(IV)–MCM-41 samples (Figure 2A, trace 3 and 4). Therefore it was concluded that the catalytic oxidation of 2-propanol is driven by the visible-light induced MMCT of Ti(IV)–O–Ce(III) assemblies. It is to be noted here that the MMCT band remains almost unchanged in intensity after the photocatalytic reaction, as can be seen from the difference optical spectrum before and after irradiation in Figure 2B, trace 1. In contrast, most of the intensity was lost and the complementary growth of absorption band of Ce(IV) was observed in the same experiment if 2-propanol is absent (Figure 2B, trace 2). These clearly demonstrate that the Ce(IV) formed by photoinduced MMCT of Ti/Ce assemblies continuously re-reduced to Ce(III) by extracting an electron from 2-propanol. Isotopic labeling experiments using ¹⁸O₂ instead of ¹⁶O₂ showed the inclusion of ¹⁸O into acetone and CO₂ (Figure S4 in Supporting Information). This implies that O₂ was reduced to O₂^{•-} by photogenerated Ti(III), though the alternative mechanism that 2-propanol-derived α -hydroxyalkyl radical reduces O₂ directly might not be excluded completely at present.

We then compared the photocatalytic activities of Ti/Ce–MCM-41 with the nitrogen-doped TiO₂(TiO_{2-x}N_x, $x = 0.002$) powder.^{3c,6} Photocatalytic oxidation of 2-propanol was made under the same conditions as those mentioned above except that the light intensity was adjusted in a way that the number of adsorbed photons at 460

nm is equivalent between Ti/Ce–MCM-41 and TiO_{1.998}N_{0.002}.⁶ It was observed that the apparent quantum efficiencies⁶ of acetone and CO₂ formation for Ti/Ce–MCM-41 are 0.035 and 0.138, respectively, while that for TiO_{1.998}N_{0.002} are 0.004 and 0.029, respectively. The TiO_{1.998}N_{0.002} is one of the most active visible-light photocatalysts for the oxidative decomposition of organic compounds reported so far.³ Therefore remarkably higher activity demonstrates the significance of the Ti(IV)/Ce(III) hetero-bimetallic photocatalysts.

Furthermore, we observed that the nanocrystalline TiO₂ (rutile) powder grafted with Ce(III) ions,⁶ whose UV–vis spectrum was shown in Figure 1D, have photocatalytic activities as well as photocurrent responses under visible-light irradiation up to 600 nm (Figure S5 and S6). The generation of cathodic photocurrent for Ce(III)-grafted TiO₂ electrodes in O₂ saturated acetonitrile solutions definitely demonstrates that the reduction of O₂ to O₂^{•-} was initiated by the photoinduced charge transfer from the Ce(III) ions to Ti(IV) of nanocrystalline TiO₂. This again confirms the aforementioned mechanism of site-specific redox reaction for bimetallic Ti/Ce assemblies and also proves the effectiveness of the method of grafting as a novel strategy for sensitization of wide-band gap photocatalysts. We have confirmed, in fact, that this grafting method can be applied also for Cr(IV)/Cr(III) redox couples, $E^0 = 2.10 \text{ V}$, in which the Cr(III)-grafted TiO₂ powder showed the photocatalytic activities under the visible-light excitation of the Ti(IV)/Cr(III) MMCT band.

In summary, the first photocatalysis operated by the visible-light induced MMCT has been demonstrated for the Ti(IV)/Ce(III) heterobimetallic assemblies synthesized on the pore of MCM-41. The combination of Ti(IV) and Ce(III) enabled to drive the photocatalytic oxidative decomposition of 2-propanol into acetone and CO₂ under visible-light irradiation. The Ti/Ce assembly is an attractive metal combination also for constructing the photosynthetic units because the Ce(IV) ion is known to be an effective oxidant to drive the oxygen evolving complexes.⁸ To date, the grafting of metal cations on the silica surface has been established for about one-fourth of the elements in the periodic table.⁵ Therefore, the abilities of hetero-bimetallic assemblies to drive photocatalysis and also their high flexibility in metal combination offers the opportunities to design and fabricate a wide variety of molecular-based inorganic photocatalysts according to the needs from the target reactions as well as their operation environments.

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Supporting Information Available: XANES, XRD, FT-IR, photocatalytic and photoelectrochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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