

Visible light water splitting using novel Al₂O₃/carbon cluster nanocomposite materials

H. Matsui · H. Miyazaki · A. Fujinami ·
S. Ito · M. Yoshihara · S. Karuppuchamy

Received: 19 February 2012 / Accepted: 7 April 2012 / Published online: 5 May 2012
© The Author(s) 2012. This article is published with open access at Springerlink.com

Abstract A novel nano-sized Al₂O₃/carbon cluster composite materials with and without doping of Pt nanoparticles are successfully prepared for the first time. The newly synthesized composites indeed very effective to split the water and produce H₂ and O₂ with the [H₂]/[O₂] ratios of ca.2. under visible light irradiation.

Keywords Nanomaterials · Nanostructures · Semiconductors · Insulator

Multi-electron transfer by visible light irradiation has been attracting attention of chemists (Zou et al. 2001; Fujishima and Honda 1972; Sayama et al. 2001; Kato et al. 2004; Konta et al. 2004; Zong et al. 2010; Zhang et al. 2010; Wang 2009; Furukawa et al. 2007; Kawahara et al. 2007a, b), because such a transfer will be a key for obtaining functional materials such as electronic and/or magnetic devices, oxidation–reduction catalysts, artificial photosynthesis catalysts, solar cells, and so on. In our previous works, we found that the calcination of hybrid materials composed of organic polymers and heavy metals such as Ti, Zr, Hf, W, Ta and V under a reducing atmosphere produced new types of carbon cluster composite materials uniformly dispersed with the corresponding nano-sized

metal oxides, i.e., SnO₂ (Matsui et al. 2007a), TiO₂ (Miyazaki et al. 2008), ZrO₂ (Miyazaki et al. 2009), HfO₂ (Matsui et al. 2009a), WO₃ (Matsui et al. 2007b) and V₂O₃ (Matsui et al. 2009b). The composite materials can stimulate the electron transfer between the metal oxides and the carbon clusters under visible light irradiation with a light-responsive oxidation–reduction function. Here, it should be indicated that these oxides essentially have too high band gaps and impossible to exhibit a visible light-responsive electron excitation. However, we assume that in our systems some bonding between the interface of oxides and carbon clusters along with the doping of carbon atom inside the oxides could be formed to affect the features of the band gaps and/or electron movements of oxides (Miyazaki et al. 2009; Matsui et al. 2007b, 2009a, b). Further, carbon clusters are considered to enhance the light-absorption ability (Zhao et al. 2010). If this assumption is true, then the combination of carbon clusters and insulating materials with higher band gaps is also expected to cause visible light-responsive electron excitation. In the present study, we selected Al₂O₃ with the band gap of 9.0 eV for a suitable insulating material to synthesize composite materials and subsequently studied their water splitting activity under visible irradiation. Here, we report a simple synthetic route for the synthesis of novel nano-sized Al₂O₃/carbon cluster composite materials and their effective water splitting activity under visible light irradiation.

A mixture of 2.95 g (9.30 mmol) of Al₂(C₂O₄)₃·H₂O, 5.34 g (56.8 mmol) of phenol, 4.61 g (154 mmol) of a 37 % formalin solution and 40 mL of a 1 mol/L sodium hydroxide solution was heated for 4 h to obtain Al₂(C₂O₄)₃-dispersed phenol resin I (Al 6.85 %, H 3.83 %, C 48.5 %. [C]/[Al] = 16). Inductively coupled plasma-atomic emission spectrometer (ICP-AES) and energy dispersive X-ray spectroscopy (EDX) measurements were

H. Matsui · H. Miyazaki · A. Fujinami · S. Ito · M. Yoshihara
Department of Applied Chemistry, Faculty of Science
and Engineering, Kinki University, 3-4-1, Kowakae,
Higashiosaka, Osaka 577-8502, Japan

S. Karuppuchamy (✉)
Department of Biological Functions and Engineering,
Kyushu Institute of Technology, 2-4, Hibikino, Wakamatsuku,
Kitakyushu, Japan
e-mail: chamy@life.kyutech.ac.jp; skchamy@gmail.com

used to analyze composition of the I and Ic. Elemental analysis was performed for C and H using Yanaco MT-6. Al composition was measured using ICP-AES using Shimadzu ICP-7500. The scanning electron microscope-energy dispersive X-ray (SEM-EDX) analysis of I showed that Al atom was uniformly dispersed in the resin. One gram of I in a porcelain crucible was heated under an argon atmosphere with a heating rate of 5 °C/min and kept at 500 °C for 1 h using a Kouyou KTF045N furnace to obtain black-colored material Ic (Al 18.9 %, H 1.48 %, C 45.1 % [C]/[Al] = 5).

The X-ray photoelectron spectroscopy (XPS) measurement of Ic revealed the presence of a peak at 74.9 eV due to the Al_{2p} orbital of Al_2O_3 . The transmission electron microscopic (TEM) image of Ic showed the presence of

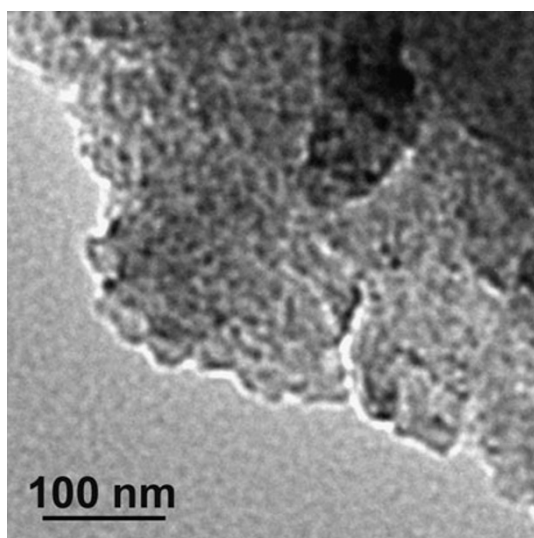


Fig. 1 TEM image of Ic

particles with the diameters of ca. 5 nm, possibly Al_2O_3 , in carbon matrix (Fig. 1). These results suggest that the calcined material was composed of nano-sized Al_2O_3 and carbon clusters. To evaluate the electron transfer process in Ic, the electron spin resonance (ESR) spectra of Ic in the presence of either a reductant (1,4-hydroquinone) or an oxidant (1,4-benzoquinone) under the irradiation of light ($\lambda > 460$ nm) were measured. The addition of the reductant to Ic decreased the ESR signal intensity and the addition of the oxidant increased the intensity (Fig. 2), suggesting that the material has a photo-responsibility and the electron transfer process in Ic is carbon clusters $\rightarrow Al_2O_3$ particles to form an oxidation site at the carbon clusters and a reduction site at the Al_2O_3 parts.

The visible light-responsive oxidation–reduction function of the present newly synthesized composite material was examined. First, the reduction reaction of methylene blue with Ic under the irradiation of visible light ($\lambda > 460$ nm) was spectrometrically performed. The absorption peak intensity of methylene blue was found to decrease with the irradiation time (Fig. 3), but essentially no degradation took place in the dark. Next, the visible light-irradiated oxidation–reduction reaction of an aqueous 0.05 mmol/L silver nitrite solution with Ic was performed to give a $[O_2]:[Ag]$ ratio of 1:4. Here, if a four-electron oxidation–reduction reaction takes place, then a $[O_2]:[Ag]$ ratio is given to be 1:4. These findings indicate an occurrence of smooth visible light-responsive oxidation–reduction ability.

It is known that the loading of Pt particles on the semiconductors increases the reduction ability. The surface of Ic was thus modified with Pt particles by reacting with a hydrogen hexachloroplatinate aqueous methanol solution under visible light irradiation to obtain Pt-loaded material

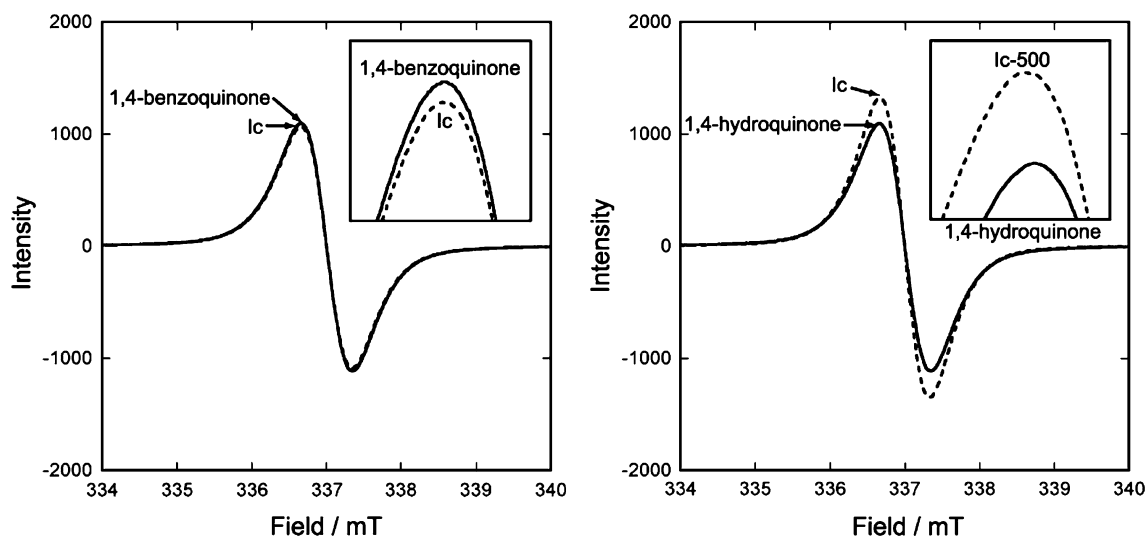


Fig. 2 ESR spectra of Ic in the presence of either 1,4-hydroquinone or 1,4-benzoquinone under the irradiation of light ($\lambda > 460$ nm)

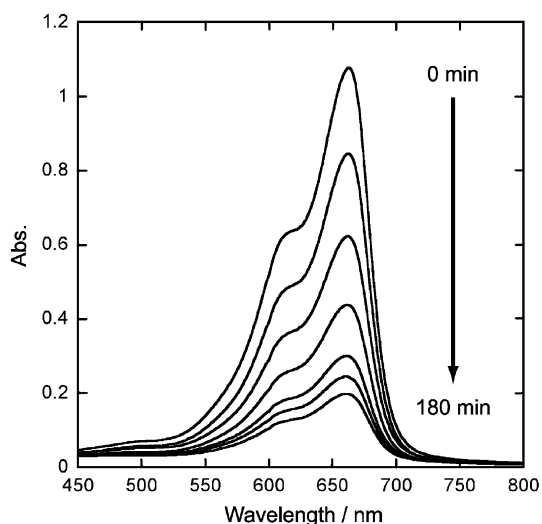


Fig. 3 UV-Vis spectra of methylene blue in the presence of Ic under the irradiation of visible light ($\lambda > 460$ nm)

Table 1 Water decomposition with the use of Ic and Ic-Pt under the irradiation of visible light ($\lambda > 460$ nm)

Materials	H ₂ (nmol)	O ₂ (nmol)	Ratio [H ₂]:[O ₂]
Ic	0	0	–
Ic-Pt	15.3	7.27	2:1

denoted as Ic-Pt. The TEM image of Ic-Pt revealed the presence of highly dispersed Pt particles of ca. 5 nm diameters on the surface of Ic (figure is not shown). The ICP-AES analysis of Ic-Pt showed a Pt content of 0.5 wt%. Water splitting experiments using Ic and Ic-Pt were performed in the following way. A stirred mixture of water (0.2 mL) and the calcined materials (10 mg) in a sealed tube was irradiated by visible light ($\lambda > 460$ nm) at room temperature for 12 h, and the evolved gases were analyzed by gas chromatography. The results are shown in Table 1. It is quite interesting to note that H₂ and O₂ were obtained with a H₂/O₂ molar ratio of 2 for Ic-Pt, while no gas was evolved with Ic.

We have fundamentally succeeded in constructing a visible light-responsive electron excitation of Al₂O₃ by simple carbonization technique. The novel nano-sized composite materials effectively split the water and produce H₂ and O₂ with the [H₂]/[O₂] ratios of ca.2. under visible light irradiation. We believe that similar photo-reactive excitation of either other insulating materials or metal oxides with high band gaps must be achieved by this approach and our observations will contribute to the development of new photoscience.

Acknowledgments This work was supported by a Grant-in-aid for scientific research (B) 21310076 from the Ministry of education, science, sport and culture, Japan.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

- Fujishima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238:37–38
- Furukawa T, Matsui H, Hasegawa H, Karuppachamy S, Yoshihara M (2007) The electronic behaviors of calcined materials from a (S-nickel-S-phenylene-O)-strontium-(O-phenylene-S-selenium-S) hybrid copolymer. *Solid State Commun* 142:99
- Kato H, Hori M, Kato R, Shimodaira Y, Kudo A (2004) Construction of z-scheme type heterogeneous photocatalysis systems for water splitting into H₂ and O₂ under visible light irradiation. *Chem Lett* 33:1348–1349
- Kawahara T, Miyazaki H, Karuppachamy S, Matsui H, Ito M, Yoshihara M (2007a) Electronic nature of vanadium nitride-carbon cluster composite materials obtained by the calcination of oxovanadylphthalocyanine. *Vacuum* 81:680
- Kawahara T, Kuroda T, Matsui H, Mishima M, Karuppachamy S, Seguchi Y, Yoshihara M (2007b) Electronic properties of calcined materials from a scandium-O-phenylene-O-yttrium-O-phenylene hybrid copolymer. *J Mater Sci* 42:3708
- Konta R, Ishii T, Kato H, Kudo A (2004) Photocatalytic activities of noble metal ion doped SrTiO₃ under visible light irradiation. *J Phys Chem B* 108:8992–8995
- Matsui H, Karuppachamy S, Yamaguchi J, Yoshihara M (2007a) Electronic behavior of calcined materials from SnO₂ hydrosol/starch composite materials. *J Photochem Photobio A Chem* 189:280
- Matsui H, Yamamoto S, Sasai T, Karuppachamy S, Yoshihara M (2007b) Electronic behavior of WO₂/carbon clusters composite materials. *Electrochemistry* 75:345
- Matsui H, Kuroda T, Kawahara T, Karuppachamy S, Kudo R, Yoshihara M (2009a) Electronic behavior of visible light sensitive ZrO₂/Cr₂O₃/carbon clusters composite materials. *Curr Appl Phys* 9:263
- Matsui H, Okajima T, Karuppachamy S, Yoshihara M (2009b) The electronic behavior of V₂O₃/TiO₂/carbon clusters composite materials obtained by the calcination of a V(acac)₃/TiO(acac)₂/polyacrylic acid complex. *J Alloy Comp* 468:L27
- Miyazaki H, Matsui H, Nagano T, Karuppachamy S, Ito S, Yoshihara M (2008) Synthesis and electronic behaviors of TiO₂/carbon clusters/Cr₂O₃ composite materials. *Appl Surf Sci* 254:7365
- Miyazaki H, Matsui H, Kita Y, Karuppachamy S, Ito S, Yoshihara M (2009) Electronic behavior of visible light sensitive ZrO₂/Cr₂O₃/carbon clusters composite materials. *Curr Appl Phys* 9:155
- Sayama K, Musaka K, Abe R, Abe Y, Arakawa H (2001) Stoichiometric water splitting into H₂ and O₂ using a mixture of two different photocatalysts and an IO₃⁻/I⁻ shuttle redox mediator under visible light irradiation. *Chem Commun* 2416–2417
- Wang XC (2009) A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat Mater* 8:76–82
- Zhang JS et al (2010) Synthesis of a carbon nitride structure for visible-light catalysis by copolymerization. *Angew Chem Int Ed* 49:441–444
- Zhao L, Chen X, Wang X, Zhang Y, Wei W, Sun Y, Antonietti M, Titirici M-M (2010) One-step solvothermal synthesis of a carbon@TiO₂ dyad structure effectively promoting visible-light photocatalysis. *Adv Mater* 22:3317

Zong X et al (2010) Photocatalytic H₂ evolution on MoS₂/CdS catalysts under visible light irradiation. *J Phys Chem C* 114:1963–1968

Zou Z, Ye J, Sayama K, Arakawa H (2001) Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. *Nature* 414:625–627