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Visible light-induced photocatalytic activity of SiO_2/carbon cluster composite materials

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Abstract

A convenient – and quick to realize – approach for the synthesis of a novel nano-sized SiO_2/carbon cluster composite photocatalyst is suggested. Since, the preparation of visible light sensitive SiO_2/carbon cluster composite photocatalyst is hitherto unreported; we performed such investigations to develop a novel catalyst from insulating materials. The synthesized composite indeed show efficient photocatalytic activity by degrading the methylene blue under visible light-irradiation.

Keywords: Composite materials; Nanostructures; Oxides; Optical materials

1. Introduction

Oxide Semiconductors have recently been the focus of intensive research owing to their use in many technological fields, such as optics and micro-electronics, but especially for the fundamental role played in photocatalysis and photoelectrochemistry. TiO_2 has been the most widely-investigated photocatalysts among other wide band gap oxide semiconductors, but suffers from low efficiency and narrow light response range [1,2]. Combining TiO_2 with carbonaceous nanomaterials is being intensively investigated in order to increase the photocatalytic activity [1–6]. The enhancement of the visible light activity has been confirmed for the carbonaceous nanomaterials coated TiO_2 [1–6]. However, the photocatalytic activity achieved with those materials is insufficient to use in practical applications. It should be indicated that the electron transfer under whole visible-light irradiation is considered to be a very important function for obtaining effective photocatalysts [7–21]. We considered that such a transfer could be achieved by the combination of carbon clusters and nano-sized semiconductors, in which carbon clusters act as a visible-light absorption site and an electron transfer bed, and semiconductors act as an electron excitation site [20,21]. We assumed that such hybrid materials could be obtained by the calcination of metal–organic moiety composite materials, and quite interestingly the formation of visible light-responsive carbon materials containing nano-sized metal oxides such as Nb_2O_5, SnO_2 and CeO_2 [7–10] were achieved. Here, it should be noted that the band gap of these metal compounds are too high and, in general, these oxides with high band gap never exhibit visible light-response abilities. The achievement of light-induced excitation in the above mentioned hybrid materials may be due to the formation of either donor level in the metal oxides due to O-deffect or a partial metal oxide–carbon bonding. It is expected that the carbonization of insulating materials containing polymeric complex could also produce carbon coated composite materials and subsequently resulting materials could show visible light-response. Therefore, in the present work, SiO_2 has been selected as a suitable stable insulating material to synthesize composite materials. SiO_2 is a typical insulating material with the band gap of 8.9 eV. Here, we report a new and simple synthetic route for the preparation of novel nano-sized SiO_2/carbon cluster composite materials for the first time.

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The photo-electronic nature of SiO_2/carbon clusters composite materials was investigated and indeed it show very effective electron transfer under visible light-irradiation.

2. Experimental

2.1. Reagents

Commercially available tetraethyl orthosilicate (TEOS), 1,8-octanediol, of bis-phenol A glycidyl ether and phthalic anhydride were used as received.

2.2. Synthesis of complex I

1.41 g (6.67 mmol) of TEOS, 1.98 g (13.53 mmol) of 1,8-octanediol, 4.61 g (13.53 mmol) of bis-phenol A glycidyl ether and 2 g (13.53 mmol) of phthalic anhydride were dissolved in 100 mL of acetone. Acetone was evaporated and subsequently the residues were heated at 130 °C for 5 h to obtain TEOS-dispersed epoxy resin denoted as complex I.

2.3. Calcination of complex I

One gram of complex I in a porcelain crucible was heated under an argon atmosphere with a heating rate of 5 °C/min and kept at 400, 500 and 600 °C for 1 h to obtain black-colored materials Ic-400, Ic-500 and Ic-600, respectively (Ic-400; Si 3.5%, C 80.7%, H 4.1%, [Si]/[C]=1/54: Ic-500; Si 4.4%, C 82.0%, H 3.0%, [Si]/[C]=1/44: Ic-600; Si 4.9%, C 81.3%, H 2.7%, [Si]/[C]=1/39).

2.4. Characterizations

The Scanning electron microscope–energy dispersive X-ray (SEM-EDX) measurement was carried out with a Hitachi S-4800 microscope. Transmission electron microscopic (TEM) observations was carried out using a Jeol JEM-3010 microscope. X-ray photoelectron spectroscopy (XPS) analysis was carried out using Shimadzu ESCA-850. Electron spin resonance (ESR) spectra were taken with a Jeol JES-TE200 spectrometer. Visible light was generated using a Hoya-Schott Megalight 100 halogen lamp. UV–vis spectra were measured using a Hitachi U-4000 spectrometer. The reduction reaction of methylene blue with the calcined materials was carried out in the following way. A mixture of 3 mg of the calcined materials and a degassed 0.03 mmol/L methylene blue-0.12 mmol/L citric acid aqueous solution was stirred in the dark for 48 h under an argon atmosphere. The mixture was irradiated with visible light ($\lambda > 460$ nm) and the concentration of methylene blue was determined by a UV–vis spectrometer. TCD gas chromatography was taken using Shimadzu GC-8 A. The oxidation-reduction reaction of an aqueous $AgNO_3$ solution with the composite materials was performed in the following way. A mixture of 10 mg of the composite and 1 mL of a degassed 0.05 mol/L $AgNO_3$ aqueous solution was irradiated with visible light ($\lambda > 460$ nm) under an argon atmosphere for 1 h, and the evolved O_2 was analyzed with gas chromatography and the obtained Ag was estimated by ICP analysis.

3. Results and discussion

SEM–EDX measurements of complex I revealed that Si atom was uniformly dispersed in the epoxy resin (Fig. is not shown). The XPS analysis of the calcined materials were found to give a binding energy at 103.2 ~103.6 eV due to the Si_{2p} orbital of SiO_2. The Transmission electron microscopic images of the materials showed ultrafine particles with the diameters of 10~15 nm, possibly SiO_2, in the matrix of carbon clusters (Fig. 1). These results suggest that the calcined materials are composed of nano-sized SiO_2 particles and carbon clusters.

The electronic behaviors of the calcined materials were examined. The Electron spin resonance spectra of the materials

Table 1
Radical spin quantities (*rsq*), reduction activities (*ra*) and photo-decomposition (*pd*) of calcined materials Ic's.

Materials	*rsq*	*ra*	*pd*		
	(spin g^{-1})	(μmol g^{-1} h^{-1})	(μmol)		Ratio
			O_2	Ag	$[O_2]$:[Ag]
Ic-400	9.58×10^{19}	6.8	38	148	1:3.9
Ic-500	2.61×10^{20}	7.2	72	290	1:4.0
Ic-600	7.76×10^{19}	5.5	48	197	1:4.1

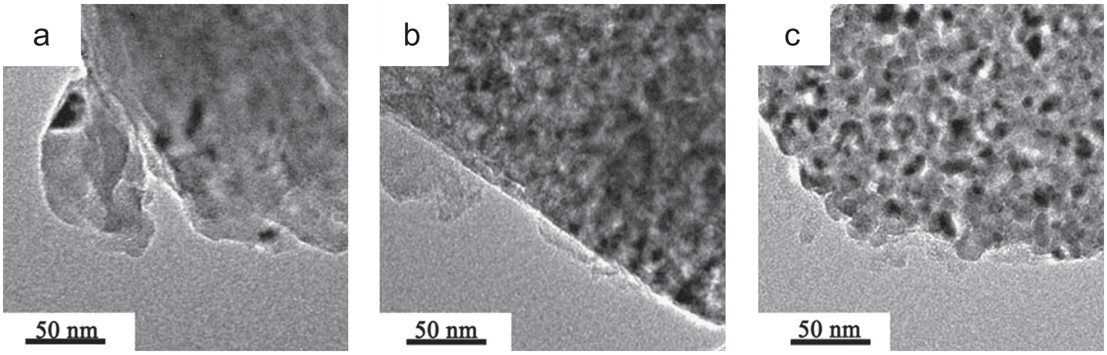

Fig. 1. TEM images of SiO_2/carbon cluster composite materials (a) heated at 400 °C (Ic-400), (b) 500 °C (Ic-500) and (c) 600 °C (Ic-600).

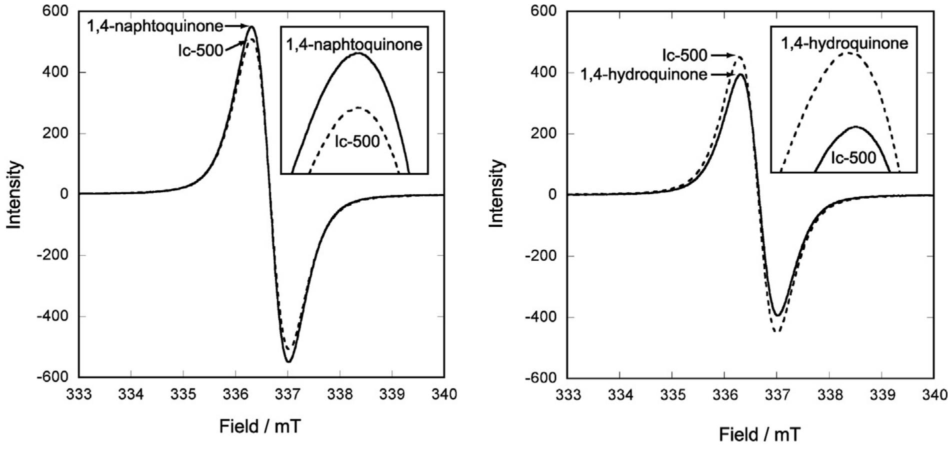

Fig. 2. ESR spectra of Ic-500 in the presence of either an oxidant or a reductant.

showed a peak at 337 mT ($g=2.003$). The radical spin quantities (rsq) of the calcined materials were determined by a double integrating calculation of the differential absorption line with the use of 1,1-diphenyl-2-picrylhydrazyl and the results are shown in Table 1. The highest rsq value was observed for Ic-500. Our understanding is that an electron transfer between SiO_2 particles and carbon clusters took place to form a free electron on carbon clusters and the highest electron transfer appeared for Ic-500.

Fig. 2 shows the ESR spectra of Ic-500 in the presence of either an oxidant (1,4-naphtoquinone) or a reductant (1,4-hydroquinone) under the irradiation of light ($\lambda > 460$ nm). The peak intensity was increased with the addition of the oxidant but decreased with the addition of the reductant, indicating that the signal is due to a cation radical. It is thus deduced that an electron transfer from carbon clusters to SiO_2 particles takes place to form an oxidation site at carbon clusters and a reduction site at SiO_2 part.

The photocatalytic ability of the calcined materials was examined. Fig. 3 is the UV–vis spectra of methylene blue in the presence of Ic-500 under the irradiation of visible light ($\lambda > 460$ nm). The absorption band of methylene blue was decreased with the increase of the irradiation time, indicating that the calcined materials have visible light-responsive reduction ability. The reduction activity (ra) of the calcined materials in the reduction reaction of methylene blue was determined by the equation $ra =$ (the amount of methylene blue) $\cdot$ (g of the calcined material)$^{-1}$ $\cdot$ (h)$^{-1}$, and the results are also shown in Table 1. Here again, the highest ra value was obtained for Ic-500, indicating that Ic-500 has the highest photo-reduction ability.

The visible light-irradiated oxidation–reduction reaction of an aqueous silver nitrate solution with the calcined materials was performed and the results are also shown in Table 1. The amounts of O_2 and Ag formed for Ic-500 was found to be higher than those for the others, indicating that Ic-500 has the highest photo-responsive oxidation-reduction ability. Here, if a four electron oxidation–reduction reaction takes place, then $[O_2]$:[Ag] ratio is given to be 1:4. The $[O_2]$:[Ag] ratios of the calcined materials were obtained to be nearly 1:4, indicating the occurrence of a smooth electron transfer with a visible light-responsive oxidation–reduction ability. We have thus achieved the construction of visible light-responsive activation of SiO_2 by a carbonization technique.

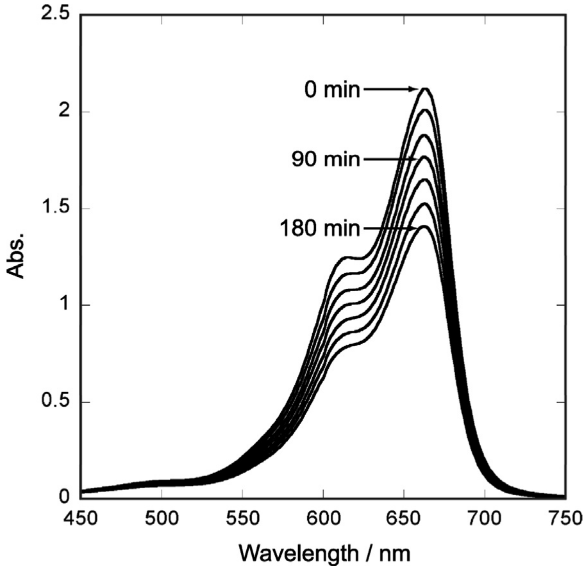

Fig. 3. UV–vis spectra of methylene blue in the presence of Ic-500 under the irradiation of visible light ($\lambda > 460$ nm).

4. Conclusions

A novel nano-sized SiO_2/carbon cluster composite materials were successfully obtained by carbonization technique for the first time. The synthesized composite indeed showed efficient photocatalytic activity by degrading the methylene blue under visible light-irradiation. It is concluded that this unique carbonization technique will be a useful tool for the development of new visible light-active materials either from insulating materials or metal oxides with higher band gaps. The present investigation will open up a new route for the development of new photo-science, including electronic and/or optical devices production, artificial photosynthesis catalysis, organic synthesis catalysis, solar cell production, and so on.

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