

Electronic behavior of calcined materials obtained from SnO₂ hydrosol/starch composite materials

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Abstract

The calcinations of SnO₂ hydrosol/starch composite materials under an argon atmosphere gave nano-sized SnO₂/Sn/carbon clusters composite materials. ESR and UV–vis spectral examinations suggest the possibility of light-responsive electron transfer from carbon clusters to SnO₂ and/or Sn particles.

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1. Introduction

An electron excitation under light irradiation is important for developing a new photo-science. Various photochemical effects have been reported with the use of semiconductors and modified inorganic metal compounds [1–7]. We have considered that such a function is given by the combination of nano-sized semiconductors and carbon clusters, resulting from the combined function of electron excitation by semiconductors and light absorption and electron transport by carbon clusters. We have recently reported that the calcination of metal–organic moiety hybrid copolymers gave nano-sized inorganic metal compounds/carbon clusters composite materials, which showed visible light-responsive electron excitation [8–11]. Here, it is expected that the combination of semiconductors and carbon clusters could also be obtained by simply calcining the mixture of semiconductors particles and organic components. In this study, we report the constituent and electronic behavior of calcined materials Ic's from SnO₂ hydrosol/starch composite materials I's (Scheme 1).

2. Experimental

2.1. Reagents

Commercially available tin oxide hydrosol (Taki Chemical Co. Ltd.), starch (Kanto Chemical Co. Ltd.), 1,4-benzoquinone, triethylamine, 1,1-diphenyl-2-picrylhydrazyl (DPPH), citric acid and 7,7,8,8-tetracyanoquinodimethane (TCNQ) were used.

2.2. Preparation of precursor I

A mixture of tin oxide hydrosol and starch in 60 mL of water was stirred at 80 °C for 2 h. Water was evaporated under a reduced pressure and the residues were dried under vacuum at 110 °C for 2 h to obtain precursor I. The charged amounts of tin oxide hydrosol and starch are shown in Table 1.

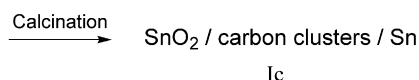
2.3. Calcination of precursor I

One gram of precursor I in a porcelain crucible was heated under an argon atmosphere with a heating rate of 5 °C/min using Denken KDF-75 electric furnace and kept for 1 h at 400 °C through 700 °C to obtain black-colored material Ic.

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Table 1
Charged amounts of tin oxide hydrosol and starch

Precursor	SnO ₂ (g)	Starch (g)
I ₁	4.52	5.01
I ₂	1.05	8.14
I ₃	0.60	9.35



Scheme 1. Syntheses of precursor I and calcined material Ic.

2.4. Apparatus and property evaluation

Elemental analysis was performed for C and H with Yanaco MT-6 and for Sn by inductively coupled plasma atomic emission spectrometry (ICP-AES) using Shimadzu ICP-7500. X-ray diffraction (XRD) spectra were measured with Rigaku Mini Flex. Transmission electron microscopy (TEM) images were taken using Joel TEM-3010. SEM-EDX observations were done using Hitachi S-300. Visible light was generated by 150 W halogen lamp (Hoya-Schott Megalight 100).

Electron spin resonance (ESR) spectra were measured with Joel JES-TE200. The ESR spectra measurements of the calcined material with the addition of an oxidant (1,4-benzoquinone) or a reductant (triethylamine) were performed in the following way. A mixture of 1 mg of the calcined material and 0.2 mL of 0.1 mmol/L 1,4-benzoquinone benzene solution or 0.1 mmol/L triethylamine benzene solution was irradiated by visible light above the wavelength of 360 nm for 3 h and subjected to the ESR spectral analysis.

UV–vis spectra were taken using Hitachi U-4000 spectrometer. The reduction of TCNQ with the calcined material Ic was performed in the following way. A mixture of 10 mg of Ic and 3.6 mL of 0.005 mmol/L TCNQ/citric acid acetonitrile solution was stirred at room temperature for 24 h and the TCNQ concentration at every 30 min under the irradiation of visible light above the wavelength of 460 nm was measured by UV–vis spectrometer.

3. Results and discussion

The results of the elemental analyses of the precursors were shown in Table 2. The Sn contents in precursors I₁, I₂ and I₃ were obtained to be 39.00, 19.00 and 7.62%, respectively. The XRD spectra measurements of the materials (Fig. 1) showed peaks at $2\theta = 26.5^\circ$, 33.5° , 51.6° and 65° due to SnO₂. TEM measurements showed that ultrafine particles with the diameters of 3–5 nm, possibly SnO₂ particles, were uniformly dispersed in the organic component phases (Fig. 2).

The calcination of precursors I₁, I₂, and I₃ were performed at 400 °C through 700 °C to obtain black-colored materials I_{1c}-400 through I_{1c}-700, I_{2c}-400 through I_{2c}-700 and I_{3c}-400 through

Table 2
Elemental analyses of precursors and calcined materials

Material	Found (%)			[C] / [Sn]
	C	H	Sn	
I ₁	17.82	3.18	39.00	4.52
I _{1c} -400	19.46	1.23	31.11	6.18
I _{1c} -500	18.41	1.15	30.91	5.89
I _{1c} -600	18.26	0.81	39.93	4.52
I _{1c} -700	18.03	0.31	38.48	4.63

I ₂	35.53	5.54	19.00	18.48
I _{2c} -400	58.40	2.36	15.89	36.32
I _{2c} -500	55.14	2.16	16.05	33.95
I _{2c} -600	57.86	1.55	16.00	35.73
I _{2c} -700	59.87	1.01	16.48	35.90

I ₃	37.83	5.99	7.62	49.06
I _{3c} -400	63.20	3.80	15.10	41.36
I _{3c} -500	64.66	2.42	15.66	40.80
I _{3c} -600	67.31	1.56	16.09	41.34
I _{3c} -700	68.41	0.98	15.50	43.61

I_{3c}-700, respectively. The results of the elemental analyses of the calcined materials are summarized in Table 2. The average C/Sn molar ratios in I_{1c}, I_{2c}, and I_{3c} were obtained to be 5.31, 38.07, and 39.66, respectively. The XRD measurements (Fig. 3) showed that every calcined material had peaks at $2\theta = 26.5^\circ$, 33.5° , 51.6° and 65° due to SnO₂, and that the 600 and 700 °C calcined materials had peaks at $2\theta = 30.4^\circ$, 31.8° and 44.7° due to metallic Sn. The SEM-EDX analysis of I_{1c}-700 (Fig. 4) showed spherical particles with the diameters of 0.5–3 μm due to metallic Sn in the matrix of the carbon clusters. The TEM images of the 600 °C-calcined materials (Fig. 5) showed ultrafine particles with the diameters of 3–5 nm, possibly SnO₂, in the matrix

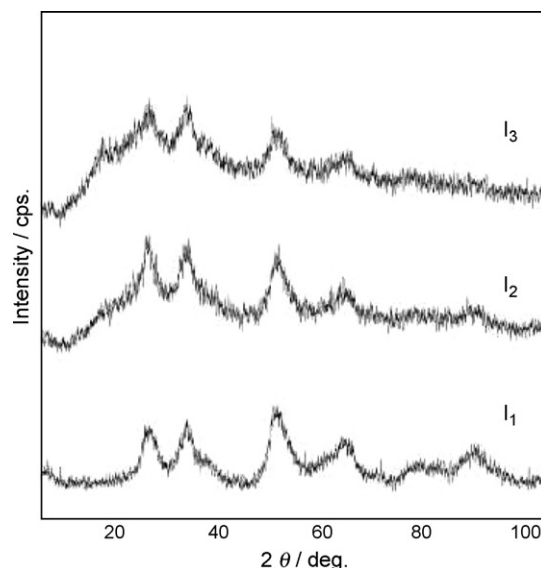


Fig. 1. XRD patterns of precursors.

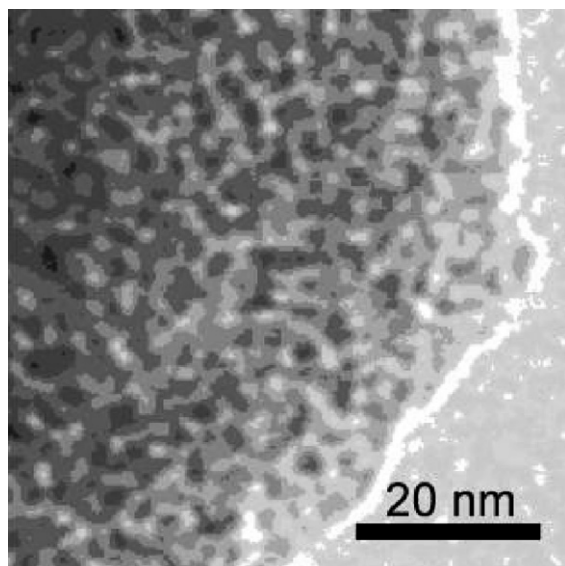


Fig. 2. TEM images of precursor I₁.

of carbon clusters. From these results, the calcined materials were considered to be composed of SnO₂ and Sn particles in the matrix of carbon clusters.

The ESR spectra of I_{1c}, I_{2c}, and I_{3c} were shown in Fig. 6. In every case, a peak at 337 mT ($g = 2.003$) was observed, and, in the I_{1c}'s and I_{2c}'s series, the highest intensity was obtained

Table 3

Radical spin quantities (rsq, $\times 10^{20}$ spins/g) of calcined material I_{2c}-600 in the presence of oxidant or reductant

I _{2c} -600	5.77
I _{2c} -600 + 1,4-benzoquinone	6.68
I _{2c} -600 + triethylamine	5.04

for the 600 °C-calcined materials and, in the I_{3c}'s series, I_{3c}-500 showed the highest intensity. The radical spin quantities (rsq) of I_{1c}-600, I_{2c}-600 and I_{3c}-500 were determined by the double integrating calculation of the differential absorption line with the use of DPPH and the plot of rsq values against the [C]/[Sn] ratios in I_{1c}-600, I_{2c}-600 and I_{3c}-500 (Fig. 7) gave a maximum rsq value for I_{2c}-600. Our suggestion is that an electron transfer between carbon clusters and SnO₂ and/or Sn particles took place to form a free electron on carbon clusters and a quantitative balance between C and metal in the calcined materials is important for the electron transfer feature.

Table 3 shows the rsq change of I_{2c}-600 in the presence of an oxidant (1,4-benzoquinone) and a reductant (triethylamine) under the irradiation of light above 360 nm. The rsq value increased with the addition of the oxidant and decreased with the addition of the reductant, indicating that the radical species was cationic. Therefore, it is deduced that the light-responsive electron transfer from carbon clusters to SnO₂ and/or Sn particles took place to form an oxidation site at carbon clusters and a reduction site at SnO₂ and/or Sn particles. Recently, we have

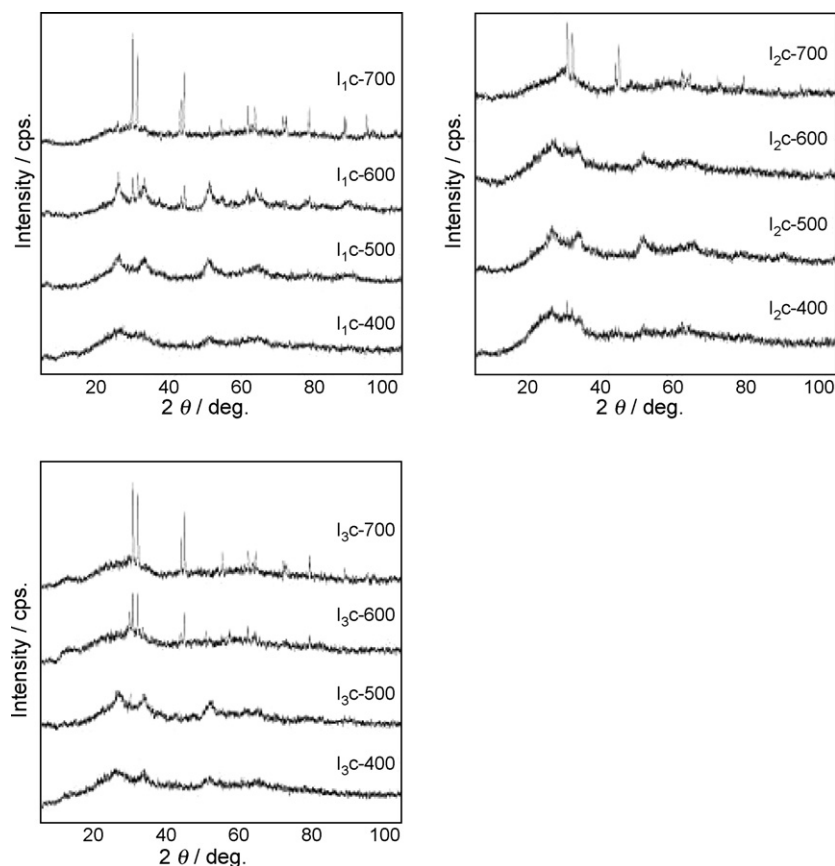


Fig. 3. XRD patterns of calcined materials.

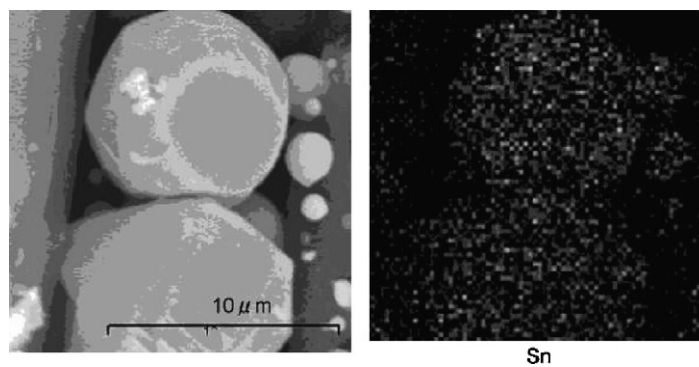


Fig. 4. SEM-EDX analysis of I₁c-700.

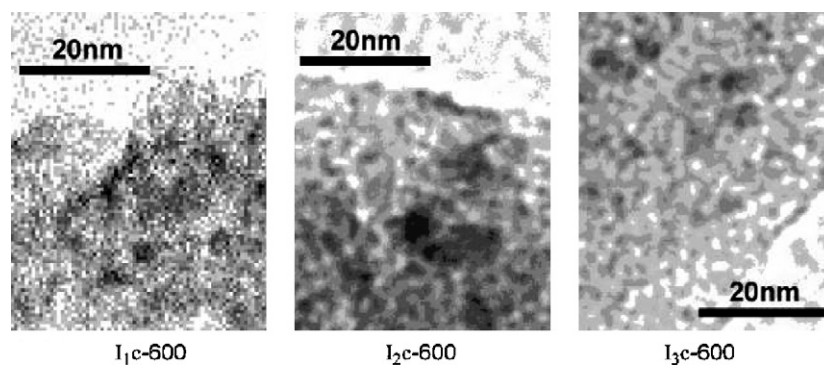


Fig. 5. TEM images of calcined materials.

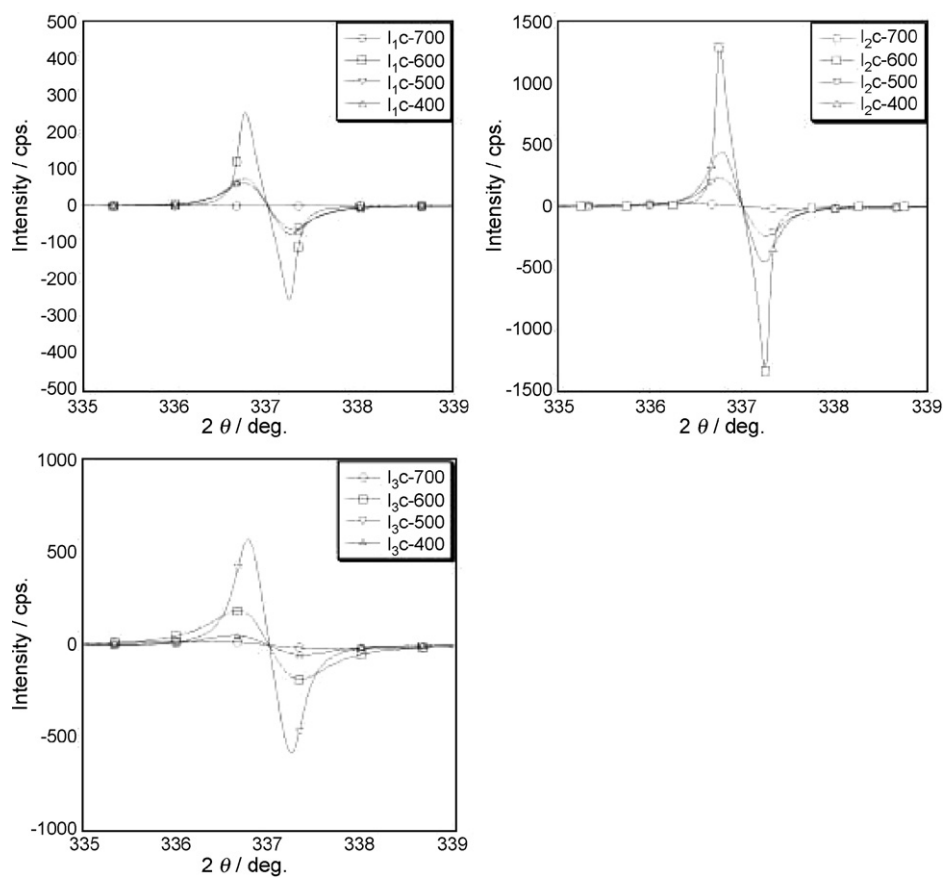


Fig. 6. ESR spectra of calcined materials.

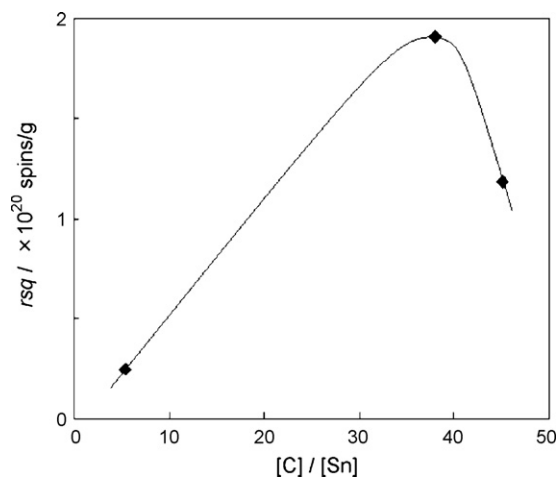


Fig. 7. Relationship between rsq values and [C]/[S] ratios.

found that the microwave treatment of Sn-*O*-phenylene hybrid copolymer II gave SnO₂/carbon clusters/Sn composite material IIc (Scheme 2), which showed similar electron transfer process of carbon clusters → SnO₂ and/or Sn particles [12].

Here, we have examined the catalytic activity of calcined materials I_{2c}-600 and IIc under light irradiation. Fig. 8 is a typical example of the UV–vis spectral change of TCNQ in the presence of I_{2c}-600 under the irradiation of light above 460 nm, in which the slight decrease of absorption band was observed with the increase of the irradiation time. Fig. 9 shows the relationships between the concentration of TCNQ and time in the presence of I_{2c}-600 and IIc either in the dark or under the light irradiation (above 460 nm). No TCNQ decomposition was observed for the I_{2c}-600/dark system, while a slight reduction of TCNQ was detected for the IIc/dark system. On the other hand, visible light enhanced the degree of decomposition of TCNQ for both I_{2c}-600 and IIc, indicating that both calcined materials had visible light-responsive catalytic activity. It is interesting to note that the degree of TCNQ decomposition for I_{2c}-600 under the visible light irradiation was smaller than that of IIc, indicating that the light-responsive electron excitation of IIc was higher than that of I_{2c}-600. Our assumption is that, in I_{2c}-600, carbonization and metallation may take place on the surface of SnO₂ particles with no reduction in the inside of SnO₂ particles, while, in IIc, the reduction to the inside of SnO₂ particles during the calcination may take place to form donor level due to O-defect in SnO₂, thus facilitating a multi-step electron transport.

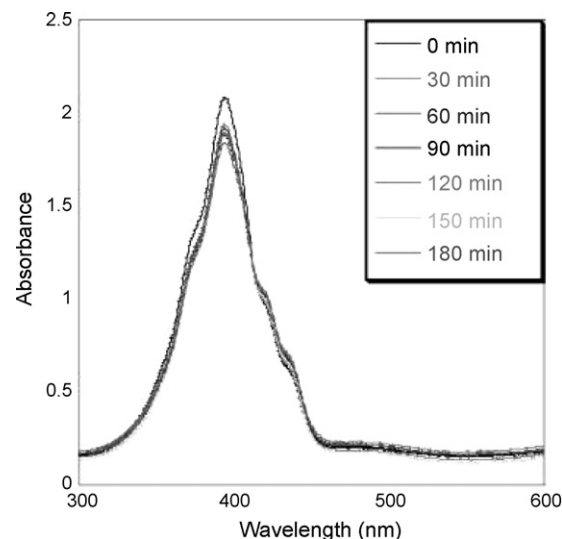


Fig. 8. UV–vis spectra of TCNQ in the presence of I_{2c}-600 under light irradiation (above 460 nm).

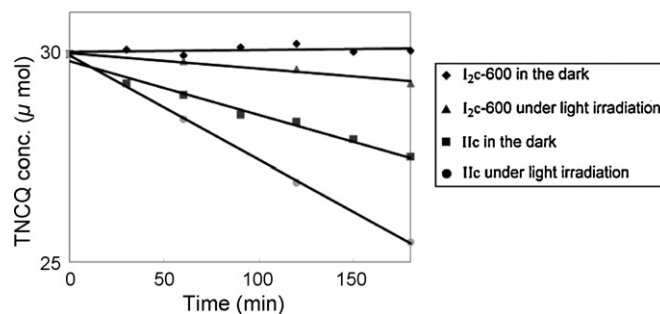


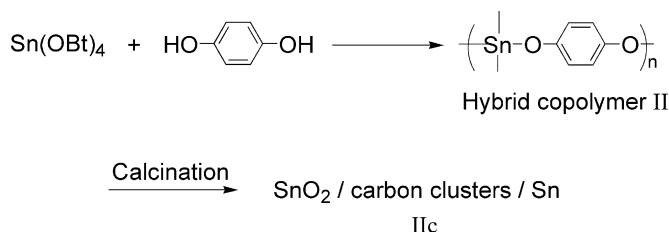
Fig. 9. TCNQ decomposition in the presence of I_{2c}-600 and IIc either in the dark or under light irradiation (above 460 nm).

4. Conclusions

The calcination of SnO₂ hydrosol/starch composite material gave nano-sized SnO₂/carbon clusters/Sn composite material, and the photo-responsive electron transfer from carbon clusters to SnO₂ and/or Sn particles was found to take place. It was observed that the light-responsive catalytic activity of the calcined material was smaller than that of calcined material obtained from an Sn-*O*-phenylene hybrid copolymer. This may be due to the formation of O-defect SnO₂ in the inside of metal oxide for the latter calcined material and thus facilitating an electron excitation.

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Scheme 2. Syntheses of hybrid copolymer II and calcined material IIc.

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