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Electronic properties of ruthenium sulfide–carbon cluster composite material obtained by calcination of an alternating ruthenium–S–phenylene hybrid copolymer

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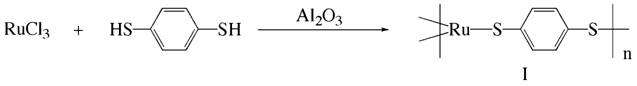
Abstract Calcination of an alternating ruthenium–S–phenylene hybrid copolymer under an argon atmosphere was found to give nano-sized ruthenium sulfide/carbon cluster composite material. ESR spectral examinations of the material revealed that an electron transfer from ruthenium sulfide particles to carbon clusters took place to raise a visible-light responsive oxidation–reduction function with an oxidation site at ruthenium sulfide particles and a reduction site at carbon clusters. The surface of the calcined material was modified with Pt particles, and the reduction ability of the resulting modified material was examined.

Introduction

Realizing a charge-separated electron transfer with photo-response function will lead to an achievement of novel photocatalysts. Such a transfer has been achieved by TiO_2 and modified semiconductors [1–8], however, an electron transport under whole visible-light irradiation does not seem to have been established yet. We consider that such an electron transfer will be achieved by a combination of carbon clusters and nano-sized semiconductors, where carbon clusters are expected to act as a visible-light absorption site and an electron transport bed and, on the other hand, semiconductors to act as an electron excitation site, resulting in the realization of visible-light responsive electron transfer. We have recently reported the syntheses of alternating metal-organic moiety hybrid copolymers [9–12], in which a charge-separated electron transport between metals and organic moieties took place. We assume that calcinations of the copolymers under a reducing atmosphere will give new types of novel hybrid materials involving nano-sized inorganic metal compounds in the matrix of carbon clusters. In the present study, we describe the composition and electronic behavior of calcined material from an alternating ruthenium–S–phenylene hybrid copolymer I (Scheme 1). Calcination of the copolymer I is expected to provide ruthenium sulfide-carbon cluster composite material. Ruthenium sulfide has a rather low band gap of 1.8 eV, and incorporation of ruthenium sulfide particles into carbon clusters will raise an effective charge-separation under visible-light irradiation.



Scheme 1. Synthesis of ruthenium–S–phenylene copolymer

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Experimental

Commercially available ruthenium chloride, 1,4-benzenedithiol, activated alumina, 1,1-diphenyl-2-picrylhydrazy(DPPH), and methylene blue were used. Other reagents and solvents were purified by standard procedures.

A mixture of ruthenium chloride (0.6 mmol) and 1,4-benzenedithiol (0.9 mmol) in the presence of activated alumina (20 g) in anhydrous ethanol (30 ml) was refluxed for 12 h. Precipitates formed were washed with anhydrous ethanol using a Soxhlet extractor and dried at 80 °C under vacuum to obtain copolymer I.

About 0.5 g of the copolymer I was heated in a porcelain crucible under an argon atmosphere with a heating rate of 5 °C/min using Denken gas convertible electric furnace KDF-75, and kept for 1 h at 400, 500, 600, 700 and 800 °C, respectively, to obtain calcined materials Ic-400, Ic-500, Ic-600, Ic-700 and Ic-800, respectively.

About 200 mg of calcined material dispersed in 50 ml of 0.5 mmol/l hydrogen hexachloroplatinate(IV)hexahydrate solution was irradiated using Hoya-Schott Megalight 100 halogen lamp (150 W) for 30 min. Into the mixture was added 10 ml of methanol, and then the mixture was irradiated by halogen lamp for 1 h. The precipitate was collected, washed with distilled water, and dried by heating under vacuum.

Elemental analyses were performed for C and H using Yanaco MT-6, for S using Yanaco YS-10, and for Ru using Shimadzu ICPS-1000III. Transmission electron microscopy (TEM) observations were done using Jeol JEM-3010. X-ray diffraction (XRD) spectra were taken using Rigaku Mini Flex. UV–VIS spectra were taken using Hitachi U-4000 spectrometer. Electron spin resonance (ESR) spectra were measured using Jeol JES-TE 200 spectrometer.

Results and discussion

The FT-IR spectral measurement of copolymer I showed frequencies of the phenylene group at 1481 and 834 cm^{-1} and of the C–S bond at 667 cm^{-1}. Table 1 summarizes the results of ICP and elemental analyses of copolymer I and calcined materials Ic. The percentage of the phenylene moiety in copolymer I was calculated to be 80.1% from the observed carbon content. Increase of calcination temperature was found to increase the carbon contents and to decrease the hydrogen contents, suggesting that the carbonization of the copolymer had proceeded. However, the ruthenium and sulfur contents of Ic-700 and Ic-800 were found to be considerably low. This probably is due to the errors in ICP analyses, since insoluble residues in acidic solutions were yielded at the analyses of Ic-700 and Ic-800.

Table 1 ICP and elemental analyses of copolymer I and calcined materials Ic

Material	% (Found)			
	Ru	C	H	S
I	21.3	27.8	2.1	23.5
Ic-400	22.9	31.7	1.4	23.7
Ic-500	22.7	30.4	1.1	24.2
Ic-600	23.0	29.2	0.9	21.7
Ic-700	16.2	35.5	0.8	19.0
Ic-800	5.4	33.6	0.5	8.5

In order to identity the ruthenium compound, XRD measurements were performed. As shown in Fig. 1, peaks due to RuS$_2$ at $2\theta = 27$, 32, 46 and 54 deg were detected for Ic-600, Ic-700 and Ic-800. TEM observations (Fig. 2) showed that copolymer I was spherical particles with diameters of ca. 200 nm and the calcined materials Ic-600–Ic-800 keep the spherical particle form with ultrafine particles of a few nm diameter which are considered to be ruthenium sulfide particles. These results indicated that the calcined material was composed of nano-sized ruthenium sulfide particles and carbon clusters.

In order to examine the electronic behaviors of the calcined materials, ESR spectra were taken (Fig. 3). A signal due to a free electron at 337 mT ($g = 2.003$) was observed. Our understanding is that an electron transfer between RuS$_2$ particles and carbon clusters took place to form a free electron on carbon clusters. The radical spin quantities of the calcined materials were determined by a double integrating calculation of the differential absorption spectrum with the use of 1,1-diphenyl-2-picrylhydrazyl (DPPH) to be in the order of Ic-600

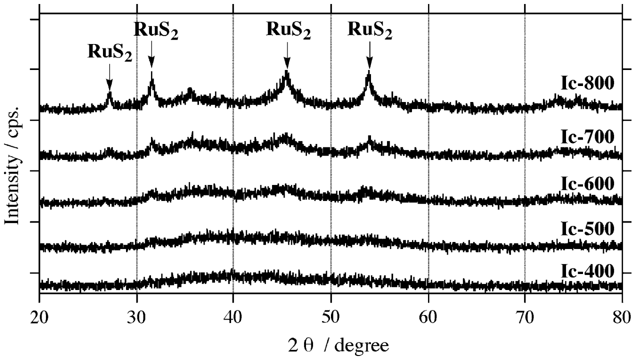
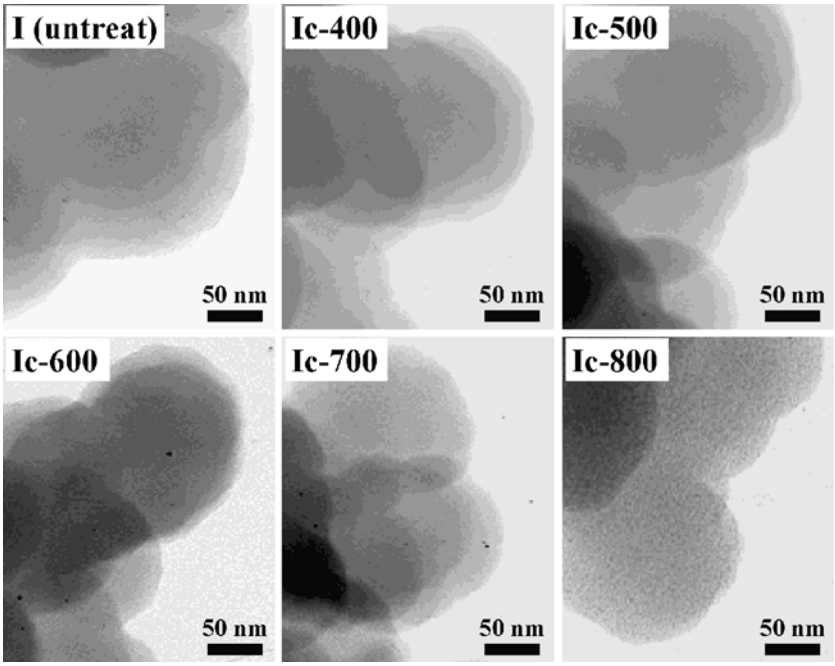


Fig. 1 X-ray diffraction of calcined materials

Fig. 2 TEM images of the copolymer I and calcined materials



(8.8 × 10^{17} spins/g) > Ic-500 (5.5 × 10^{16} spins/g) > Ic-700 (2.8 × 10^{16} spins/g), indicating that the most effective charge separation took place in Ic-600. The signal intensity of Ic-600 was found to decrease in response to 15 min visible-light irradiation, but to increase back to the initial intensity when kept in dark for 15 min after the irradiation had stopped (Fig. 4), indicating that Ic-600 has a photo-response characteristic. The addition of oxidants (1,4-naphtoquinone, anthraquinone, and 7,7,8,8-tetracyanoquinodimethane) to Ic-600 decreased the signal intensity, but the intensity increased with the addition of reductants (pyrogallol, hydroquinone, and triethylamine) (Fig. 5), indicating that the peak signal is due to an anion radical formed on carbon clusters.

The HOMO potentials of the reductants are plotted against the increase in ESR spin quantity of Ic-600 to give linear correlation as shown in Fig. 6. The oxidation potential of Ic-600 was estimated to be –9.35 eV by extrapolating this linear plot to the ordinate. Similarly, the reduction potential of Ic-600 was estimated to be 2.22 eV by extrapolating the linear correlation between the LUMO potential of the oxidants and the decrease in ESR spin quantity of Ic-600 to the ordinate (Fig. 7). It was thus deduced that calcined material shows a photo-responsive oxidation–reduction behavior.

It is known that Pt-modification on semiconductor surface improves their reduction ability. Pt particles were thus loaded on the surface of Ic-600 by a photo-electrodeposition procedure, and the TEM image of the resulting Pt-loaded Ic-600 (Ic-600/Pt) was found to have highly dense cores with diameters of ca. 3 nm,

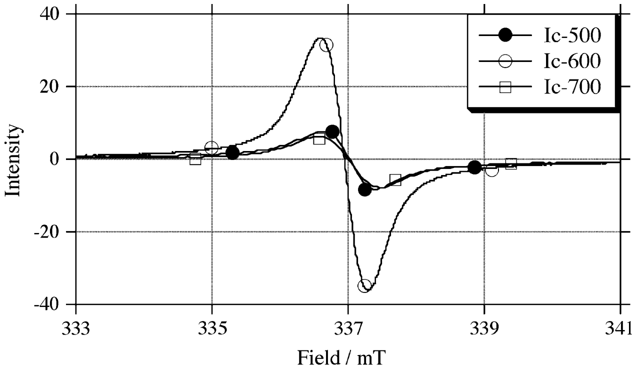


Fig. 3 ESR spectra of calcined materials

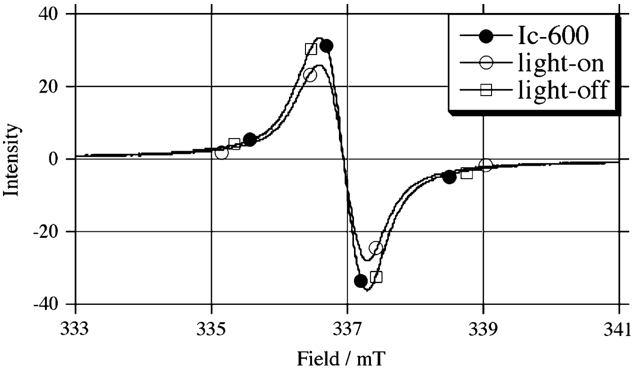


Fig. 4 ESR spectra of Ic-600 under visible-light irradiation

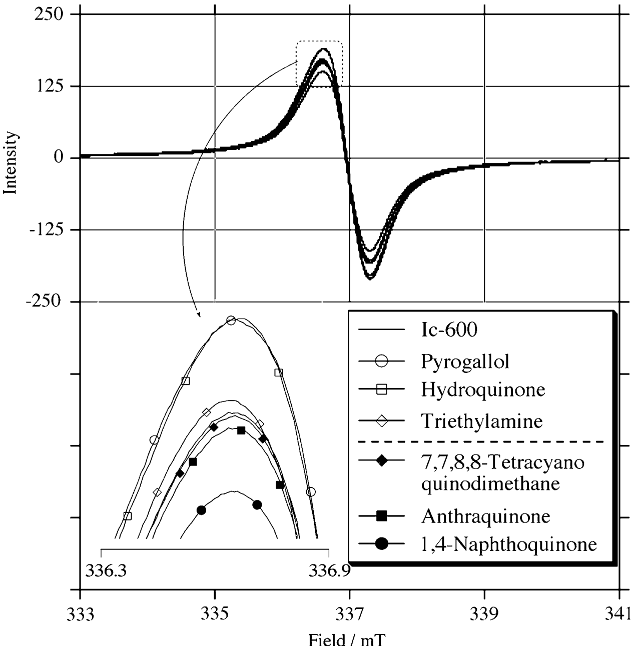


Fig. 5 ESR spectra of Ic-600 in the presence of oxidants and reductants

possibly due to Pt particles. In order to evaluate the reduction ability of Ic-600/Pt, the degradation of methylene blue were measured in the presences of Ic-600 under visible-light irradiation (Fig. 8a), Ic-600/Pt in dark (Fig. 8b), and Ic-600/Pt under visible-light irradiation (Fig. 8c). The absorption peak intensity of methylene blue at 664 nm decreased with time. In the two experimental runs under visible-light irradiation, the peak intensity decreased rapidly in the beginning, and reached constant decreasing rate after 30 min. Thus, the reduction ability indexes (*rdi*) of calcined materials were determined by the equation $rdi = [(C_{30}–C_{180})/150] \times 10^3$ (nmol l^{-1} min^{-1}), where C*t* is the concentration of methylene blue at *t* (min). As shown in Table 2, the *rdi* values were in the decreasing order; Ic-600/Pt under visible-light irradiation (Run 3) > Ic-600 under visible-light irradiation (Run1) > Ic-600/Pt in dark (Run 2), indicating that Ic-600 and Ic-600/Pt have a visible-light induced reduction function and loading Pt increased the degree of charge separation and hence the reduction ability of Ic-600. According to the present results, it is likely that an electron transfer from ruthenium sulfide particles to carbon clusters through possibly the unsaturated chemical bond formed by the partial calcination of copolymer I took place to form an oxidation site at ruthenium sulfide particles and a reduction site at the Pt cores loaded on carbon clusters (Scheme 2). Either effective electron transfer or charge separation is presumed to be achieved by both sufficiently low band gap of ruthenium sulfide and stabilization with carbon clusters capable of accommodating transferred electrons.

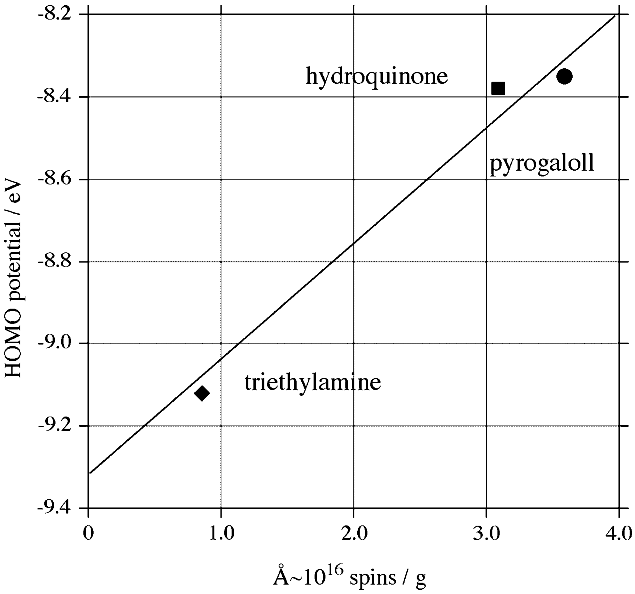


Fig. 6 Relationship between HOMO potentials of reductants and ESR spin concentration of Ic-600

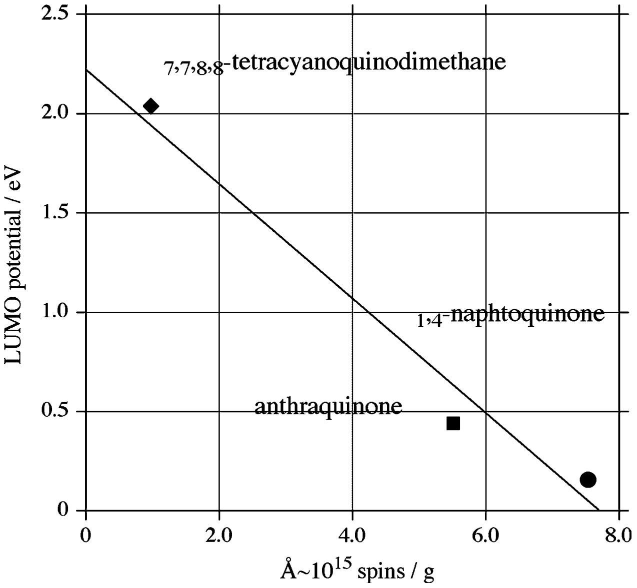


Fig. 7 Relationship between LUMO potentials of oxidants and ESR spin concentration of Ic-600

Conclusion

In conclusion, calcination of a ruthenium–S–phenylene hybrid copolymer under an argon atmosphere gave

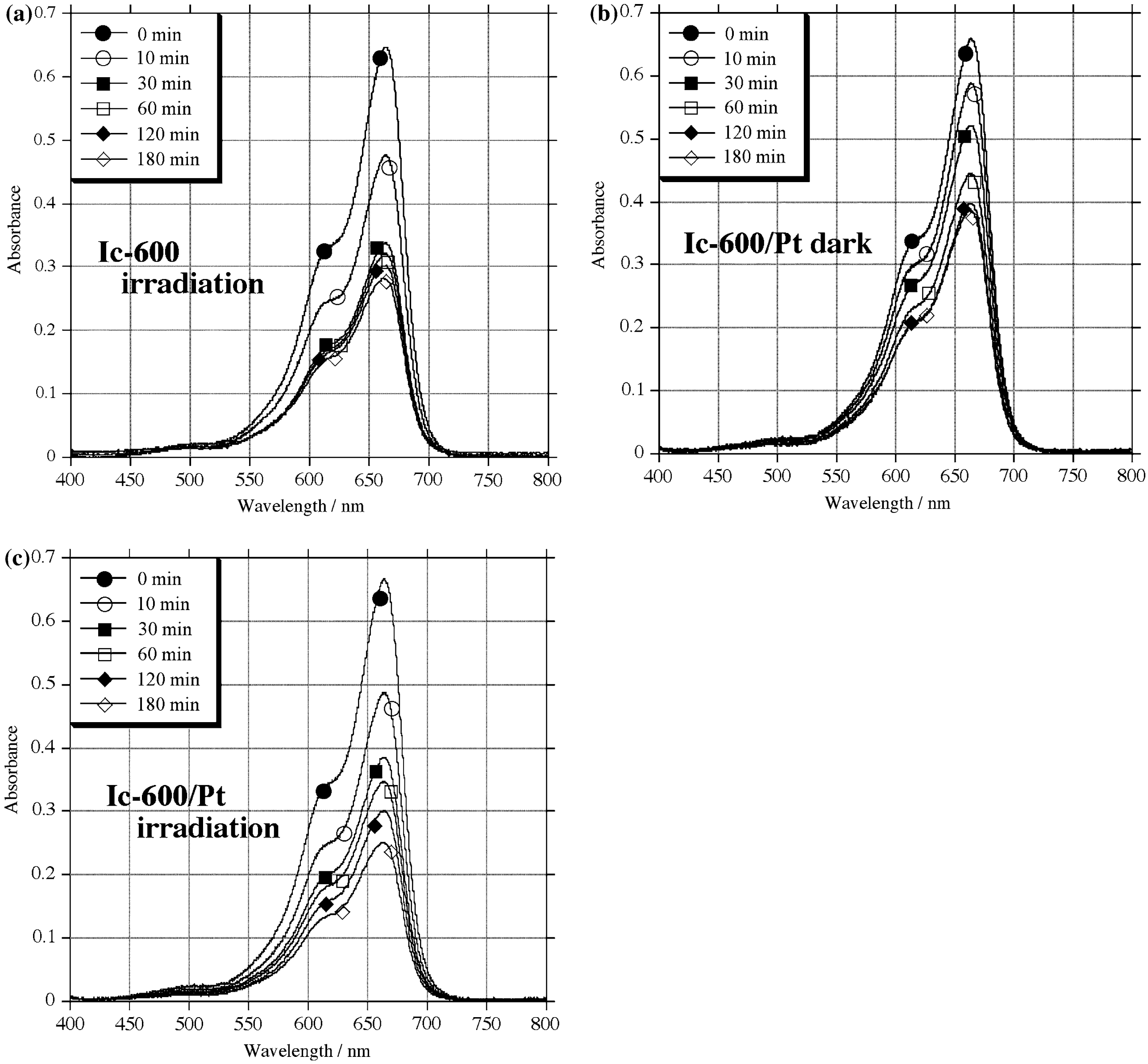


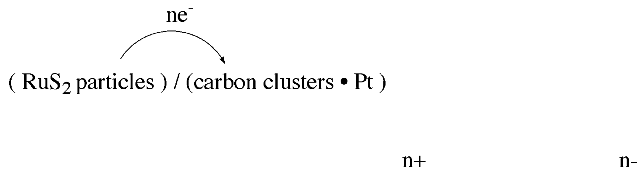
Fig. 8 (**a**) UV–VIS spectral change of methylene blue in the presence of Ic-600 under visible-light irradiation. (**b**) UV–VIS spectral change of methylene blue in the presence of Ic-600/Pt in dark. (**c**) UV–VIS spectral change of methylene blue in the presence of Ic-600/Pt under visible-light irradiation

nano-sized ruthenium sulfide/carbon cluster composite material, which showed a visible-light responsive oxidation–reduction function through an electron transfer from ruthenium sulfide particles to carbon clusters.

Table 2 Reduction ability indices (*rdi*) of the calcined materials

Run	Material	Condition	*Rdi*	
			(nmol/l/min)	Ratio
1	Ic-600	Under visible-light irradiation	6.9	1.3
2	Ic-600/Pt	In dark	5.4	1.0
3	Ic-600/Pt	Under visible-light irradiation	13.0	2.4

We believe that such an electron transport will be achieved by combinations of carbon clusters and various photosensitive semiconductors, and our findings will provide a valuable source for many useful materials



Scheme 2. Electron transfer process

including optical, magnetic, and/or electronic devices, oxidation and/or reduction catalysts, organic synthesis catalysts, artificial photosynthesis catalysts, and so on.

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