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The electronic behavior of calcined material obtained from a manganese-*O*-phenylene-*S*-rhenium-*S*-phenylene hybrid copolymer

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Abstract

The calcinations of a manganese-*O*-phenylene-*S*-rhenium-*S*-phenylene hybrid copolymer under an argon atmosphere at 600–900 °C were carried out. Calcined materials were found to be composed of MnS particles and metallic Re in a matrix of carbon clusters. ESR spectra reveal the calcined materials to have a photoresponsive oxidation–reduction function via the electron transfer process MnS → Re and/or carbon clusters. The surface of the calcined materials was modified with Pt particles and the reduction ability of the resulting materials was examined. It has been found that the material calcined at 800 °C loaded with Pt particles could decompose water under visible-light irradiation.

Keywords: MnS; Re; Carbon clusters; Electron transport

1. Introduction

Semiconductors such as TiO_2 [1–3] and modified inorganic oxides [4–7] with photoresponsive oxidation–reduction functions have been shown to split water to H_2 and O_2 under photoirradiation; however, their quantum yields were low and only limited wavelengths were used. The construction of an effective and stable charge-separation is considered to be one of the most important factors for obtaining a high oxidation–reduction function, and the absorption of visible light is also desired for the efficient utilization of sunlight. We have recently reported the synthesis of heavy metal–organic moiety hybrid copolymers [8–11], in which electron transfer from organic moieties to metal atoms takes place. We consider that the calcination of such copolymers under a reducing atmosphere will give new types of nano-sized inorganic semiconductor/carbon cluster composite materials, in which some bonding on the interface of semiconductors and carbon clusters could be formed and affect the features of the band gaps of semiconductors and/or electron movements. Further on carbon clusters are expected to enhance the light-absorption ability.

In this paper, we describe the compositions and electronic properties of calcined material obtained from a manganese-*O*-phenylene-*S*-rhenium-*S*-phenylene hybrid copolymer I (Scheme 1). The calcination of I is expected to provide the composite material of carbon clusters and inorganic compounds derived from Mn and Re, in which unique electronic feature will appear.

2. Experimental

2.1. Reagents

Commercially available manganese chloride, rhenium chloride, 1,4-hydroquinone, 4-mercaptophenol, 1,4-benzenedithiol, and 1,8-bis(dimethylamino)naphthalene (proton sponge) were used. Other reagents and solvents were purified by standard procedures.

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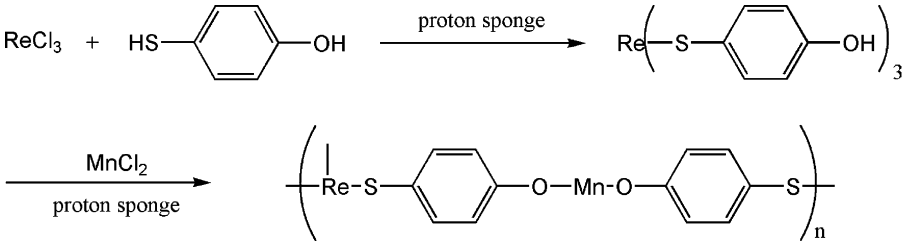
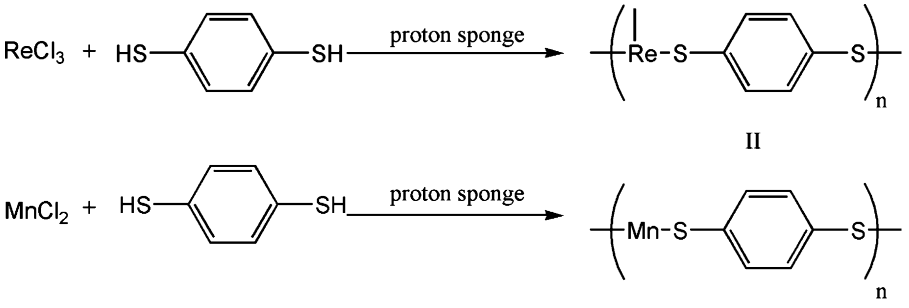


Scheme 1. Synthesis of hybrid copolymer I.



II

III

Scheme 2. Syntheses of hybrid copolymers II and III.

2.2. Syntheses of copolymers I, II and III (Schemes 1 and 2)

A solution of 1 mmol of rhenium chloride, 3 mmol of 4-mercaptophenol and 50 mmol of proton sponge in 60 mL of anhydrous ethanol was stirred at room temperature for 24 h. A solution of 1.5 mmol of manganese chloride in 10 mL of anhydrous ethanol was added into the above reaction mixture and then the resulting mixture was stirred at room temperature for 24 h. The obtained precipitate was washed with anhydrous ethanol using a Soxhlet extractor and dried with heating under vacuum to obtain copolymer I. Similar treatment of either rhenium chloride (1 mmol) with 1,4-benzenedithiol (3 mmol) or manganese chloride (1 mmol) with 1,4-benzenedithiol (2 mmol) in the presence of proton sponge (50 mmol) gave copolymer II or III.

2.3. Calcination of copolymers

One gram of copolymer in a porcelain crucible was heated under an argon atmosphere with a heating rate of 5 °C/min and kept for 1 h at a fixed temperature using Denken KDF 75 furnace.

2.4. Modification of calcined material with Pt particles

A mixture of 250 mg of the calcined material and 50 mL of aqueous 0.5 mmol hydrogen hexachloroplatinate hexahydrate solution in 10 mL of methanol was stirred under visible-light irradiation at room temperature for 30 min. The precipitates were washed with distilled water and dried with heating under vacuum.

2.5. Water decomposition

A mixture of the calcined material and degassed water was sealed in a 1-mL glass tube and irradiated with a 150-W halogen lamp at room temperature for a fixed time. Evolved gas was analyzed by using gas chromatography.

3. Apparatus

Elemental analyses were performed for C and N and for S with Yanaco MT-6, and Yanaco YS-10 analyzers, respectively, and for Re and Mn by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Shimadzu ICP-1000 apparatus. Transmission electron microscopy (TEM) images were taken by a Jeol/TEM-3010 microscope. X-ray diffraction (XRD) spectra were measured by a Rigaku Mini Flex. UV–vis spectra were taken with a Hitachi U-4000 spectrometer. Electron spin resonance (ESR) spectra were measured with a Jeol JES-TE 200 spectrometer. X-ray photospectrometry spectra (XPS) were measured with a Shimadzu ESCA-850 apparatus. Visible light was generated by a Hoya-Schott Megalight 100 halogen lump (150 W). H_2 and O_2 analyses were performed with a Shimadzu GC-8A gas chromatograph. Linear sweep voltammogram (LSV) was taken with a BAS 100 B/W unit, in which the calcined material was used as a working electrode.

4. Results and discussion

In order to find a procedure for synthesizing copolymer I, the reactivity of the starting metal chlorides with 1,4-hydroquinone and 1,4-benzenedithiol were examined. Manganese chloride was found to react with both 1,4-hydroquinone and 1,4-

Table 1
ICP and elemental analyses of copolymers and calcined materials

Run	Material	Found (%)					Molar ratio Mn/Re
		Mn	Re	C	H	S	
1	I	7.7	32.3	33.9	2.6	13.9	0.81
2	Ic-600	7.7	33.7	31.3	1.0	13.0	0.77
3	Ic-700	9.2	36.6	30.6	0.6	14.2	0.85
4	Ic-800	10.3	45.0	10.6	0.4	15.3	0.78
5	Ic-900	13.0	52.8	9.8	0.4	12.2	0.83
6	II	–	49.1	22.5	1.5	20.3	
7	IIc-800	–	49.9	13.1	1.0	8.9	
8	III	28.1	–	28.8	2.1	26.4	
9	IIIc-800	53.6	–	29.9	0.9	17.5	

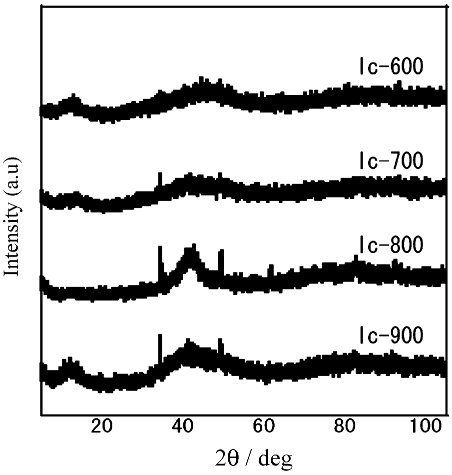


Fig. 1. X-ray diffraction of calcined materials.

benzenedithiol in the presence of proton sponge in anhydrous ethanol to give precipitates. On the other hand, rhenium chloride did not react with 1,4-hydroquinone in the presence of proton sponge but reacts with 1,4-benzenedithiol in the presence of proton sponge to give the precipitate. Therefore, copolymer I was synthesized by an initial reaction of rhenium chloride with 4-mercaptophenol in the presence of proton sponge followed by a second reaction with manganese chloride. ICP and elemental analyses of copolymer I (Table 1, Run 1) revealed the composition of Mn:Re:C_6H_4 = 0.81:1:2.71. Since the expected ratio is Mn:Re:C_6H_4 = 1.5:1:3, 54% manganese and 90% rhenium units were calculated to be introduced into the obtained copolymer.

Copolymer I was calcined with a heating rate of 5 °C/min under an argon atmosphere for 1 h at 600, 700, 800 and 900 °C to obtain black-colored materials Ic-600, Ic-700, Ic-800 and Ic-900, respectively. The results of ICP and elemental analyses of the calcined materials are shown in Table 1. Increase in calcination temperature decreased the hydrogen contents, suggesting that the carbonization of copolymer I proceeded. The Mn/Re molar ratios in the materials were found to be 0.77–0.85, suggesting that each metal compound was involved in the calcined materials. The XRD measurements (Fig. 1) reveal the presence of manganese sulfide due to the sharp peaks at $2\theta = 34.4^\circ$ and 49.4° in Ic-700, Ic-800 and Ic-900, and metallic rhenium due to a peak at $2\theta = 41.8^\circ$. TEM images of the calcined materials (Fig. 2) show that Ic-700 and Ic-800 have ultrafine particles with few nanometer diameters, and that particles aggregation for Ic-900. These findings suggest the calcined materials Ic-700 and Ic-800 to have nano-sized manganese sulfide and metallic rhenium which are uniformly distributed in the matrix of carbon clusters.

In order to examine the electronic properties of the calcined materials, the ESR spectra were taken (Fig. 3). A broad peak at 337 mT ($g = 2.003$) was observed due to Mn^{2+} of MnS [12], and the peak intensities of the calcined materials varied by the calcination temperature. Variation in the peak intensity may be due to the changes in the valence number of manganese atom. XPS spectra were thus performed to examine the electronic state of the manganese atom. As shown in Fig. 4, a peak of $2p_{3/2}$ of manganese atom in Ic-700 and Ic-800 appeared at 640.5 and 641.1 eV, respectively, indicating that the electron density of the manganese atom in Ic-800 was lower than that of in Ic-700. Such a decrease may occur by the partial oxidation of the manganese atom possibly through electron transfer from the manganese atom to the metallic rhenium and/or carbon clusters.

In order to investigate further, the electron transfer process in calcined materials Ics, rhenium-*S*-phenylene hybrid copolymer II and manganese-*S*-phenylene hybrid copolymer III [13] (Scheme 2) were calcined at 800 °C under an argon atmosphere to obtain black-colored materials of IIc-800 and IIIc-800,

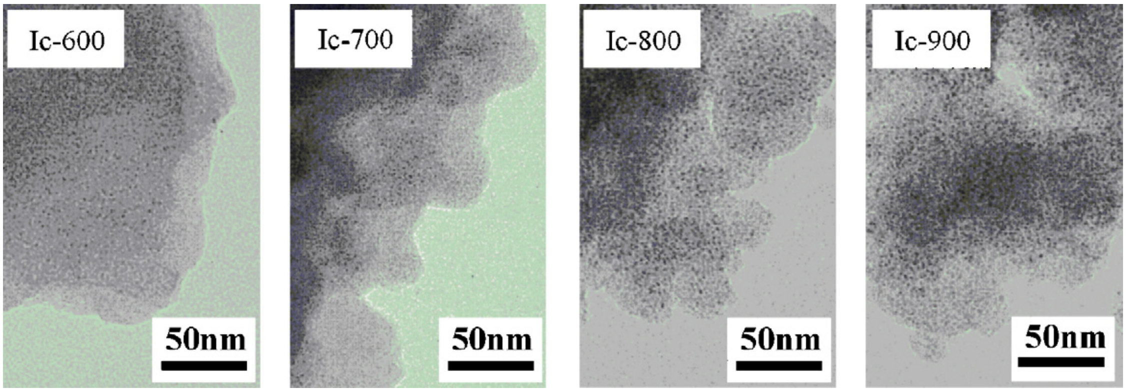


Fig. 2. TEM images of calcined materials.

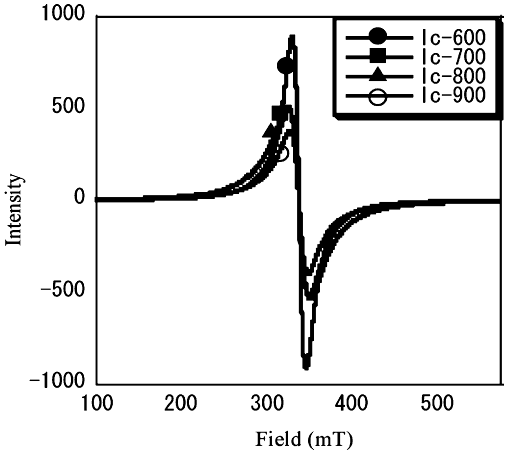


Fig. 3. ESR spectra of calcined materials.

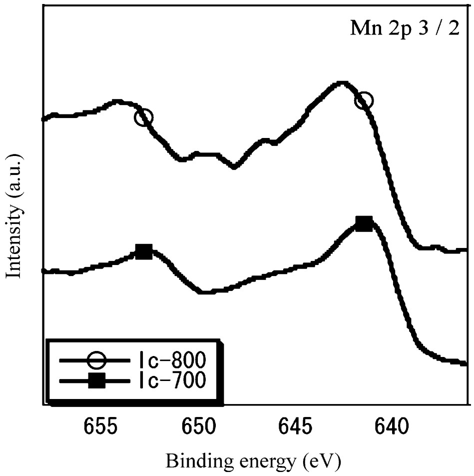


Fig. 4. XPS spectra of calcined materials Ic-700 and Ic-800.

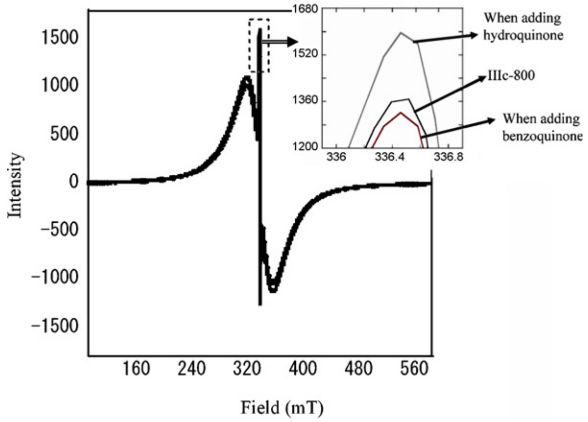


Fig. 6. ESR spectra of IIIc-800 in the presence of oxidant (benzoquinone) and reductant (hydroquinone).

respectively [14] (Table 1). The ESR spectra showed no ESR signal for IIc-800, whereas, in IIIc-800, a broad peak due to Mn^{2+} and also a small sharp peak at 337 mT ($g = 2.003$) were observed (Fig. 5). Our opinion is that the sharp peak is due to the generation of a free electron on carbon clusters. Intensity of the sharp peak in IIIc-800 was found to decrease with the addition of an oxidant (benzoquinone) but it increases with the addition of a reductant (hydroquinone) (Fig. 6), suggesting that the radical species is anionic. These findings suggest that in Ic-800, the occurrence of electron transfer from manganese sulfide particles to metallic rhenium and/or carbon clusters provides an oxidation–reduction ability with the oxidation site at manganese sulfide particles and the reduction site at the metallic rhenium and/or carbon clusters. Oxidation–reduction of Ic-800 was also investigated. First we have examined the UV–vis spectral change of methylene blue (MB, 4 mL of an 0.015 mmol/L aqueous solution) in the presence of Ic-800 (100 mg) either in the dark (Fig. 7) or under visible-light irradiation (Fig. 8). Fig. 9 shows that the absorbance of MB decreases more quickly under visible-light irradiation than in the dark, indicating the higher degree of reduction ability of Ic-800. Next, the oxidation of Ic-800 was also examined. As shown in Fig. 10, the intensity of the ESR peak due to Mn^{2+} was found to increase with the addition of reductants (pyrogarole, hydroquinone, and triethylamine) under visible-light irradiation, suggesting that Mn^{3+} was partially involved in the reduction of MnS core by the reductants and thus

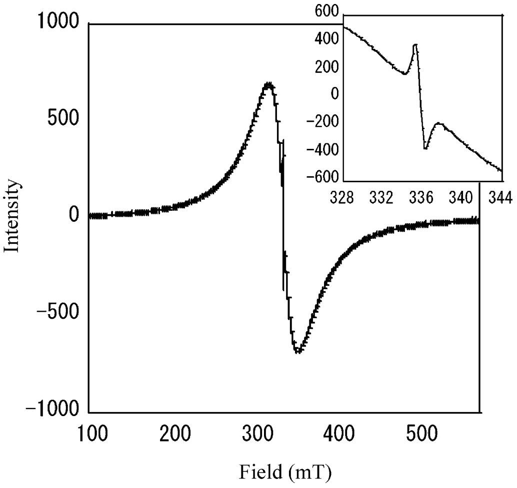


Fig. 5. ESR spectrum of calcined material IIIc-800.

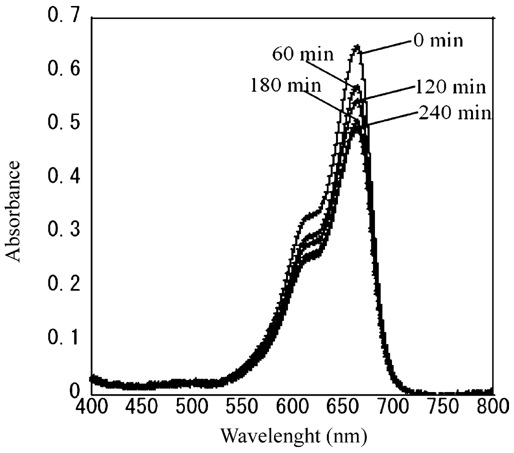


Fig. 7. Change in absorption spectrum of methylene blue in the presence of Ic-800 in the dark.

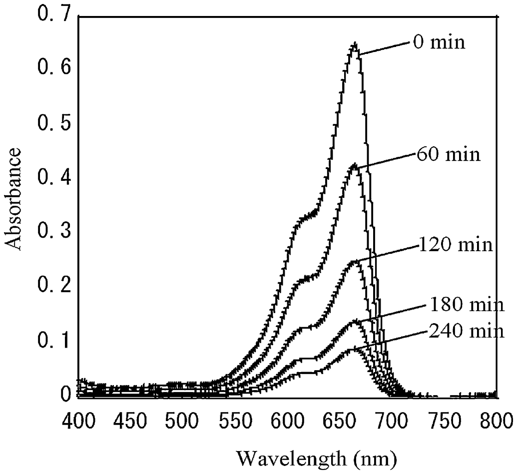


Fig. 8. Change in absorption spectrum of methylene blue in the presence of Ic-800 under visible-light irradiation.

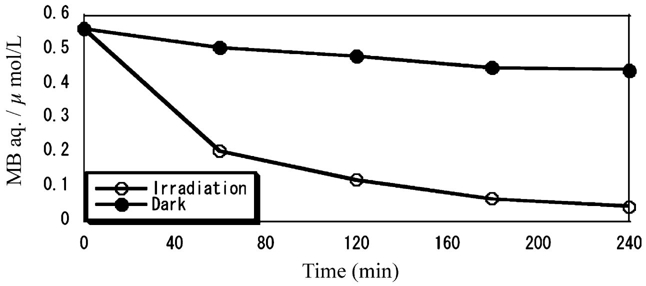


Fig. 9. Decrease in methylene blue concentration in the presence of Ic-800 in the dark and under visible-light irradiation.

the MnS part may act as an oxidation site. A linear relationship was obtained between the redox potentials of the reductants and the ESR spin quantities of Ic-800 (Fig. 11). From the intercept of the linear plot, the oxidation potential of Ic-800 was estimated to be +0.82 V, which is slightly higher than that of water (+0.80 V). These findings suggest that Ic-800 has an oxidation–reduction function and may decompose water under visible-light irradiation. However, neither H_2 nor O_2 were detected by the irradiation of a stirred mixture of water (0.3 mL) and Ic-800 (50 mg) with a 150-W halogen lamp at room temperature for 3 days.

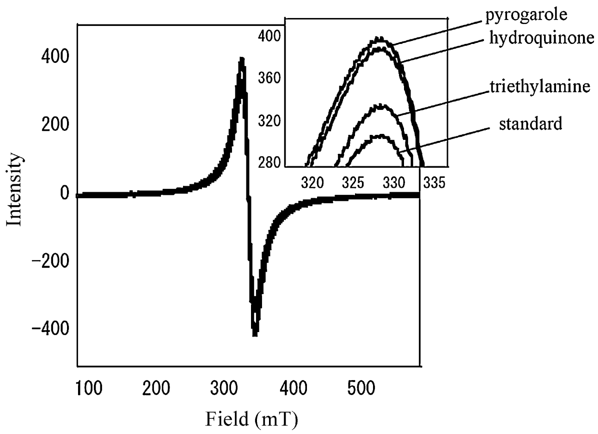


Fig. 10. ESR spectra of Ic-800 in the presence of reductants.

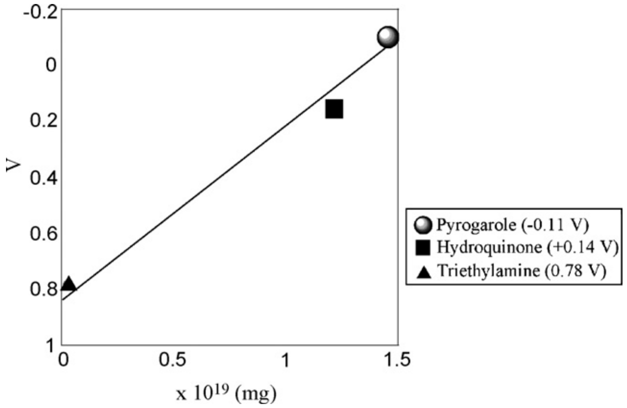


Fig. 11. Relationship between redox potentials of reductants and increased areas of ESR spectra.

It is known that the loading of Pt on semiconductors increases the reduction ability. The surface of Ic-800 was thus modified with Pt particles by reaction with a methanolic solution of hydrogen hexachloroplatinate under visible-light irradiation to obtain Pt-loaded Ic-800 (Ic-800-Pt). TEM image of Ic-800-Pt reveals the presence of highly dispersed Pt particles ca. 5 nm diameter on the surface of Ic-800 (Fig. 12). XPS spectra of Ic-800-Pt (Fig. 13) show a peak of $4f_{7/2}$ of Pt at 70.9 eV. It is noteworthy that a peak signal of $4f_{7/2}$ of Re in Ic-800-Pt was observed at 41 eV which was higher than that of in Ic-800 (40 eV), indicating the decrease of electron density of Re in Ic-800 due to the loaded Pt, possibly by electron transfer from Re to Pt. LSV examinations of Ic-800 and Ic-800-Pt in 0.5 M H_2SO_4 solution under visible-light irradiation were performed (Fig. 14 and Table 2). The Pt loading was found to shift the value of H_2 generation potential to a positive side,

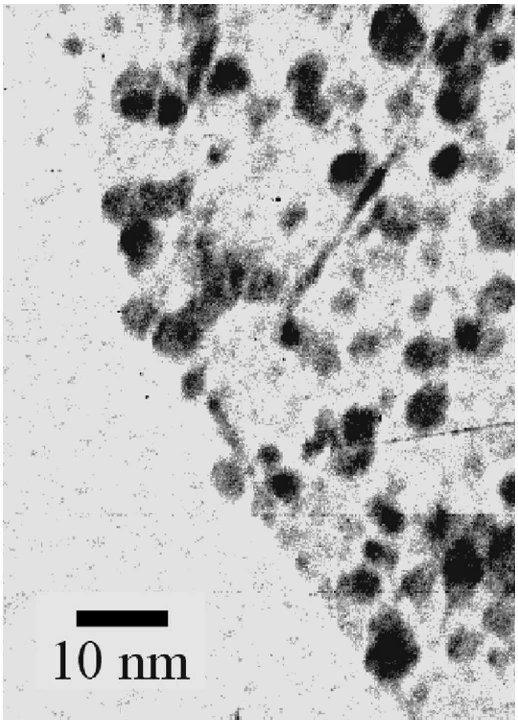


Fig. 12. TEM image of Ic-800-Pt.

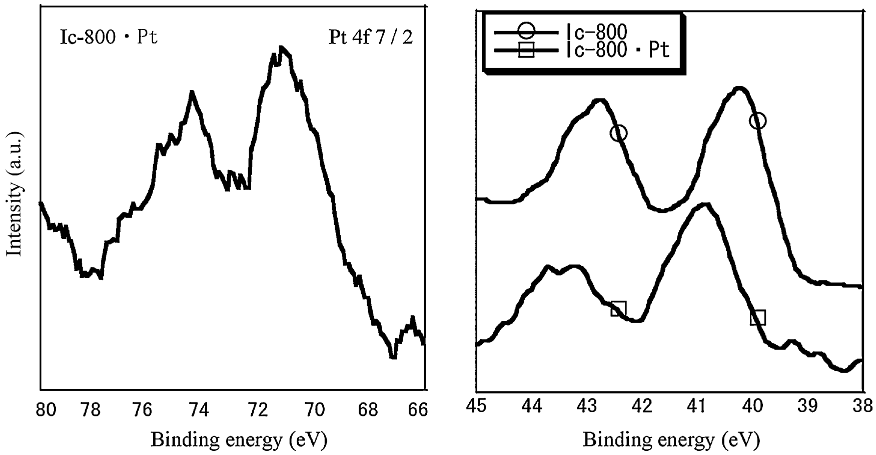


Fig. 13. XPS spectra of Ic-800 and Ic-800-Pt.

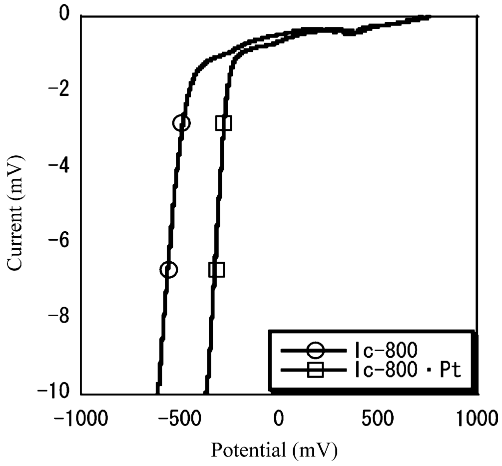


Fig. 14. Linear sweep voltammogram of Ic-800 and Ic-800-Pt.

Table 2
H_2 generation potentials of Ic-800 and Ic-800-Pt

Electrode	H_2 generation potential (mV)
Ic-800	−425
Ic-800-Pt	−215

indicating that Pt acts as an effective reduction site. Water-decomposition experiment has also been carried out by irradiating the mixture of water (1 mL) and Ic-800-Pt (50 mg) with a 150-W halogen lamp at room temperature for 24 h to obtain H_2 of 9.2×10^{-2} μmol. H_2 evolution is considered to take place as follows: MnS particles first absorb the light to excite an electron, which passes through the carbon clusters to reach the metallic Re core and/or carbon clusters, from which the electron arrive at the Pt core, thus allowing water decomposition to take place. Ic-800-Pt is thus found to yield H_2 from water under visible-light irradiation. However, it is noted that no evolution of O_2 was observed. A possible explanation for non-generation of O_2 is that an activated oxygen species formed at the oxidation site could react with the MnS particles, although no evidence was obtained yet to support this assumption.

5. Conclusions

Calcinations of manganese-*O*-phenylene-*S*-rhenium-*S*-phenylene hybrid copolymer under an argon atmosphere gave nano-sized MnS particles and metallic Re in a matrix of carbon clusters. ESR spectra reveal the calcined materials to have a photoresponsive oxidation–reduction function via the electron transfer process MnS → Re and/or carbon clusters. Similar functions will be obtained by the combination of carbon clusters and various semiconductors.

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[13] II: Re 49.1%, C 22.5%, H 1.5%, S 20.3%.;
III: Mn 28.1%, C 28.8%, H 2.1%, S 26.4%.
[14] IIc-800: Re 49.9%, C 13.1%, H 1.0%, S 8.9%.;
IIIc-800: Mn 53.6%, C 29.9%, H 0.9%, S 17.45%.