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Electronic properties of calcined materials from a scandium-O-phenylene-O-yttrium-O-phenylene hybrid copolymer

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Abstract Calcination of a scandium-O-phenylene-O-yttrium-O-phenylene hybrid copolymer under an argon atmosphere at 400–800 °C was performed. The calcined materials were found to be composed of nano-sized Sc_2O_3 and Y_2O_3 particles in the matrix of carbon clusters. ESR spectral examinations of the calcined materials suggest that a two-step electron transfer of $Y_2O_3 \rightarrow$ carbon clusters $\rightarrow Sc_2O_3 \rightarrow$ carbon clusters took place to provide a photo-responsive oxidation–reduction function with an oxidation site at Y_2O_3 particles and a reduction site at carbon clusters.

Introduction

Construction of a stable charge-separated electron excitation under visible light irradiation is required to achieve an artificial photosynthesis function, and semiconductors such as TiO_2 and other metal oxides [1–10] have been expected to provide such a function. Effective oxidation–reduction function will be achieved by increasing the stability of charge-separation state without recombination of holes and excited electrons. In this context, we have recently reported the syntheses of metal–organic hybrid copolymers, in which an electron transfer from the organic moieties to the metal atoms took place [11–15]. We have assumed that the calcination of the hybrid copolymers will provide new types of nano-sized metal compound–carbon cluster composite materials, in which some bondings on interfaces of metal compounds and carbon clusters will be formed to affect the features of band gaps and/or electron transfer, and further, carbon clusters will enhance the light absorption ability.

In the present work, we describe the composition and electronic properties of calcined materials from a scandium-O-phenylene-O-yttrium-O-phenylene hybrid copolymer **I** (Scheme 1).

Synthesis of copolymer **I** was reported in a previous work [16], in which an electron transfer in the process of phenylene group → Y → Sc was shown to take place. Calcination of copolymer **I** is expected to provide the material composed of Sc_2O_3 and Y_2O_3 particles in the matrix of carbon clusters.

Experimental

Reagents

Commercially available scandium isopropoxide and yttrium isopropoxide were used. Other reagents and solvents were purified by standard procedures.

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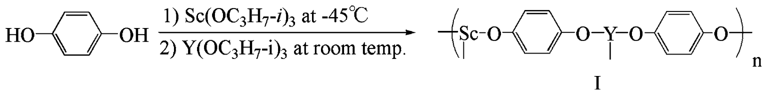
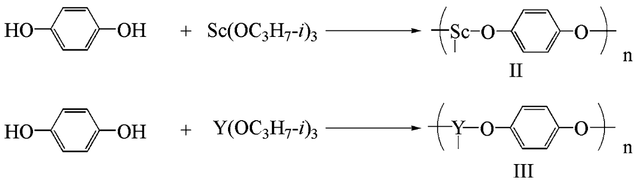


Scheme 1 Synthesis of copolymer **I**



Scheme 2 Syntheses of copolymers **II** and **III**

Syntheses of copolymers

Procedures of the copolymer syntheses were previously reported in detail [16]. Copolymer **I** was synthesized by the first reaction of 1,4-hydroquinone (12 mmol) with scandium isopropoxide (4 mmol) at –45 °C followed by the second reaction with yttrium isopropoxide (4 mmol) at room temperature. Copolymers **II** and **III** (Scheme 2) were synthesized by the reaction of 1,4-hydroquinone (6 mmol) with scandium isopropoxide (4 mmol) or yttrium isopropoxide (4 mmol), respectively, at room temperature.

Calcination of copolymers

0.3 g of copolymer **I** was heated in a porcelain crucible under an argon atmosphere with a heating rate of 5 °C/min and kept for 1 h at 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C using an electric furnace, Denken KDF-75, to give calcined materials **Ic-400**, **Ic-500**, **Ic-600**, **Ic-700**, and **Ic-800**, respectively. For the sake of comparison, copolymers **II** and **III** were processed similarly at 600 °C to give **IIc-600** and **IIIc-600**, respectively.

Apparatus

TG–DTA analysis of copolymer **I** was performed using Rigaku TG–DTA–MS 8010. Elemental analyses were performed for C and H using Yanaco MT-6, and for Sc and Y by inductively coupled plasma atomic emission spectrometry (ICP–AES) using Shimadzu ICP-7500. X-ray diffraction (XRD) spectra were taken using Rigaku Mini Flex. Transmission electron microscopy (TEM) observations were done using Jeol JEM-3010 microscope. CP/MAS ^{13}C-NMR spectra were taken using Bruker Avance–DSX 400. Electron spin resonance (ESR) spectra were measured using Jeol JES–TE 200. Visible light was generated using Hoya–Schott Megalight 100 halogen lamp.

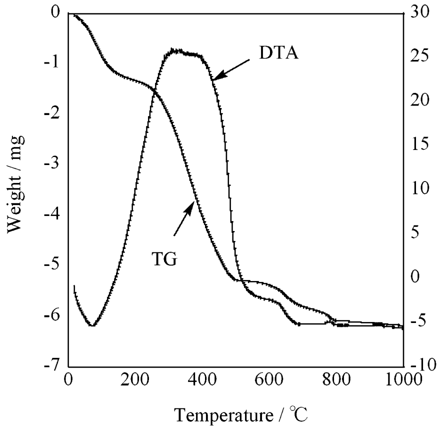


Fig. 1 TG–DTA analysis of the copolymer **I**

Results and discussion

Characterization of the prepared materials

The TG–DTA measurement of copolymer **I** with a heating rate of 5 °C/min under a nitrogen atmosphere (Fig. 1) showed an endothermic reaction below about 150 °C due to evaporation of volatile components and an exothermic reaction at 150–500 °C probably due to the carbonization of copolymer **I**. Copolymer **I** was thus calcined with a heating rate of 5 °C /min under an argon atmosphere for 1 h at 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C, to obtain black-colored materials **Ic-400**, **Ic-500**, **Ic-600**, **Ic-700**, and **Ic-800**, respectively. Results of ICP and

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

Material	Found (wt%)				Molar ratio Sc: Y
	Sc	Y	C	H	
I	7.80	13.24	33.26	3.47	1.17:1
Ic-400	8.81	14.90	36.30	2.74	1.17:1
Ic-500	9.43	16.00	36.72	2.27	1.17:1
Ic-600	9.06	15.40	36.43	1.51	1.16:1
Ic-700	12.53	22.03	36.69	1.35	1.12:1
Ic-800	12.64	22.14	35.35	0.99	1.13:1

elemental analyses of the materials were shown in Table 1. Increase in calcination temperature was found to decrease hydrogen contents, suggesting that carbonization of copolymer **I** proceeded. It is noted that Sc:Y molar ratios in the materials were 1.12–1.17:1, which were close to the expected ratio of 1:1, indicating that each metal component was involved in the materials.

The XRD spectral measurement (Fig. 2) revealed that the calcined materials had broad peaks at 2θ = ca. 32° and 53°. Individual metal hybrid copolymers, i.e. scandium-O-phenylene copolymer **II** and yttrium-O-phenylene copolymer **III** (Scheme 2), were calcined at 600 °C under an argon atmosphere to obtain black-colored materials **IIc-600** and **IIIc-600** and their XRD spectral examinations showed the presences of Sc_2O_3 at 2θ = ca. 32° and 52° and of Y_2O_3 at 2θ = ca. 30° and 51°, respectively (Fig. 3). Therefore, the observed peaks for **Ic-600** are considered to be an overlapped signal of Sc_2O_3 and Y_2O_3. TEM observations of the calcined materials (Fig. 4) showed that the materials had highly dense particles with diameters of a few nm

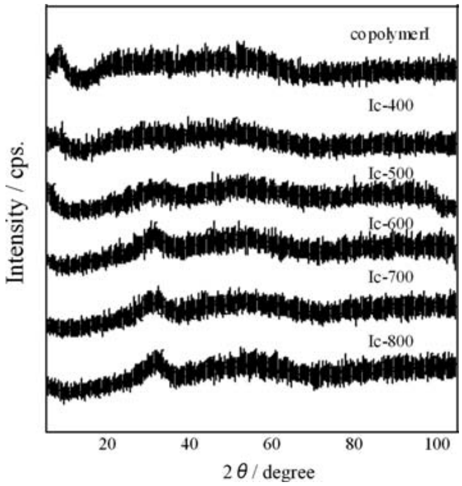


Fig. 2 XRD spectra of copolymer **I** and calcined materials **Ic**'s

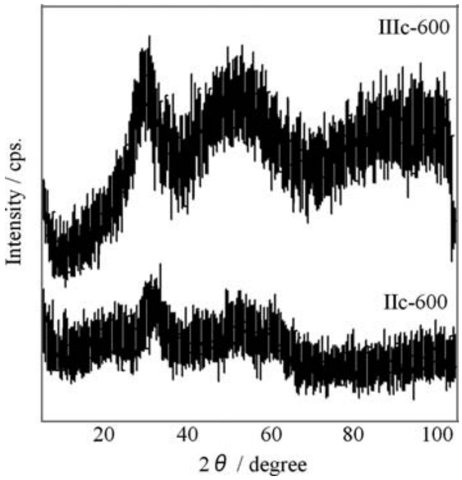
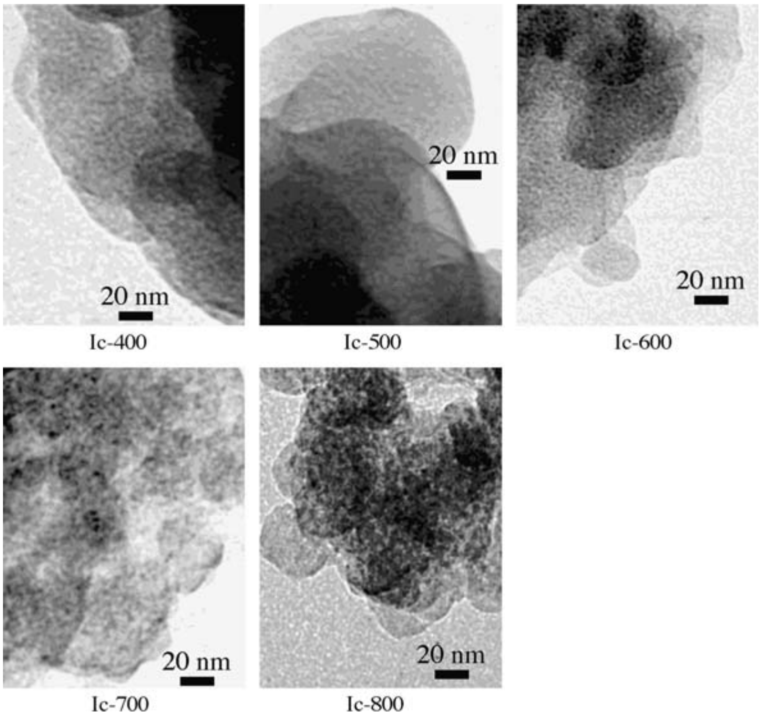


Fig. 3 XRD spectra of copolymers **IIc-600** and **IIIc-600**



Ic-400 Ic-500 Ic-600

Ic-700 Ic-800

Fig. 4 TEM images of calcined materials **Ic**'s

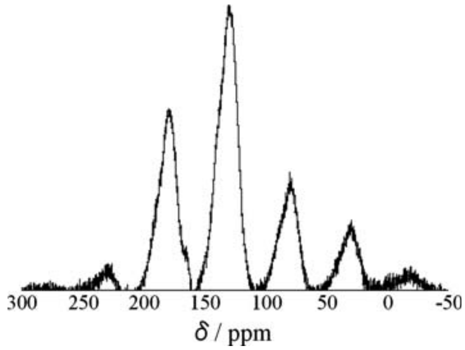


Fig. 5 CP/MAS ^{13}C-NMR spectra of **Ic-600**

in the matrix of carbon clusters, and that increase in calcination temperature caused the aggregation of the particles. The CP/MAS ^{13}C-NMR spectral analysis of **Ic-600** (Fig. 5) showed a signal due to carbon at 129 ppm which was higher than that of 1,4-hydroquinone (115 ppm), suggesting the formation of unsaturated carbon cluster in **Ic-600**. These results suggest that the calcined materials were composed of Sc_2O_3, Y_2O_3, and carbon clusters.

Electronic nature

In order to examine the electronic properties of the calcined materials, their ESR spectra were measured (Fig. 6). Copolymer **I** or the calcined materials all showed a signal at 337 mT ($g = 2.003$) which is considered to be a free electron formed on the phenylene group for copolymer **I** and on carbon clusters for the calcined materials, and the intensities for calcined materials **Ic-400**, **Ic-500**, and **Ic-600** were higher than that of copolymer **I**, suggesting that the calcination treatment had enhanced the degree of the electron transfer, i.e., charge separation. The ESR signal intensity of **Ic-600** slightly decreased in response to visible light irradiation, but recovered towards the initial intensity when kept in dark after the irradiation had stopped (Fig. 7). This indicates that **Ic-600** has a photo-response characteristic, although the effect is weak. Wide band gaps of Sc_2O_3 and Y_2O_3 (5.88 eV and

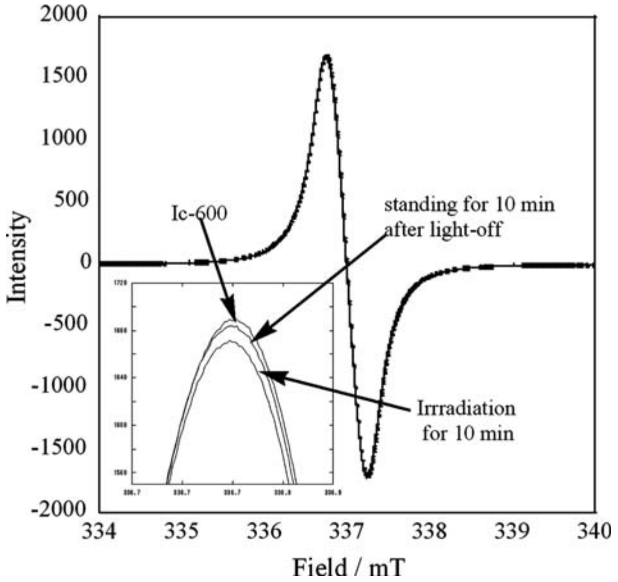


Fig. 7 ESR spectrum changes of **Ic-600** under visible light irradiation

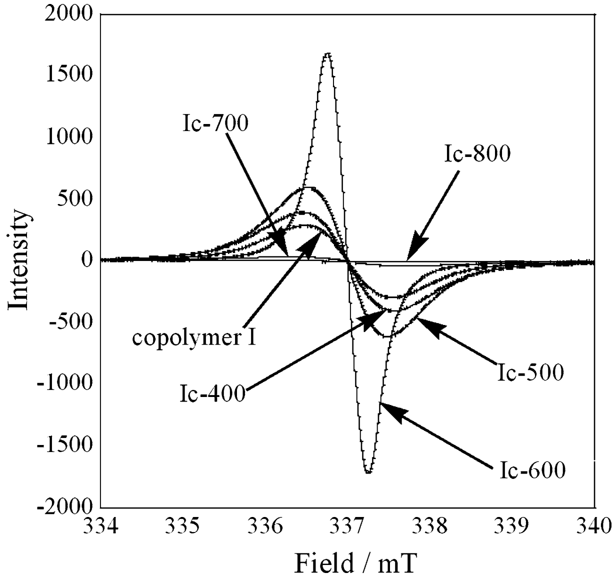


Fig. 6 ESR spectra of copolymer **I** and calcined materials **Ic**'s

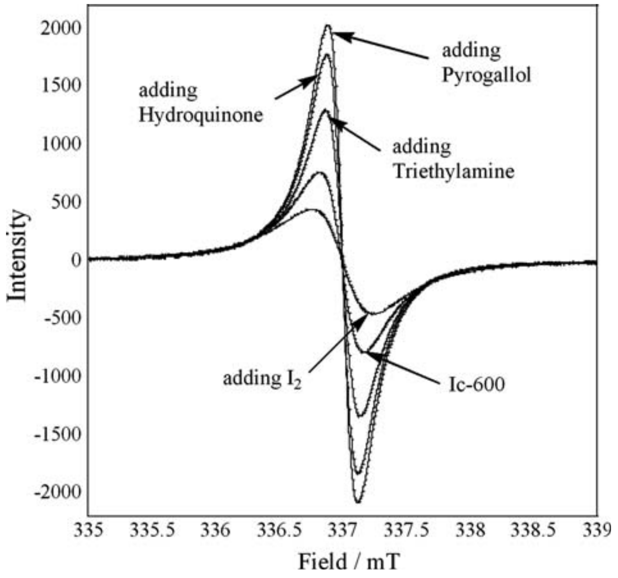


Fig. 8 ESR spectrum changes of **Ic-60**0 in the presence of oxidant or reductant

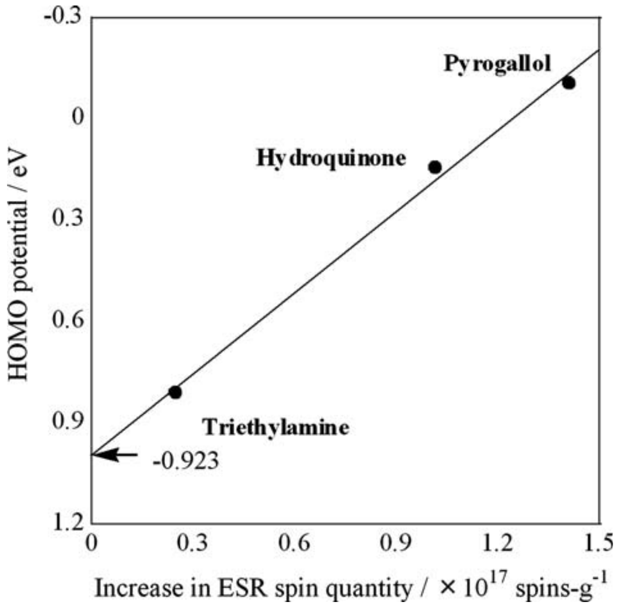


Fig. 9 Relationship between HOMO potentials of reductants and ESR spin quantities

5.65 eV, respectively, for bulk materials) might be responsible for the weak photo-response.

It was found that the ESR signal intensity of **Ic-600** decreased with the addition of an oxidant (I_2) but increased with the addition of reductants (pyrogallol, hydroquinone, and triethylamine) (Fig. 8), indicating that the radical species is anionic. By the extrapolation of linear correlation between the HOMO potentials of the reductants and the increase in ESR radical spin quantity (*rsq*) of **Ic-600** by a double integrating calculation of the differential absorption line with the use of DPPH, the critical oxidation potential of **Ic-600** was estimated to be –0.923 eV (Fig. 9).

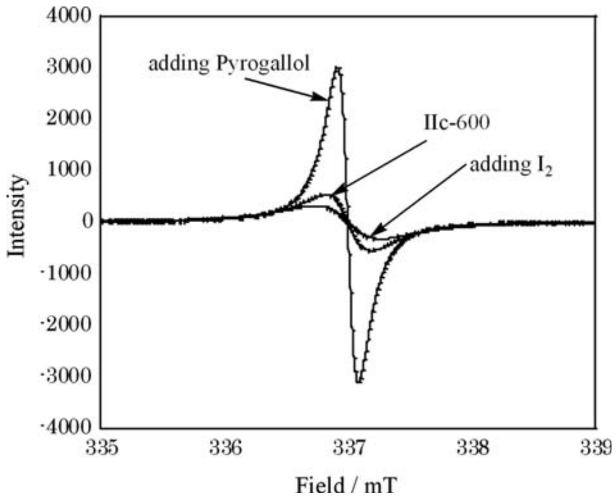


Fig. 10 ESR spectrum changes of **IIc-600** in the presence of oxidant or reductant

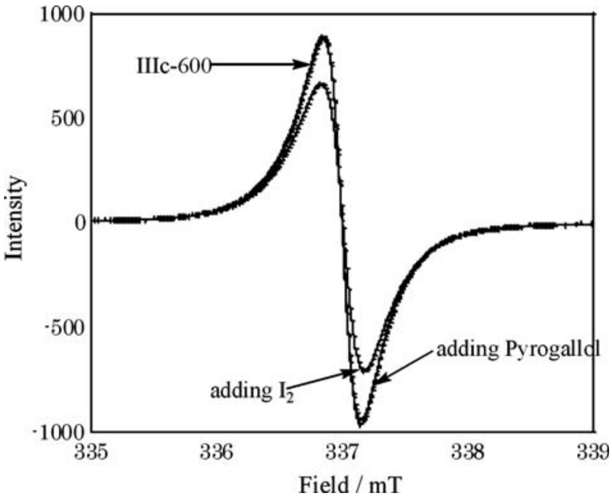


Fig. 11 ESR spectrum changes of **IIIc-600** in the presence of oxidant or reductant

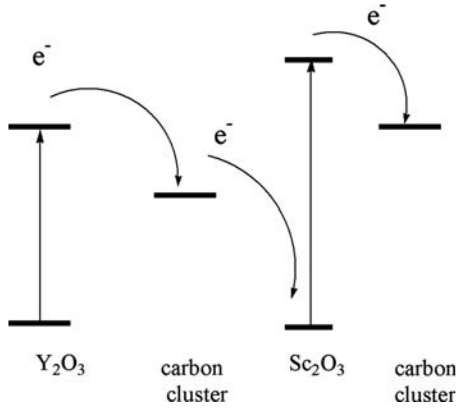
In order to investigate the electron transfer process in **Ic-600**, the ESR spectral examinations of **IIc-600** and **IIIc-600** in the presence of a reductant (pyrogallol) or an oxidant (I_2) were performed (Figs. 10, 11). Table 2 summarizes the *rsq* values of **Ic-600**, **IIc-600** and **IIIc-600**. The *rsq* values were found to decrease with the addition of an oxidant and increase with the addition of a reductant, indicating that electron transfers from metal oxides, Sc_2O_3 and Y_2O_3, to carbon clusters took place. Table 3 shows the results of XPS analyses of metal oxides and **Ic-600**. The value of $2p_{3/2}$ of Sc in **Ic-600** was lower than that in Sc_2O_3, indicating that the electron density of Sc atom in **Ic-600** was higher than

Table 2 Radical spin quantities (*rsq*) of calcined materials **Ic-600**, **IIc-600** and **IIIc-600** in the presense of reductant (pyrogallol) and oxidant (I_2)

Additive	Ic-600 (*rsq* additive/*rsq* none)	IIc-600 (*rsq* additive/*rsq* none)	IIIc-600 (*rsq* additive/*rsq* none)
None	2.47×10^{20}	2.00×10^{20}	1.88×10^{20}
Pyrogallol	3.40×10^{20}(1.38)	3.20×10^{20}(1.60)	1.91×10^{20}(1.02)
I_2	2.22×10^{20}(0.90)	1.88×10^{20}(0.94)	1.69×10^{20}(0.90)

Table 3 XPS analyses of metal oxides and calcined material **Ic-600**

Material	Sc($2p_{3/2}$)	Y($3d_{5/2}$)
Sc_2O_3	401.9	–
Y_2O_3	–	156.8
Ic-600	401.6	157.5



Scheme 3 Plausible electron transfer process

that in Sc_2O_3. On the other hand, the value of $3d_{5/2}$ of Y in **Ic-600** was higher than that in Y_2O_3, indicating that the electron density was lower than that in Y_2O_3.

Summary

As a conclusion, all these results suggest that a plausible electron transfer process in **Ic-600** is electron transfers of Y_2O_3 → carbon clusters → Sc_2O_3 → carbon clusters (Scheme 3), and **Ic-600** is deduced to have a photo-responsive oxidation–reduction function with a major oxidation site at Y_2O_3 and a reduction site at carbon clusters.

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