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# Electronic behavior of calcined material obtained from 2,2-diphenylphosphino-1,1-binaphthyldichloro palladium

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## 1. Introduction

Construction of a charge-separated electron transfer with photo-responsive function is important for obtaining novel photocatalysts and many works on semiconductors have been reported [1–7]. However, an electron transport under whole visible light irradiation does not seem to have been established yet. We assumed that such a transport will be obtained by combining semiconductors and carbon clusters, since carbon clusters are considered to act as a visible-light absorption and electron transport sites, and semiconductors to act as an electron excitation site. We have recently reported that the calcination of metal-organic moiety hybrid copolymers under a reducing atmosphere gave nano-sized inorganic metal compound/carbon clusters composite materials and an electron transfer between the metal compounds and the carbon clusters took place to exhibit a visible light-responsive oxidation-reduction function [8-13]. Here, we consider that such composite materials will be obtained

ABSTRACT

The calcinations of 2,2-diphenylphosphino-1,1-binaphthyldichloro palladium under an argon atmosphere gave nano-sized Pd<sub>5</sub>P<sub>2</sub>/carbon cluster composite material. The ESR spectral examination of the material, and the reaction of either methylene blue or 2,3,5-trimethylhydroquinone in the presence of the material revealed that the calcined material has a visible light-responsive oxidation-reduction function through an electron transfer from the carbon clusters to the Pd<sub>5</sub>P<sub>2</sub> particles.

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by the calcination of common organometallic compounds. In the present work, we describe the composition and electronic behavior of material obtained by the calcination of 2,2-diphenylphosphino-1,1-binaphthyldichloro palladium I (Scheme 1).

# 2. Experimental

Commercially available chemicals, 2,2-diphenylphosphino-1,1binaphthyl (BINAP), bis (acetonitrile) dichloropalladium, anhydrous dichloromethane, anhydrous cyclohexane, anthraquinone, pyrogallol, methylene blue, and 2,3,5-trimethylhydroquinone were used.

A solution of 0.623 g (1 mmol) of BINAP in 10 ml of anhydrous dichloromethane was added into a solution of 0.229 g (1 m mol) of bis(acetonitrile)dichloropalladium in 10 ml of anhydrous dichloromethane, and the mixture was stirred at room temperature for 24 h to obtain precipitates. The obtained precipitates were recrystallized from cyclohexane by vapor diffusion method to obtain orange-colored compound I (90%).

0.1 g of compound I in a porcelain crucible was heated 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 300,



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

$$(Pd_5P_2) / (carbon clusters) \longrightarrow (Pd_5P_2)^{n(-)} / (carbon clusters)^{n(+)}$$

Scheme 2. Plausible electron transfer process.

Table 1
Elemental analyses of compound I and calcined materials

Materials	Found (%)					Color
	Cb	Н	Pd	Р	Cl	
I <sup>a</sup>	65.83	4.17	12.99	8.06	8.36	Orange
Ic-300	59.18	3.52	15.10	7.68	0	Dark green
Ic-400	53.44	3.14	17.46	8.69	0	Black
Ic-500	55.10	2.81	17.84	9.79	0	Black
Ic-600	45.52	1.77	20.73	7.36	0	Black
Ic-700	48.77	1.44	8.53	4.88	0	Black

<sup>a</sup> Calcd (%): C 66.06, H 4.03, Pd 13.30, P 7.74, Cl 8.86.

 $^{\rm b}$  C value is within the range of +/-0.3% from the given value while repeating the experiment.

400, 500, 600 and 700  $^{\circ}$ C to obtain calcined materials Ic-300, Ic-400, Ic-500, Ic-600, and Ic-700, respectively.

The reduction and oxidation abilities of Ic-600 were examined in the following way: A mixture of 50 mg of Ic-600 and 20 mL of 10  $\mu$ M methylene blue aqueous solution or 10  $\mu$ M 2,3,5-trimethylhydroquinone acetonitrile solution was kept in the dark overnight. The mixture was irradiated by visible light for fixed time and then the absorbance of methylene blue or 2,3,5trimethylhydroquinone was determined by UV-VIS spectrometry.

Elemental analysis was performed for C and H using Yanaco MT-6, for Cl using Yanaco YS-10, and for P and Pd using Shimadzu ICP-7500. FT/IR spectra were measured using Nihon Bunko FT/IR-470. <sup>31</sup>P-NMR spectra were taken using Jeol ECA500. X-ray diffraction (XRD) spectra were obtained using Rigaku Mini Flex. Transmission electron microscopy (TEM) observations were carried out using Jeol JEM-3010 spectrometer. UV-VIS spectra were measured using Hitachi U-4000 spectrometer. Electron spin resonance (ESR) spectra were taken using Jeol JES-TE200 spectrometer. Visible light was generated using Hoya–Schott Megalight 100 halogen lamp.

## 3. Results and discussion

Compound I was synthesized according to the procedure reported by Sannicola [14] and the results of elemental analyses of I are shown in Table 1. The observed values were nearly equal to the calculated values. FT/IR spectra of I showed frequencies at 1567 and 1512 cm<sup>-1</sup> due to the naphthyl and phenyl groups and at 1447 cm<sup>-1</sup> due to the P–C bond. The <sup>31</sup>P-NMR spectra of I showed a peak at 28.6 ppm due to the P atom. These results suggest the formation of compound I.

The results of the elemental analyses of the calcined materials are summarized in Table 1. The total amounts of the observed



Fig. 1. XRD patterns of calcined materials.

contents for the calcined materials were below 100%. A reason is incomplete elemental analyses, since insoluble residues in acidic solutions were yielded at the ICP analyses of the materials and partly black-colored residues after the elemental analyses operations were observed. Fig. 1 is the XRD patterns of the calcined materials and peaks at  $2\Theta = 33^{\circ}$ ,  $39^{\circ}$  and  $43^{\circ}$  due to  $Pd_5P_2$  were observed. It should be indicated that the XRD spectra showed a peak at  $2\Theta = 22^{\circ}$  due to a graphite and at  $2\Theta = 12^{\circ}$  due to a layered structure of graphite with the basal space of 8.23 Å. The TEM images (Fig. 2) showed that the calcined materials have ultrafine particles with the diameters of a few nm, possibly metal compound  $Pd_5P_2$ , in the matrix of carbon clusters. These results suggest that the material was composed of nano-sized  $Pd_5P_2$  and carbon clusters.

In order to examine further the electronic behavior of the calcined materials, their ESR spectra were measured (Fig. 3). A peak at 337 mT (g = 2.003) due to a free electron was detected and the highest intensity was observed for Ic-600. Our opinion is that an electron transfer between the metal compound and the carbon clusters took place to form a free electron on the carbon clusters. The peak intensity of Ic-600 at 337 mT slightly decreases in response to 15 min visible light irradiation but almost

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Fig. 2. TEM images of calcined materials.

lc-600

50nm



50nm

lc-500

Fig. 3. ESR spectra of calcined materials.

increased back to the initial intensity when kept it for 15 min after the irradiation had stopped (Fig. 4), suggesting that Ic-600 had a visible-light responsive function. The peak intensity of Ic-600 increases with the addition of an oxidant (anthraquinone) but decreases with the addition of a reductant (pyrogallol) (Fig. 5), indicating that the peak signal was due to a cation radical. These results suggest that an electron transfer from the carbon clusters to the  $Pd_5P_2$  particles took place to form an oxidation site at the carbon clusters and a reduction site at the  $Pd_5P_2$  particles (Scheme 2).

The photoresponsive oxidation–reduction ability of Ic-600 was also examined. Fig. 6 shows the UV-VIS spectral change of methylene blue in the presence of Ic-600 under visible light-irradiation and the absorbance was found to decrease with the increase of the irradiation time. Fig. 7 shows the relationships



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

between the concentrations of methylene blue and the irradiation time either in the dark or under the visible light irradiation. The  $Pd_5P_2$  have high electron density compared to the methylene blue and hence a slight electron movement may occur from  $Pd_5P_2$ to methylene blue in the dark. So the reduction of methylene blue could occur in the dark. However, the degree of decrease of methylene blue under the light irradiation was higher than that in the dark, indicating that Ic-600 had visible light-responsive reduction ability. Fig. 8 shows the UV-VIS spectral change of 2,3,5trimethylhydroquinone in the presence of Ic-600 under the visible light irradiation and the absorbance was found to decrease with the increase of the irradiation time. Fig. 9 shows the relationships between the 2,3,5-trimethylhydroquinone concentrations and the irradiation. The 2,3,5-trimethylhydroquinone have rather high



Fig. 5. ESR spectra of Ic-600 in the presence of oxidant or reductant.



**Fig. 6.** UV-VIS spectra of methylene blue in the presence of Ic-600 under visible light irradiation.



**Fig. 7.** Relationships between methylene blue concentration and time in the presence of Ic-600 either in the dark or under visible light irradiation.



**Fig. 8.** UV-VIS spectra of 2,3,5-trimethylhydroquinone in the presence of Ic-600 under visible light irradiation.



**Fig. 9.** Relationships between 2,3,5-trimethylhydroquinone concentration and time in the presence of Ic-600 either in the dark or under visible light irradiation.

electron density and hence the electron transfer may occur from 2,3,5-trimethylhydroquinone to the positive charge containing Carbon. Thus, the concentration of 2,3,5-trimethylhydroquinone slightly decreases by the oxidation in the dark. However, here again, the visible light effectively decreases the concentration of 2,3,5-trimethylhydroquinone compared to the same in the dark, indicating that Ic-600 had a visible light-responsive oxidation function.

In conclusion, the calcinations of 2,2-diphenylphosphino-1,1binaphthyldichloropalladium I under an argon atmosphere gave nano-sized  $Pd_5P_2$ /carbon clusters composite material. ESR spectral examination of the material and the reaction of methylene blue or 2,3,5-trimethylhydroquinone in the presence of the material showed that the composite material have visible light-responsive oxidation-reduction ability through an electron transfer from the carbon clusters to the  $Pd_5P_2$  particles. We believe that such an electron transfer will be achieved by the combination of carbon clusters and various semiconductors, and our findings will contribute to the development of new photo-science, including electronic and/or optical devices production, organic synthesis catalysts, artificial photosynthesis catalysis, solar cells production, and so on.

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