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SHORT COMMUNICATION

P. H. Wang
C.-Y. Pan

Ultrafine palladium particles immobilized on polymer microspheres

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P. H. Wang · C.-Y. Pan (✉)
Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei
Anhui 230026, China
e-mail: pcy@ustc.edu.cn

Abstract Ultrafine palladium particles immobilized on submicrometer copolymer microspheres were prepared by reduction of palladium ions in the presence of the copolymer microspheres. Copolymer microspheres with surface carboxylic or cyano functionality were used. Transmission electron microscopy observation and X-ray diffraction analysis indicated that ultrafine palladium particles of nanometer size were formed and were attached on the surface of the copolymer microspheres. The interaction between palladium particles and surface functionality of the copolymer microspheres was studied by IR spectroscopy and X-ray photoelectron spectroscopy.

Key words Copolymer microspheres · Surface functionality · X-ray photoelectron spectroscopy

Introduction

Fine metal particles immobilized on various materials have attracted considerable interest since these composites have applications as active catalysts in various chemical reactions, such as hydrogenation and hydrogenolysis [1–3].

Hirai et al. [4, 5] reported the preparation of noble metal particles with a particle size of 1–5 nm by reducing the corresponding metal salts with primary or secondary alcohols or ether in an aqueous solution of poly(vinyl-2-pyrrolidone). They found that palladium particles of nanometer size catalyzed partial hydrogenation of cyclopendadine and methyl esters of unsaturated fatty acids to the corresponding monoenes.

Fine polymer particles having high surface area and fluidity have also been used as supporting materials for the immobilization of fine metal particles. Tamai and coworkers [6, 7] reported the preparation of ultrafine metal particles, such as palladium or rhodium particles, immobilized on polymer microspheres by reduction of copolymer–metal ion complexes. The composite particles thus obtained were tested for their catalytic activity toward some hydrogenation reactions, such as hydrogenation of 1-hexene.

In this work, ultrafine palladium particles immobilized on copolymer microspheres of styrene (St)/acrylic acid (AA), St/methacrylic acid (MAA), and St/acrylonitrile (AN) were prepared by refluxing an ethanol/water solution of palladium ions in the presence of the copolymer microspheres. The interaction between the palladium particles and the surface functionality of the copolymer microspheres was studied by Fourier transform (FT) IR spectroscopy and X-ray photoelectron spectroscopy (XPS).

Experimental

Materials

St, AA, MAA, and AN were purified by distillation under reduced pressure. Ammonium persulfate (APS), $PdCl_2$ and NaOH were all analytical grade and were used without further purification.

Preparation of copolymer microspheres

St/AA [P(St-*co*-AA)], St/MAA [P(St-coMAA)], and St/AN [P(St-*co*-AN)] copolymer microspheres were prepared by emulsifier-free emulsion copolymerization using APS as initiator. The recipes of the copolymerization are given in Table 1. The procedures for the preparation of the copolymer microspheres were the same as in our

Table 1 Conditions for the preparation of the copolymer microspheres from styrene (*St*), acrylic acid (*AA*), methacrylic acid (*MAA*), acrylonitrile (*AN*), ammonium persulfate (*APS*), and H_2O. Polymerization temperature: 70 °C; time: 7 h

Sample	St (g)	AA (g)	MAA (g)	(g)	APS (g)	H_2O (g)	Conversion (%)	*D* (nm)
AA	20	3			0.1	200	89.1	330
MAA1	20		3		0.1	200	96.1	175
MAA2[a]	20		3		0.1	200	90.3	227
AN	12			12	0.084	200	85.0	446

[a] MAA was partially neutralized by NaOH (molar ratio of NaOH/MAA = 0.2)

previous reports [8, 9]. For the preparation of MAA2, a prescribed amount of aqueous NaOH solution (equivalent ratio of NaOH/MAA = 0.2) was added to the polymerization system containing St, MAA, APS, and water. Then polymerization was performed at 70 °C for 7 h. The microspheres obtained were purified by centrifugation–dispersion in distilled water at least three times.

Immobilization of palladium particles on the surface of copolymer microspheres

The copolymer microspheres (0.5 g) dispersed in water were purged into a three-necked round-bottom flask fitted with a condenser, a nitrogen inlet, a constant-pressure funnel, and a magnetic bar. Ethanol (25 ml) was added to afford 50 ml solution (ethanol/water = 1:1 in volume). Then 25 mg $PdCl_2$ in acid aqueous solution was dropped in from funnel, and the mixture was stirred for 1 hour at room temperature under a nitrogen atmosphere. Then, the temperature was raised, and refluxing of the mixture was maintained for 2 h. For Sample AA-Pd, 50 mg $PdCl_2$ was used. The composite particles obtained were purified by dialysis for about 24 h and were dried below 40 °C. The composite particles were designated correspondingly as AA-Pd, MAA1-Pd, MAA2-Pd, and AN-Pd.

Characterization

The size and the morphology of both the copolymer microspheres and the composite particles were investigated, and the electron diffraction patterns of the composite particles were obtained using a Hitachi-800 transmission electron microscope. IR spectra in KBr pellets were recorded on a VECTOR-22 spectrometer. XPS measurements were conducted on an ESCALAB MarkII system with a residual pressure of 3×10^{-9} mbar. The analyzer was in the constant resolution mode, at a pass energy of 20 eV. The slit width of the analyzer was 6 mm. A Mg Kα radiation source ($h\nu = 1253.6$ eV) was used with an overall energy resolution of 1.0 eV. X-ray diffraction (XRD) analysis was carried out on a Rigaku rotating-anode X-ray powder diffractometer of D/Max-γA type using Cu Kα radiation.

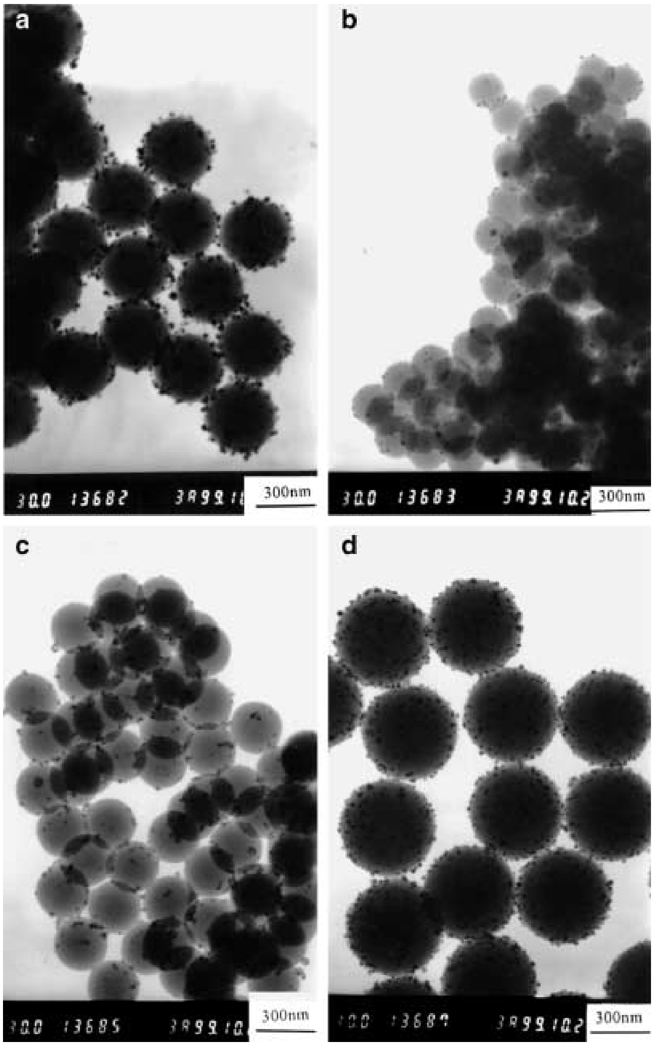


Fig. 1a–d Transmission electron microscope photographs of the composite particles

Results and discussion

TEM photographs of the copolymer microspheres supporting palladium composite particles prepared by refluxing the ethanol/water solution of Pd ions in the presence of the copolymer microspheres are shown in Fig. 1. Ultrafine palladium particles of nanometer size were quite uniformly immobilized on the surface of the copolymer microspheres. It is noted from Fig. 1 that in the case of AN, the amount of palladium immobilized was relatively higher than that in the St/AA and St/MAA systems. The electron diffraction patterns of these composite particles are shown in Fig. 2, which reveals four diffraction rings. A typical XRD diffraction profile of sample MAA1-Pd is shown in Fig. 3. In addition to the scattering of the copolymer microspheres centered at about $2\theta = 19.5°$, two additional quite broad peaks appear at $2\theta = 39.6°$ and 46.2°, respectively. These two

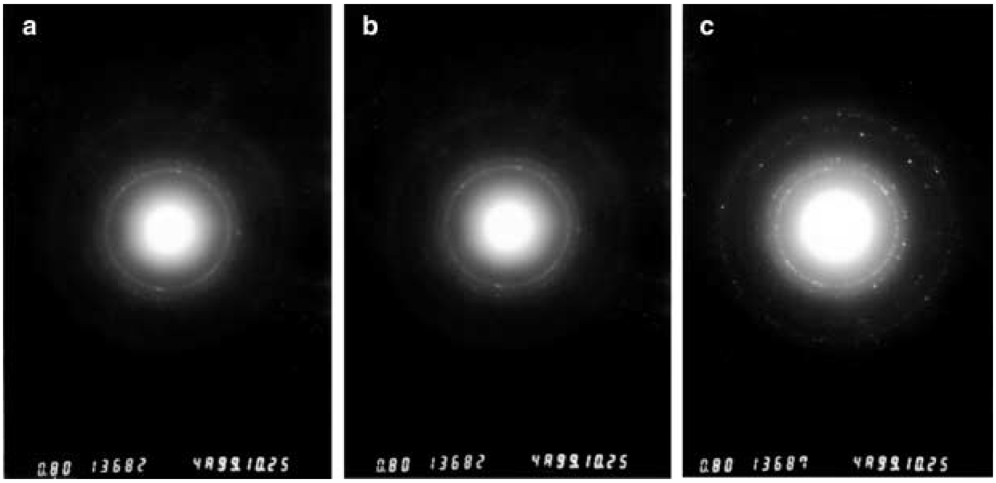


Fig. 2a–c Electron diffraction patterns of the composite particles

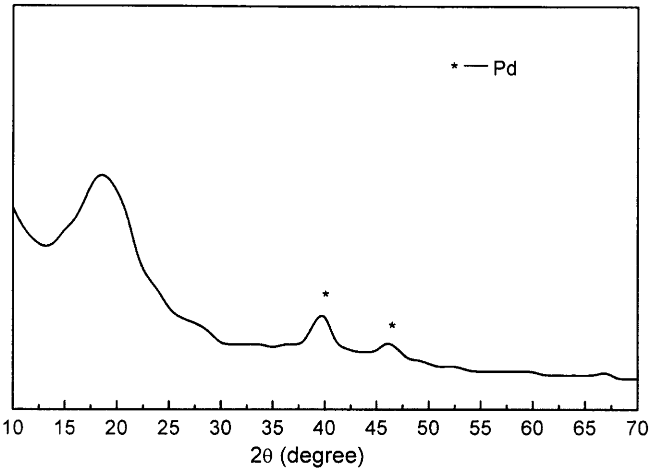


Fig. 3 X-ray diffraction profile of methacrylic acid (*MAA*) MAA1-Pd

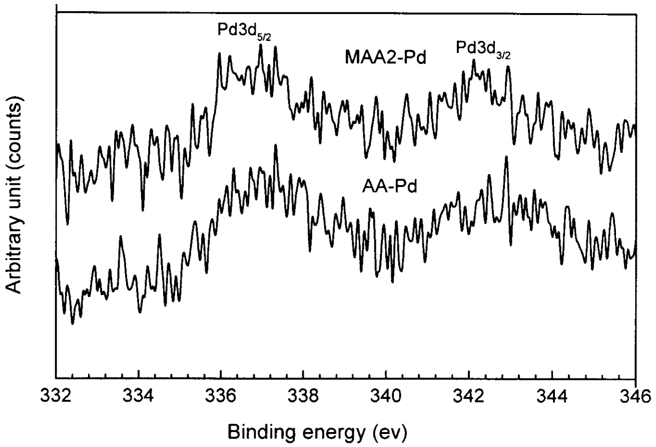


Fig. 4 X-ray photoelectron spectroscopy (*XPS*) Pd3*d* spectra of acrylic acid (*AA*)-Pd and MAA2-Pd particles

peaks can be attributed to the diffractions of the (111) (40.1°) and (200) (46.6°) planes of palladium, respectively. The broad diffraction peaks observed in Fig. 3 suggested the formation of highly ultrafine metal particles as confirmed by TEM observation in Fig. 1. The diffraction rings in Fig. 2 are thus attributed to arise from inner reflections of the (111), (200), (311), and (222) planes of palladium. All these observations proved that ultrafine palladium particles were formed and immobilized on the surface of the copolymer microspheres. The valence of the palladium particles on the copolymer microspheres was examined by XPS analysis. The Pd3*d* spectra of the AA-Pd and MAA2-Pd composite particles are shown in Fig. 4. The broad peak of Pd3$d_{5/2}$ suggests more than one type of palladium. A typical curve-fitted palladium spectrum of AN-Pd is shown in Fig. 5. Three peaks are found with binding energies of 335.5, 336.5,

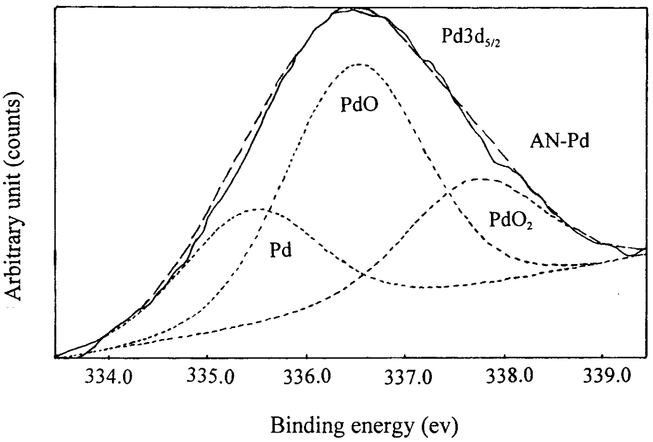
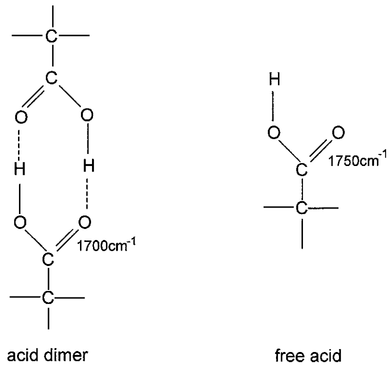


Fig. 5 Curve-fitted Pd3*d* spectrum of acrylonitrile (*AN*)-Pd composite particles

and 337.7 eV at an atomic ratio of 1:2:1. These three peaks correspond to Pd(0) (Pd3*d* = 335.2 eV), PdO (Pd = 336.3 eV), and PdO_2 (Pd3*d* = 337.9 eV) (11, 12). These results indicate that Pd(2 +) was reduced to Pd(0) and that the surface of palladium particles was partially oxidized in air to PdO and PdO_2.. The reason might be that ultrafine palladium particles are very active, which is a common feature for nanometer-sized metal particles. Tamai et al. [7] found that PdO_2 and PtO_2 was predominant on the surface of metal particles after reduction of microsphere–palladium ion or microsphere–platinum ion complexes. They concluded that after formation of palladium or platinum particles, spontaneous oxidation of the resulting ultrafine metal particles in air produced PdO_2 and PtO_2.

After confirmation of the immobilization of the ultrafine palladium particles on the copolymer microspheres, a question therefore arises, i.e., whether the deposition of palladium particles was random on the surface of the copolymer microspheres having various functional groups. In order to answer this question, transmission IR spectroscopy and XPS were employed to obtain some information regarding the interfacial characteristics between palladium particles and the copolymer microspheres. Reflection IR is of no use in the present cases because the size of the copolymer microspheres was so small (less than 1 μm) that the reflection could not be strictly controlled within the surface layer of the copolymer microspheres. The IR spectra of both copolymer microspheres and the corresponding composite particles are shown in Figs. 6, 7, 8, and 9. The IR spectra of the MAA microspheres (Fig. 7, curve a, Fig. 8, curve a) reveal two bands appearing at 1739.6 and 1697.9 cm^{-1}, which correspond to C=O stretching of free carboxylic acid groups and dimerized carboxylic acid groups, respectively [13, 14]. Comparison of the intensity of these two peaks suggests that most of the carboxylic acid groups existed in dimerized form owing to mutual hydrogen bonding rather than free carboxylic acid groups as shown in Scheme 1 [13].



Comparatively, the peak at 1740 cm^{-1} due to free carboxylic acid group is nearly absent in the AA microspheres (Fig. 6, curve a). This indicates that the carboxylic acid groups existed predominantly in the acid

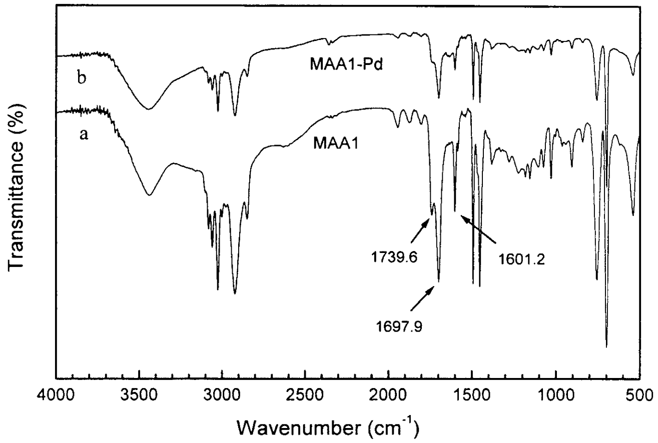


Fig. 7 IR spectra of MAA1 (*a*) and MAA1-Pd (*b*) particles

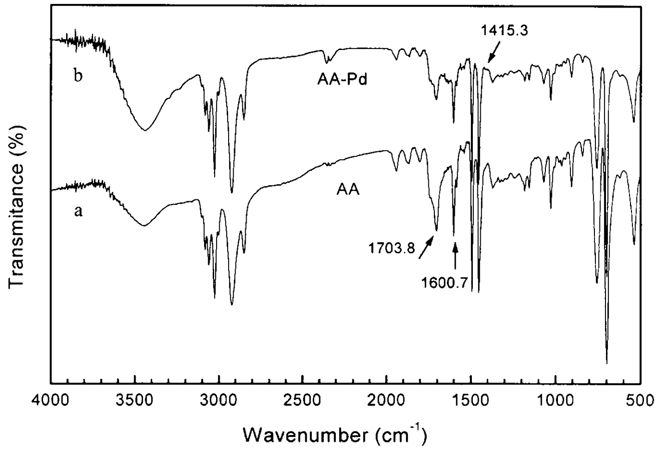


Fig. 6 IR spectra of AA (*a*) and AA-Pd (*b*) particles

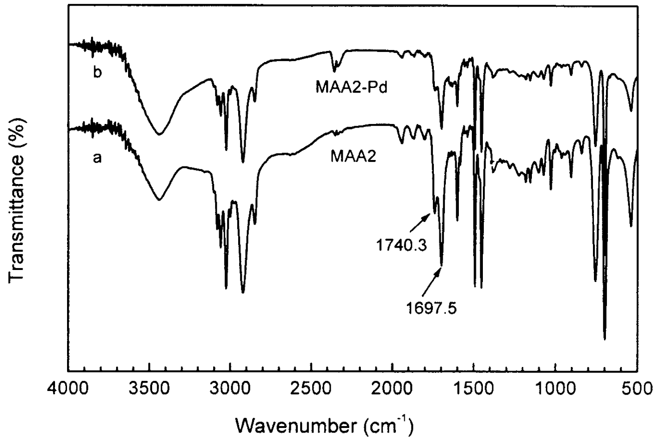
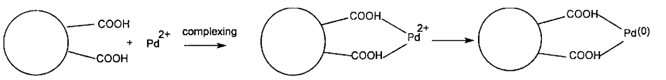


Fig. 8 IR spectra of MAA2 (*a*) and MAA2-Pd (*b*) particles

dimer form. It should be noted that the IR spectra of these microspheres were obtained in the dried state. It was reported [13] that increasing temperature could somewhat increase the amount of free carboxylic acid, while the amount of the dimer form decreased. Comparison of the IR spectra in Fig. 6, curve a and Fig. 7, curve a and Fig. 8, curve a indicates that MAA-based copolymer microspheres contained many more carboxylic acid units than the AA microspheres did. The detailed studies on the distribution of carboxylic acid groups on the surface and inside the AA and MAA microspheres demonstrated that the surface region of the AA copolymer microspheres contained higher carboxylic acid groups than the MAA microspheres did [10].

In Fig. 6, it is observed that immobilization of palladium particles on the AA microspheres reduced significantly the peak intensity at 1704 cm^{-1}. A weak peak at about 1415 cm^{-1} appeared. Generally, when a carboxylic acid group is transformed to a carboxylate group, the peak at 1700 cm^{-1} disappears, while two peaks at 1610–1550 and 1400 cm^{-1} appear, which are attributed to asymmetrical and symmetrical stretching vibrations of the COO– group, respectively [15]. The decrease in the peak intensity at 1704 cm^{-1} and the appearance of a weak peak at 1415 cm^{-1} in Fig. 6 suggest transformation of some carboxylic acid groups to carboxylate groups during the course of the immobilization of palladium particles on AA microspheres. Sugama et al. [16] reported that the formation of metal carboxylate from poly(acrylic acid) and metal oxide was verified on the basis of the absorption bands at 1550 and 1400 cm^{-1} in the IR spectra. Our observation in the IR spectrum here suggests that some of the carboxylic acid groups on the surface of the AA microspheres were transformed to their carboxylate forms, probably resulting from complexing with Pd(II) ions, successive reduction, forming carboxylate–palladium complexes as shown in Scheme 2.



Examination of Figs. 7 and 8 reveals that upon immobilization of palladium particles, the peak at 1740 cm^{-1} in both cases nearly disappears. These data seem to suggest that some carboxylic acid groups might interact with palladium particles. The IR spectra of AN copolymer microspheres and AN-Pd composite particles are shown in Fig. 9. No obvious difference can be discerned from this spectra. Kim and Jo [17] claimed that when St/4-vinylpyridine (4VP) copolymer in tetrahydrofuran solution was placed onto a copper or an aluminum surface, the peak at 1069 cm^{-1} due to the in-plane ring bending mode of the pyridine ring was enhanced in intensity on the copper surface, while there was no significant change on the aluminum surface. In

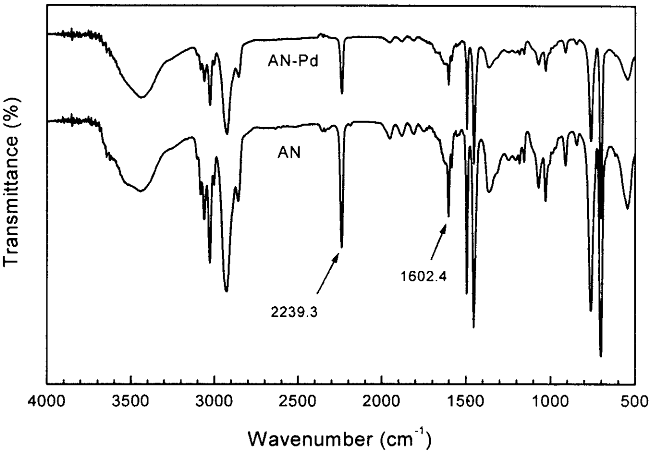


Fig. 9 IR spectra of AN and AN-Pd particles

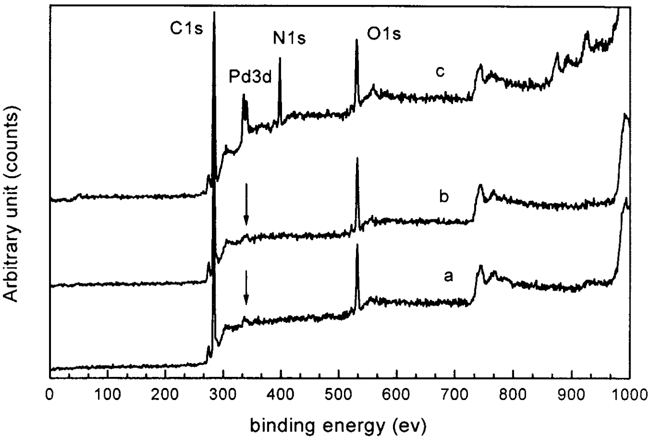


Fig. 10 XPS full-scan spectra of AA-Pd (*a*), MAA2-Pd (*b*), and AN-Pd (*c*) composite particles

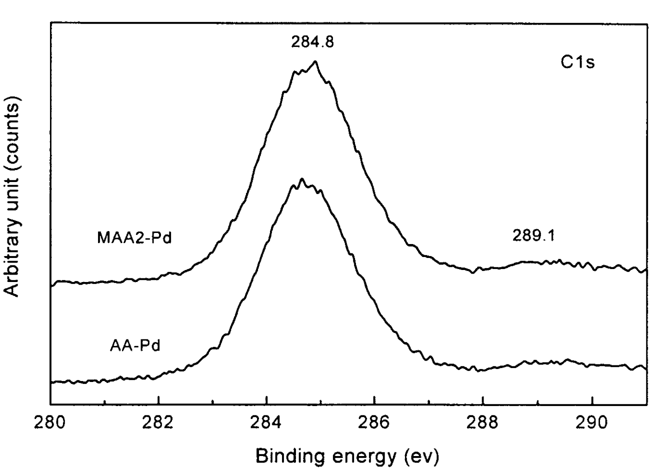


Fig. 11 C1*s* spectra of AA-Pd and MAA2-Pd composite particles

Table 2 Results of X-ray photoelectron spectroscopy analysis

Sample	AA	AA-Pd	MAA2	MAA2-Pd	AN	AN-Pd
C_{COOH}/C_{TOTAL}	0.066	0.035	0.051	0.030		
N1*s*/C1*s*					0.25	0.18

addition, the peak at 1557 cm^{-1} due to C=N stretching shifted to a lower frequency of 1550 cm^{-1} when on copper. They concluded that the 4VP unit in St/4VP was adsorbed on the metal surface nearly in a vertical direction and that the 4VP groups interacted more strongly with copper substrate than with aluminum substrate.

Further information on the interfacial characteristics between copolymer microspheres and palladium particles was obtained by XPS analysis. The XPS full-scan spectra of the composite particles are shown in Fig. 10. The peak at a binding energy of about 336.2 eV is observed in all composite particles, indicating the formation and immobilization of palladium particles on the copolymer microspheres as discussed previously. The C1*s* spectra of AA-Pd and MAA2-Pd composite particles in Fig. 11 show two peaks at binding energies of 284.8 and 289.1 eV, respectively, corresponding to carbon in C–C or C–H linkages and carbon in COO groups. The C_{COOH}/C_{TOTAL} ratios calculated from the C1*s* spectra for both the copolymer microspheres and the composite particles are given in Table 2. Interestingly, the C_{COOH}/C_{TOTAL} ratio was dramatically lessened after immobilization of the palladium particles. We think that when the palladium particles are randomly distributed on the surface of the AA or MAA microspheres, the C_{COOH}/C_{TOTAL} ratio would not vary significantly because the photoelectrons ejected from the surface region (several tens of angstroms) when passing through the layer of palladium particles are subjected to similar attenuation owing to inelastic scattering of metal atoms. On the other hand, when the metal particles are distributed preferentially onto the sites of surface carboxylic acid groups owing to complexation or mutual interaction, the photoelectrons ejected form below these sites are subjected to more attenuation in signal intensity. This would lead to a decrease in the C_{COOH}/C_{TOTAL} ratio compared with bare copolymer microspheres. The results in Table 2, therefore, suggest a preferential distribution of palladium particles on the sites of surface carboxylic acid groups of the copolymer microspheres. This observation supports the interaction mechanism between palladium particles and the copolymer microspheres as illustrated in Scheme 2.

The curve-fitted C1*s* spectrum of AN-Pd composite particles reveals mainly three types of carbons similar to those of AN copolymer microspheres as reported in Ref. [9]. The atomic ratios of N1*s*/C1*s* obtained on the basis of the C1*s* and N1*s* spectra of both AN and AN-Pd particles are also given in Table 2. It is seen that this value decreased upon immobilization of the palladium particles. Similarly, as discussed previously, this indicates a preferential distribution of palladium particles onto the sites of cyano groups. The interaction mechanism is tentatively assumed to occur through the formation of complexes as illustrated in Scheme 3.

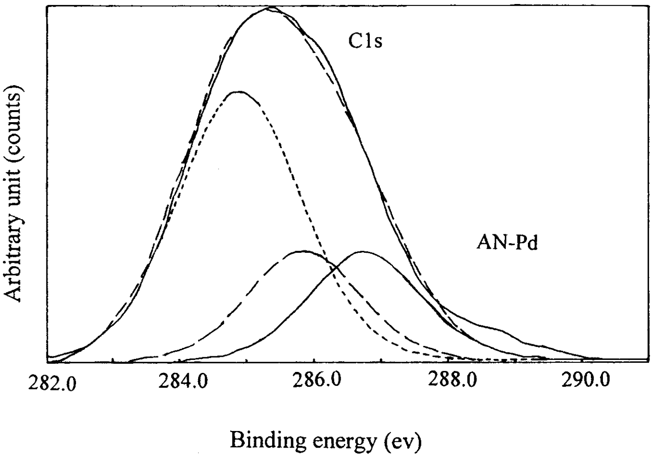
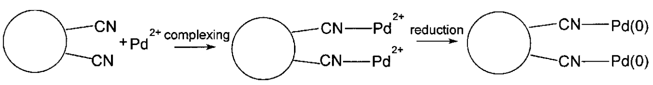


Fig. 12 C1*s* spectra of AN-Pd composite particle



Conclusion

Ultrafine palladium particles immobilized on submicrometer copolymer microspheres were prepared by refluxing $PdCl_2$ in ethanol/water solution in the presence of the copolymer microspheres. TEM observation and XRD analysis confirmed the formation of nanometer-sized palladium particles on the surface of the copolymer microspheres. XPS analysis indicated the presence of three types of palladium: Pd(0), PdO, and PdO_2, respectively. The interaction between immobilized palladium particles and surface functionality of the copolymer microspheres was studied by FTIR spectroscopy and XPS. The formation of functional group–Pd(0) complexes was tentatively assumed on the basis of both the FTIR spectroscopy and XPS results.

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