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Study of Cu^{2+}-poly(itaconic acid-*co*-acrylic acid) complex and copper-polymer nanocomposites

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Summary

Ultrafine copper particles with diameters in the range of nanometer scale have been prepared in a polymer matrix, using ionic aggregates in Cu^{2+}-random poly(itaconic acid-co-acrylic acid) complex precursor films as "microreactors" of controllable size.The morphology and formation of metallic copper particles were studied by transmission electron microscopy and X-ray diffraction techniques. Results from the measurements indicate the copper ions were transformed into nanocrystalline by in situ chemical reduction. It was also found that the polymer chains prohibited the excessive aggregation of the metal atoms and have protective effect on the ultrafine copper particles.

Introduction

Nanocrystalline composites are composed of ultrafine particles, which diameters ranging from 1 to 20nm, dispersed in a matrix(1). These materials exhibit novel electronic, optical, magnetic, and chemical properties due to the extremely small dimensions of these ultrafine particles. Polymer matrix-mediated synthesis of ultrafine particles, which results in ultrafine particles/polymer nanocomposites in the solid state, has been systematically investigated lately (2-4), e.g., ultrafine copper particles were prepared in a polymer matrix by the thermal decomposition of a copper formate-poly(2-vinypyridine)complex(1), and nanocrystalline γ-Fe_2O_3 has been synthesized in an ion-exchange resin(5). Recently noble metal nanoclusters such as Ag , Au , Pd and Pt have been able to synthesized in lamellar or cylindrical microphase-separated precursor block copolymer films(2-4,6-9) in which metal complexes initially were attached to the monomer comprising one block of the block copolymer. However, the greatest control over the number of atoms or molecules in a cluster should be possible in spherical microdomains. Synthesis of metal clusters in spherical microdomains is related to synthesis of metal and metal sulfide clusters in solution within micelles and vesicles. We have also prepared transition metal ultrafine particles within spherical microdomains from the hard segments of the multiphase block polyurethane ionomers by in situ chemical reduction (10). However, in multiphase block polyurethane ionomers the metal ions aggregated in hard domains and the metal ion content was limited by the low concentration of ionic groups in polymer precursors. Therefore it is difficult to prepare the metal-polymer nanocomposite containing higher content of metal nanoparticles in a polymer matrix.

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For random ionomers or some other macromolecule-metal complexes, it has been proved that the metal ions have a tendency to form ionic domains(11) in which the anionic groups and their associated cations are microphase separated from the typical hydrophilic portions of the polymer(12).Usually, the diameter of these metal ionic aggregates ranges from 2 to 10 nm(13). Using the ionic subphase, metal sulfide semiconductor nanoclusters have been synthesized in some commercial ionomer membranes(14-15). Our attention was focused on the study of the ionic clusters in metal-coordination polymers and the use of ionic aggregates as "microreactors" of controllable size to form the metallic particles dispersed in polymer matrix which has protective effect for ultrafine metal powders. In this paper we tried to prepare a Cu^{2+}-random poly(itaconic acid-co-acrylic acid) complex precursor, which contained more than 42wt% of metal ions and carboxylic groups. It is hoped that the copper-polymer nanocomposite containing high content and homogeneously dispersed metal nanoparticles can be formed in the solid state by in situ chemical reduction, and that the polymer chain can prevent the metal particles from oxidation and excessive aggregation during reduction.

Experimental

Materials

The random copolymer of itaconic acid(IA) and acrylic acid(AA) was synthesized by solution polymerization(16) with a number-average molecular weight of about 50 000. $Cu(CH_3CO_2)_2\cdot H_2O$ was used as received from Aldrich Chemical Co. and sodium borohydride ($NaBH_4$) was purchased from Merck-Schuchardt Chemical Co.. Dimethylformamide(DMF) and hydrazine hydrate($NH_2NH_2\cdot H_2O$) used in the present work were all analytical grade agents.

Formation of Copper-polymer nanocomposites

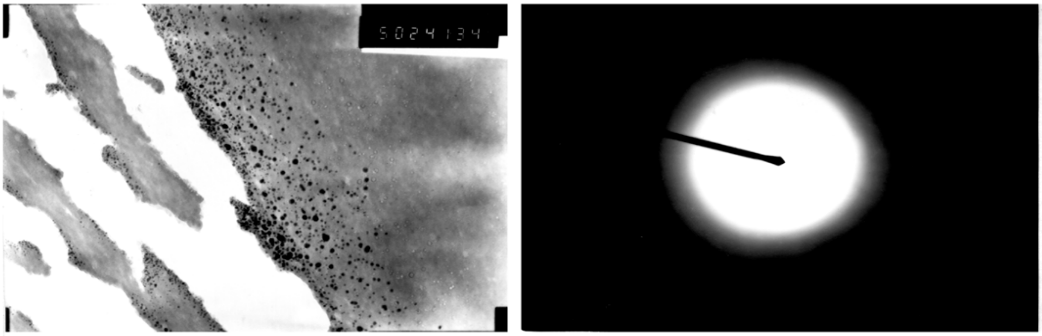
Blends of PIA-AA with metal salt were prepared by dissolving the precursor polymer in DMF(5wt%), then mixing with a stoichometric amount of copper acetate at 80°C. The solutions were poured into Teflon-casting plates and the solvent was evaporated , which result in films of Cu^{2+}-polymer complexes. Then the metal chelate films, 20um thickness, were reduced by 1wt% sodium borohydride aqueous solution or hydrazine hydrate at room temperature. The reduced films were washed with distilled water, then dried under vacuum at room temperature and stored in a desiccator for subsequent use.

Characterization

Transmission electron microscopic(TEM) observation and selected area electron diffraction(SAED) were performed on a JEOL JEM-200CX Transmission Electron Microscope. The accelerating voltage is 200 kV. X-ray Diffraction (XRD) patterns were measured using a Rigaku D/Max-RA X-Ray Diffractometer with graphite-filtered Cu-Kα radiation, operated at 40 kV and 150 mA.

Results and discussion

Fig.1(a) shows the TEM micrograph of poly(itaconic acid-co-acrylic acid)-Cu^{2+} complexes films, which is no obvious micromorphology observed. However, we found some black spherical dots emerging from the edges of the cracked films, which can be considered



(a) × 50 000 (b)

Fig.1.(a)TEM micrograph for Cu^{2+}-poly(itaconic acid-co-acrylic acid) complexes films; (b) Selected area diffraction pattern for the area shown in Fig.1(a).

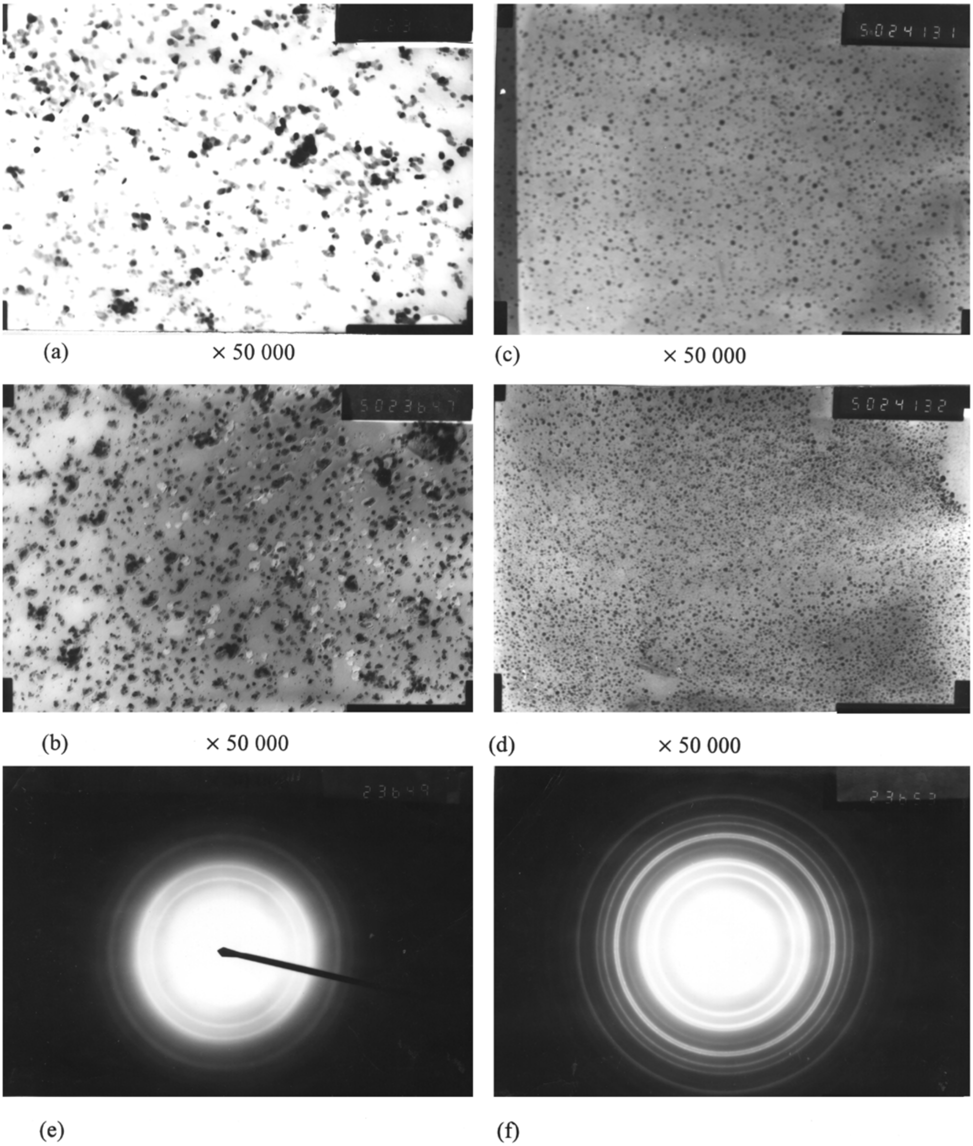
as ionic aggregates or may be related to the preparative techniques of specimens on carbon-coated copper grids. SAED (Fig. 1(b)) shows they were not in crystal state. Fig.2 shows TEM micrographs for polymer-metal nanocomposites and different initial molar ratio of $Cu^{2+}$to carboxylic groups in polymer precursors, where (a) (b) and (c) (d) show the TEM micrographs for samples prepared by different reductants $NaBH_4$ and hydrazine. The initial molar ratio of Cu^{2+} to carboxylic groups is 1:4 in (a) (c), and 1:2 in (b) (d) respectively. Monodispersed nanoparticles are observed in the polymer films. Fig. 2(e)and(f) are the selected area electron diffraction patterns obtained from the micrographs shown in Fig. 2(b)and(d), respectively. The values of interplanar spacings have been calculated from the diameters of these rings and are given in Table I. The standard ASTM d_{hkl} values for copper are also listed in this table. The observed data indicate that the lattice parameter in the nanoparticles is almostly consist with that in copper crystal. Fig.3 shows the X-ray diffraction (XRD) patterns of the films of nanocomposites, which further confirmed that the nanocrystalline copper are formed in the polymer matrix. The formation of these copper particles can be understood from the following equations:

$$4Cu^{2+} + BH_4^- + 8OH^- = 4Cu + BO_2^- + 6H_2O,$$

$$2Cu^{2+} + N_2H_4 + 4OH^- = 2Cu + N_2^{\uparrow} + 4H_2O.$$

It has been known that the ultrafine amorphous Fe-B and Ni-B alloys are formed in the previous work (10)because the chemical reduction takes place below the glass transition temperature Tg , and an appropriate quantity of boron atoms exist in those particles(17). However , there is no stabilizing element to be incorporated into the copper particles during the chemical reduction by $NH_2{\cdot}NH_2$, and boron has such low solid solubility to the bulk copper that the copper particles reduced by $NaBH_4$ generally only form crystal structure.

For random ionomers , it is well known that a number of models for the morphology have been proposed, which have been reviewed recently (18-19), and it has been widely accepted that there are ionic aggregates in ionomers, and that ion pairs can be transformed into ionic clusters when it reaches a certain critical ion content. However, even for the samples of Cu^{2+}-poly(itaconic acid-co- acrylic acid) complexes, in which the ion contents are up to 40



(a) × 50 000 (c) × 50 000

(b) × 50 000 (d) × 50 000

(e) (f)

Fig.2. TEM micrographs for polymer-metal nanocomposites films by reduction treatment of (a) (b) $NaBH_4$ and (c) (d) hydrazine. The initial molar ratio of Cu^{2+} to Carboxylic groups in polymer precursors (a) (c) 1:4 and (b) (d) 1:2 , respectively; (e) (f) Selected area diffraction patterns for the area shown in Fig. 2 (b) and (d) , respectively.

TABLE I. Comparison of d_{hkl} values with ASTM data for copper nanocrystalline obtained from Fig. 2(b) [I] and (d)[II].

Debye-Scherrer rings	d_{hkl}, observed (nm)		d_{hkl}, ASTM (nm)
	I	*II*	
1. (111)	0.2084	0.2092	0.20880
2. (200)	0.1801	0.1810	0.18080
3. (220)	0.1277	0.1278	0.12780
4. (311)	0.1084	0.1105	0.10900
5. (222)		0.1048	0.10436
6. (400)		0.0970	0.09038
7. (331)			0.08293
8. (420)			0.08093

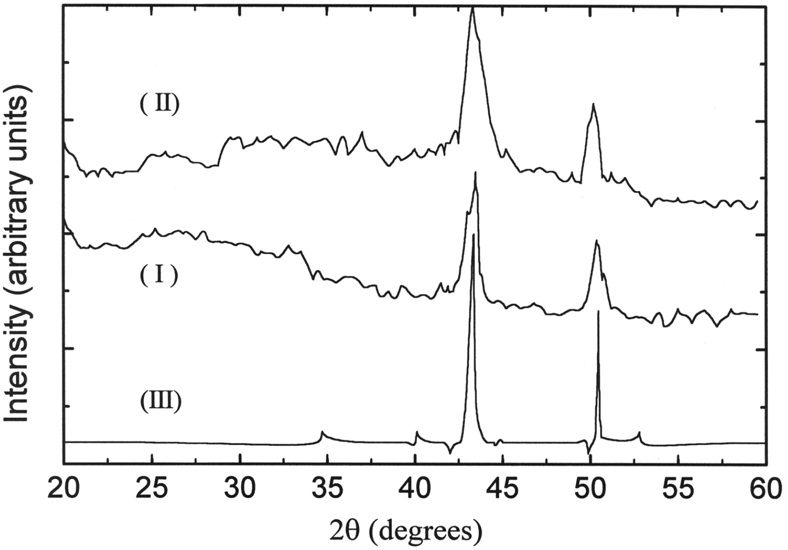


Fig. 3. XRD patterns of 1:2 complex films reduced by $NaBH_4$(I) and $NH_2{\cdot}NH_2$ (II). The pattern for bulk copper metal(III) is shown for comparison.

wt%, we have not found exact microstructures in these complexes system by TEM, while it is reasonable to postulate that ionic aggregates exist in polymer matrix, but the loose ionic domain structure in the polymer-Cu^{2+} complexes has no enough electron density in contract with the polymer matrix. But upon reduction, the metal ions in domains were transformed into compact structures such as nanocrystalline, which could be observed easily by TEM.

Furthermore, the polymer matrix takes an important role to prevent metal particles from oxidation and excessive aggregation during reduction. By comparing with Fig.2 (a)(b) or (c)(d), the particle size almost keeps equal which seems that the particle size is independent of the concentration of the metal ions in the polymer precursors, and more monodispersed particles were obtained with the increase of ion contents(Fig. 2(b)(d)). However, by comparing with Fig.2(a)(b) or (c)(d), there are different micromorphologies of particles , which are attributed to the effect of the reducing agents. We have tried to fit the experimental data of particle size from Fig.2 with a Log-normal distribution function(20):

$$\Delta n = \frac{1}{\sqrt{2\pi}\, Ln\sigma} \exp\left\{ -\frac{1}{2} \left[Ln\left(\frac{x}{\bar{x}}\right) \Big/ Ln\sigma \right]^2 \right\} \Delta(Lnx),$$

where Δn is the fractional number of particles, x is the diameter, $\bar{x}$ is the median diameter and σ is the geometric standard deviation. The histograms of these particles are compared in Fig.4. Moreover, to obtain the satisfactory results, we have calculated the average diameter $\bar{x}$ using the following equation(21)

$$\bar{x} = \sum_{j=1}^{n} x_j n_j \,/\, N,$$

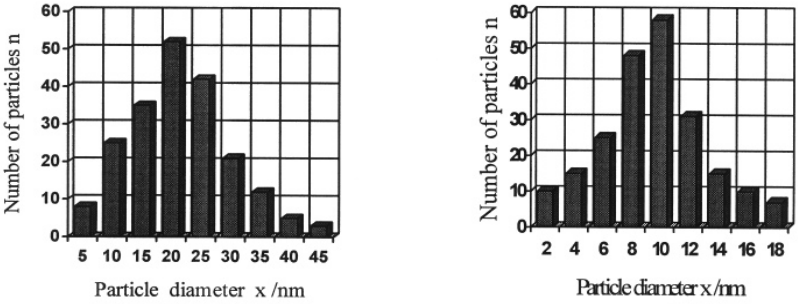
where xj is the diameter in the jth interval of the histogram, nj is the number in the jth interval, n is the total number of intervals and

$$N = \sum_{j=1}^{n} n_j .$$

The standard deviation of the particle diameter is calculated from

$$\sigma = \sqrt{\sum_{j=1}^{n} (x_j - \bar{x}) \Big/ (N-1)}.$$

Table II summarized these values of $\bar{x}$ and σ, calculated by the both above methods for the samples treated by different reducing agents. The simple statistical averaging gives a smaller value of the standard deviation than that obtained from the Log-normal distribution function, which can be related to the growth of copper particles(22).

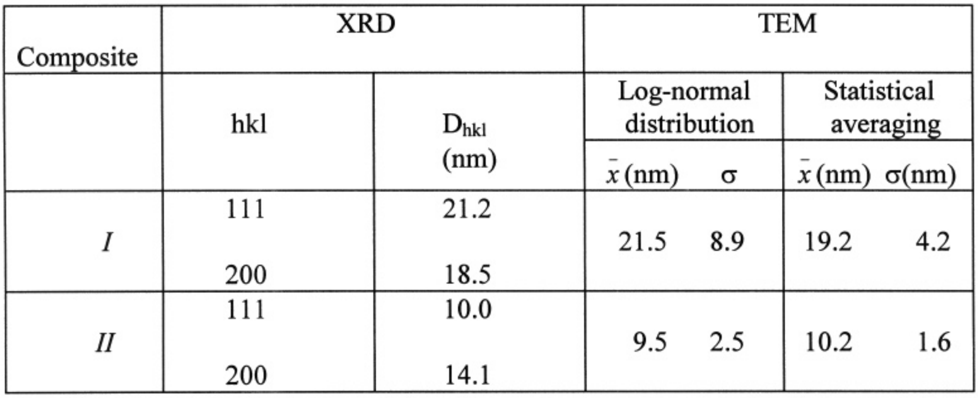


(I) (II)

Fig.4. Histograms of copper particles determined from Fig. 2(b)and (d).

Both the molar ratios of Cu^{2+} to carboxylic groups before reduction are 1:2.
The complexes are reduced by $NaBH_4$ for Fig.4(I) and by hydrazine for Fig.4(II).

TABLE II. Evaluation of particle sizes of the nanocomposites measured by different methods. *I.* and *II.* are 1:2 complexes reduced by $NaBH_4$ and $NH_2 \cdot NH_2$, respectively.



Composite	XRD		TEM			
	hkl	D_{hkl} (nm)	Log-normal distribution		Statistical averaging	
			$\bar{x}$ (nm)	σ	$\bar{x}$ (nm)	σ(nm)
I	111 200	21.2 18.5	21.5	8.9	19.2	4.2
II	111 200	10.0 14.1	9.5	2.5	10.2	1.6

The evaluation of the particle size is also determined from the line width of the diffraction peaks in the X-ray diffraction patterns(Fig.3) using Scherrer's equation(23):

$$D_{hkl} = k \bullet \lambda / \beta \cos\theta ,$$

where D_{hkl} is the linear dimension of coherent areas in different crystallographic planes (hkl),which dominantly influence the broadening of diffraction lines neglecting the influence of microstresses on the basis of our preparation method of the experimental materials. λ is the X-ray wavelength (λ= 0.1542nm). θ is the Bragg diffraction angle of the diffraction peak,and k is geometric factor taken to be 0.9 if β is the half width of the diffraction peak. The physical broadening β is determined by the separation of instrument broadening Bs from the total width B_M of the diffraction line by the following relationship:

$$ß = B_M - B_S,$$

where B_S, the instrumental broadening was determined by a standard sample.

Diffraction coherent area sizes D_{hkl} for different crystallographic directions of the different samples are listed in Table II. It is shown that the particle sizes calculated from XRD are correspond well with the data obtained by TEM. In general, the particles reduced by hydrazine are typically smaller than those reduced by $NaBH_4$, which may be related to the reductibility or nature of the reducing agents(24).

Conclusions

The ionic aggregates in the random polymer-metal complex films can be brought to the metal nanoparticles by in situ chemical treatments, and the polymer matrix takes an important role to prevent metal particles from excessive aggregation and oxidation; TEM, ED and XRD show that the copper particles reduced by either hydrazine or $NaBH_4$ are in crystal state, different from ultrafine amorphous metal borides; In general , the shape and size of these copper particles seem to be independent of the concentration of the metal ions in the polymer prosecutors, while they are affected by different reducing agents.

Acknowledgment

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