

Synthesis of 10 Nanometric Copper Clusters in a Polymer Matrix by a Solution-Reduction Synthesis (SRS)

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ABSTRACT: Nanometric metal clusters in a polymer host were synthesized by a solution-reduction route in a swelling cathode film (SCF) containing metal ions (such as Cu²⁺). The TEM results show that the scale of the clusters is about 10 nanometers and the distribution of their diameter is very narrow. The X-ray diffraction and the electron diffraction patterns confirm that the reduced clusters are the crystallites of metal (copper). The scale of nanometric clusters is affected by the electrochemical conditions in the reactions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1857–1864, 2000

Key Words: nanometric; cluster; composite; solution; copper; poly(vinyl chloride)

INTRODUCTION

Nanometric clusters display a variety of useful properties including catalysis, magnetism, and size-dependent light absorption^{1,2} because their special structures are different from the general materials. In this field, many studies have focused on inorganic^{3,4} and metallic^{5–8} nanometric clusters or their related composite materials, but the importance of nanometric metal clusters in a polymer host makes the study of these materials more desirable. There has been some research in this field^{9–12}; however, systematic work on the methodology is yet to be investigated.

In our group, “a solution-reduction synthesis” (SRS) was developed initially for the preparation of a metal-in-polymer gradient composite (MPGC).^{13,14} The near monodispersed nanometric metal clusters were found by observation with transmittance electron microscopy (TEM) when a flexible polymer

host—poly(vinyl chloride) (PVC)—was used. SRS solves two key problems in the preparation of these materials, which are the phase separation between a polymer host and the nanometric clusters and the aggregation of the clusters. It has more advantages in controlling cluster aggregation and the morphology than have the conventional methods, such as the electrochemical synthesis of surfactant-stabilized clusters,¹⁵ *in situ* formation of metal clusters in the polar segments of diblock copolymers,¹⁶ and metal vapor deposition.^{15,17} The SRS method involves the design of a three-component solution including metallic ions, a polymer, and a solvent, the preparation of a swelling cathode film (SCF), and the electrochemical reduction of the SCF. With the above serial operations, a metal-in-polymer nanometric composite (MPNC) can be obtained.

EXPERIMENTAL

Materials

A commercial PVC (made by the Qingdao Chemical Factory, Qingdao, China) was used as the polymer host, reagent-grade tetrahydrofuran

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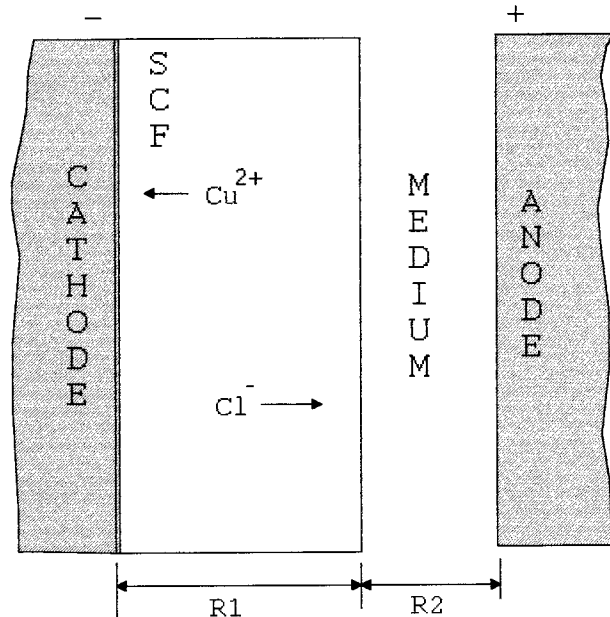


Figure 1 Scheme of electrochemical reactor.

(THF) was used as the solvent for PVC, reagent-grade copper chloride and nickel chloride were used as the ion resource, and reagent-grade ferrous salt and ferric salt were used as redox agents in the electrolyte of sulfuric acid in the electrochemical reactor. None of the reagents or materials were pretreated before use.

Synthesis of the Samples

The electrochemical reactor used in this article is shown in Figure 1. All samples were synthesized by SRS, as established in our previous articles,^{13,14} but the experimental and major electrochemical conditions were ameliorated.

The synthesis of the samples included three steps: First, PVC and copper ions (Cu^{2+}) were dissolved in THF in the same vessel at $60 \pm 2^\circ\text{C}$ for at least 24 h to obtain an appropriate solution. The ratio of copper ion to the monomer unit of vinyl chloride was 1:1.6 and the concentration of PVC in THF was about 15–16 % wt. Second, the solution was spread on a cathode which was a copperized column ($\Phi 20 \times 50$ mm) or a graphite column and the spread film was dried in air at ambient ($25 \pm 1^\circ\text{C}$) for 16–24 h. The thickness of the film was about 150–500 μm . The films were called “swelling cathode films” (SCF). Third, the SCFs were reduced electrochemically under the proper electrochemical conditions. The electrochemical reactions were started at a designed

temperature, 30–60°C. The reaction time was 3 h. In this study, the power voltage was 3.6 V or less.

Measurements

The morphology in the cross section of MPNC was tested by a TEM, JEM-2000 EX (JEOL Ltd., Tokyo, Japan). The samples were cut into extremely thin chips (about 100 nm thick) on a slicer of MT6000 (Sorvall Instruments, USA). The images were recorded by taking photographs and the electronic diffraction patterns were taken at the same time on the TEM measurement mentioned above.

The reduced metal in the sample films was measured by a wide-angle X-ray spectrometer, D/max - rB (Japan). The Fourier transform infrared (FTIR) spectrometer used to measure the components of MPNCs was a Nicolet 750 (USA). All samples were dried at 85°C for 16 h before they were finely chipped for KBr pellets.

RESULTS AND DISCUSSION

Morphology of MPNC

We carried out nanometric measurements by transmittance electron microscopy (TEM) and show the results in Figure 2. The image displays a spread distribution of black dots and their diameters are about 10 nm. According to phase-contrast (bright-field) and Z -contrast (dark-field) (Z is atomic number) rules,⁴ the dark dots are the deposited nanometric crystals.

Figure 3 shows a photograph of the electron diffraction pattern (EDP) of nanometric clusters in the polymer host. It presents the bright dots of multicrystals of the deposited nanometric clusters. The X-ray diffraction pattern (Fig. 4) of the sample reveals the deposited copper crystals (Cu^0). The peaks at $\approx 2\theta = 43.4^\circ$ (θ is the dispersion angle; the interatomic d spacing is 2.08 Å), 50.54° (d 1.804 Å), 74.16° (d 1.227 Å), and 90° (d 1.089 Å) are in accordance with the unit cell parameters of copper [Fig. 4(A)].¹⁸ This suggests that the clusters are the outcome of the reduction of Cu^{2+} and their simultaneous deposition in the plexus of molecular chains in the polymer host. To exclude any effect of PVC crystallization [Fig. 4(B)], we tested a comparable sample of PVC from $2\theta = 5^\circ$ to 80° by the same method and similar diffraction peaks could not be found in the PVC

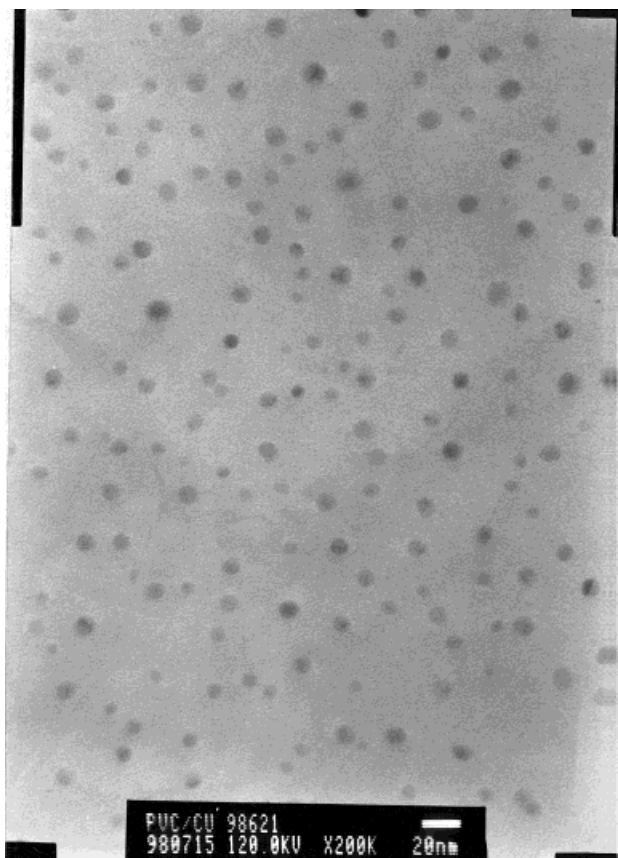


Figure 2 TEM image of sample (scale bar, 20 nm). Synthesized conditions: power voltage, 2.4 V; predrying time of SCF at ambient temperature, 24 h; ratio of molar side —Cl groups on PVC to molar copper ions, 1.6:1; copperized column as cathode.

sample. This indicates that the host PVC has no crystalline occurrence in the processes of the preparation and electrochemical reaction of SCF.

Effects of Electrochemical Factors on Morphology of MPNC

In design of the sample preparation, the important factors which control the micromorphological structures of MPNC should be considered. In our previous articles, we reported that when the host is polyacrylonitrile (PAN) the morphology in the film cross section is the gradient distribution of copper. However, when the matrix is PVC, there is no gradient distribution of copper in the cross section but nanometric clusters in the polymer host are obtained (Fig. 2). In comparing these two polymers, the major difference between them is the flexibility of the macromolecular chain. The PVC chain is more flexible than is the PAN

chain¹⁹ and it should be a closer conglomeration than that of PAN. This close structure inhibits the dispersion of ions in the nanometric domain.²⁰ On the other hand, the complex of side groups of macromolecular chains with metal ions is also very important, which causes the ions to become domain-fixed in nanometers. Although many polymers are used, such as PVC, PAN,^{13,14} poly(vinyl alcohol), and so on, the ideal one in our experimental range is PVC for MPNC.

The family of metal ionic sources chosen is represented as MX ($M = \text{Ni}^{2+}$ and Cu^{2+} ; $X = \text{Cl}^-$, Br^- , SO_4^{2-} , NO_3^- , and so on). Table I lists the results of the reduction of Ni^{2+} and Cu^{2+} ionic sources. Although they are the salts which can be reduced into metal crystals in common electrochemistry, there are obvious differences in this experiment. Cu^{2+} can easily be reduced into copper crystals but nickel cannot be obtained from the reduction of Ni^{2+} because the reduction reactions

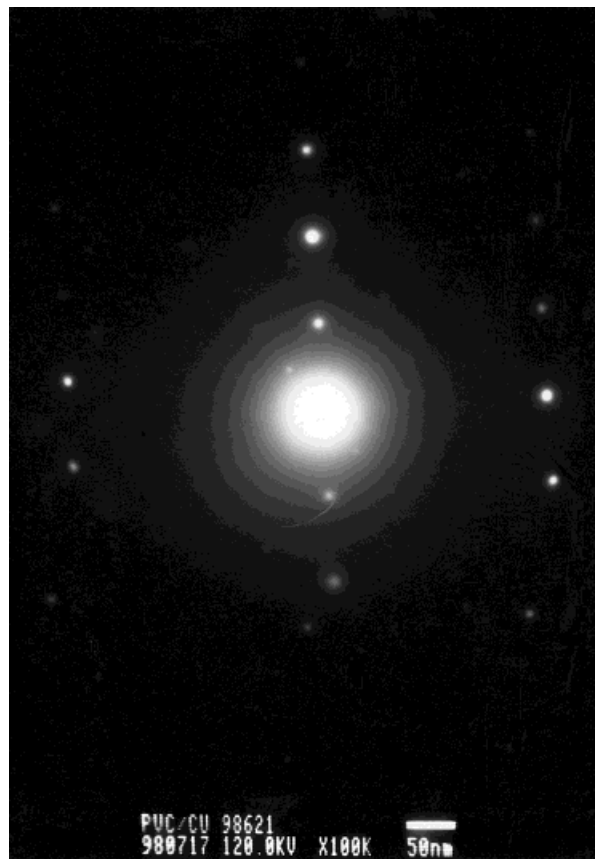


Figure 3 Electron diffraction pattern. Synthesized conditions: power voltage, 2.4 V; predrying time of SCF in ambient temperature, 24 h; ratio of molar side —Cl groups on PVC to molar copper ions 1.6:1; copperized column as cathode.

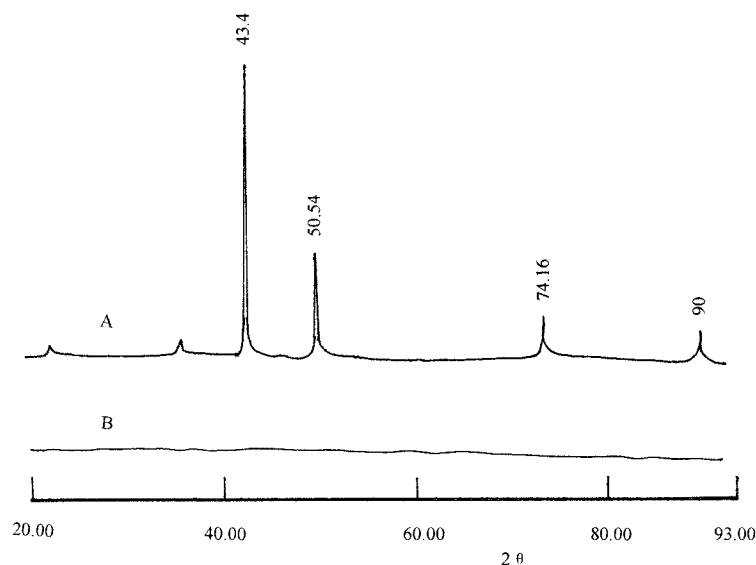


Figure 4 X-ray diffraction of MPNC. Synthesized conditions—(A) MPNC sample: power voltage, 3.6 V; predrying time of SCF in ambient temperature, 24 h; ratio of molar side —Cl groups on PVC to molar copper ions, 1.6:1; copperized column as cathode. (B) PVC sample was prepared by dissolving PVC powder in THF and drying at 80°C under a vacuum for 4 h.

in the polymer host are more complex than is the electrolysis in an aqueous solution. Obviously, the negative reduction potential of Ni^{2+} made it difficult to reduce into crystalline metal. Sohn and Cohen's work²⁰ described a similar electrochemical principle in which a positive ionic source, Ag^+ , was used to obtain nanometric clusters in a copolymer matrix.

The electrolytes in an electrochemical reactor play a very important role in the electrochemical reaction. They assist the recycle of current and convey the side products, such as Cl_2 and so on. The electrolytes used in our experiments are listed in Table II. The data show that the different electrolytes cause differences of power voltage when we maintain the current density constant. To prevent a side reaction of electrolyzing water and releasing of H_2 on the cathode, the applied power voltage should be as low as possible. The data in groups 1 and 2 in Table II can meet this

rule, while the value of the power voltage in group 3 in Table II causes a porous structure in MPNC due to electrolyzing water.

Table III shows the effect of electrode materials—copperized and graphite cathodes—on the morphology of MPNC. The clusters of deposited copper obtained in PVC hosts with these cathodes are 10 and 50 nm, respectively. This shows that the different cathode materials largely affect the morphological structures in MPNC. The explanation for it is very complex because it concerns the roughness of the electrode surface, the releasing function of electronics in the electrode, and so on. According to the experimental results, one factor at least can be confirmed, that the copperized cathode has the smoother surface.

Table IV shows the effect of electrochemical conditions, such as power voltage and temperature in the electrochemical reactor, on the scale of the clusters. Under higher power voltage (3.6 V), the lower diameter (2.2 nm) metal clusters can be obtained. This should be understood by the nucleation rule of reduced metal. Higher potential may produce more nuclei of metal in the nanometric domain in the cross section of SCF. Naturally, the more clusters there are, the smaller scales the clusters have. The temperature in the electrochemical reactor, however, has little effect on the scale of clusters in the experiments.

Table I Effects of Different Ions on the Preparation of MPNC

	Cu^{2+}	Ni^{2+}
Reduction potential (V)	+0.34	-0.25
Scale of clusters (nanometer)	10	No nickel (0)

Table II Electrolytes Used in the Electrochemical Experiments

Electrolytes	Applied Power Voltage (V)	Scale of Clusters (nm)	Potential Drop Ratio of SCF to Medium
1. Sulfuric acid	3.6	10	0.80
2. Fe ²⁺ /Fe ³⁺ + sulfuric acid	2.0	50	1.15
3. Water	20	No clusters	0.74

Forming Mechanisms of MPNC

In Figure 2, the nanometric clusters can be seen in the cross section of MPNC as mentioned above. The results help to define a forming mechanism of MPNC according to the electrochemical process of reduction of SCF. The nucleation of deposited copper is initiated when the reduction voltage meets the requirement of reducing Cu²⁺ to Cu⁰ in the nanometric range (about 10 nm) in SCF and the growth of those nuclei resulting from dispersion and reduction of Cu²⁺ in the nanometric range. We called this process the nanometric cell-reduction (NCR) mechanism. Obviously, it differs from the conventional mechanism of ionic reduction.

Figure 5 shows that the active ionic transfer can be divided into two periods: One is before 75 min and the other is after 75 min. When the power voltage is constant, the current in the electric loop has a larger value in the first period. Correspondingly, the movable ions in this period should have greater activity to disperse in SCF. We associate this result with the photograph of Figure 2 and suggest that this period corresponds to the nucleation of crystal of copper nanometric clusters and the major growth of crystals. The ion transfer in SCF in this period should come from the change of macromolecular chain conformation in the related nanometric region.²¹ After 75 min, the current in the electric loop becomes lower and

almost constant. In this period, the reduction reaction of Cu²⁺ has a lower rate.

Effects of Metal Clusters on Polymer Host Matrix

Figure 6 shows the results of FTIR of the PVC film (curve 1) and the electrolyzed PVC film (curve 2) under the electrochemical conditions of preparing MPNC. In comparing curves 1 with 2, all the absorption bands of the characteristic groups appear and the intensities of these peaks are similar. Thus, the electrochemical conditions do not cause side reactions on the PVC chains.

The results of DSC are depicted in Figure 7. In comparing curve 1 with curve 2, the glass transition temperature and the thermal degradation temperature are decreased from 123°C of PVC to 92°C of MPNC and from 233°C of PVC to 201°C of MPNC, respectively. We analyzed the change of the glass transition temperature in the previous article¹⁴ and the change of the thermal degradation temperature should be ascribed to the catalyzing effect of copper(II) and/or copper(I), as mentioned in many references.^{22–28} Another difference between curves 1 and 2 is the thermal absorption peaks at 110 and 201°C. They show

Table III Effect of Electrode Materials on Morphology of MPNC

	Scale of Clusters (nm)	Applied Power Voltage (V)
Copperized column (Φ 20 × 50 mm)	10	3.6
Graphite column (Φ 30 × 50 mm)	50	2.0

Table IV Effect of Electrochemical Conditions on Morphology of MPNC^a

	Applied Power Voltage (V)		Temperature (°C)	
	2.8	3.6	30	60
Scale of clusters (nm)	9	2.2	9	8.8

^a The cathode material is a copperized column.

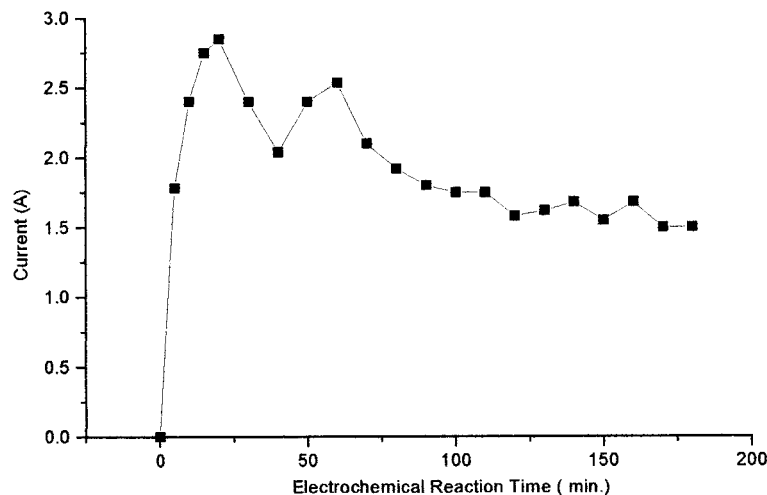


Figure 5 Change of current versus electrochemical reaction time with constant voltage. The synthesized conditions are the same as in Figure 2.

the shapes of an inverse bell and are explained as the retarded movement of the related macromolecular units,²⁹ which are macromolecular segments at 110°C and macromolecular chain movement at 201°C, respectively.

CONCLUSIONS

This study demonstrates the validity of SRS by which an MPNC can be prepared. SRS has more predominance than have other methodologies, re-

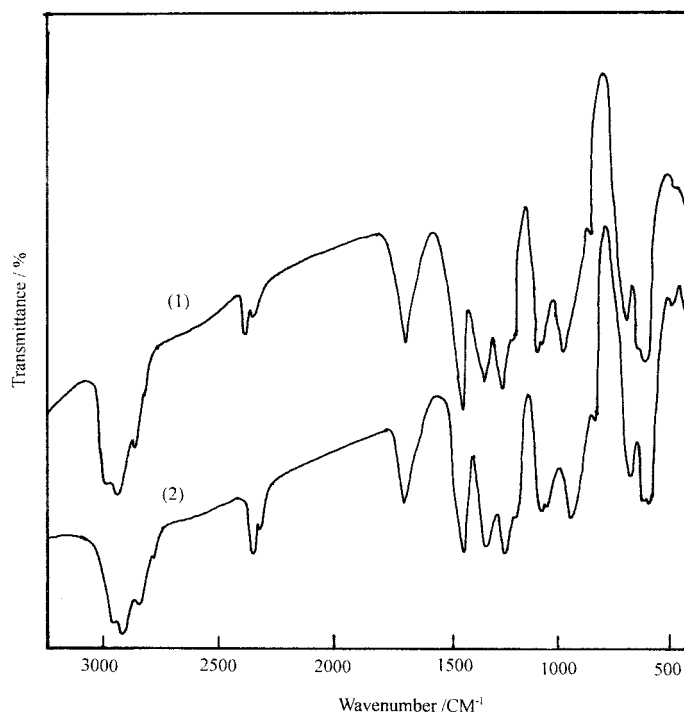


Figure 6 FTIR of MPNC and PVC matrix. Synthesized conditions—(A) sample of MPNC: power voltage, 20 V; predrying time of SCF at ambient temperature, 24 h; ratio of molar side —Cl groups on PVC to molar copper ions, 1.6:1; copperized column as cathode. (B) PVC sample was prepared by dissolving PVC powder in THF and drying at 80°C under a vacuum for 4 h.

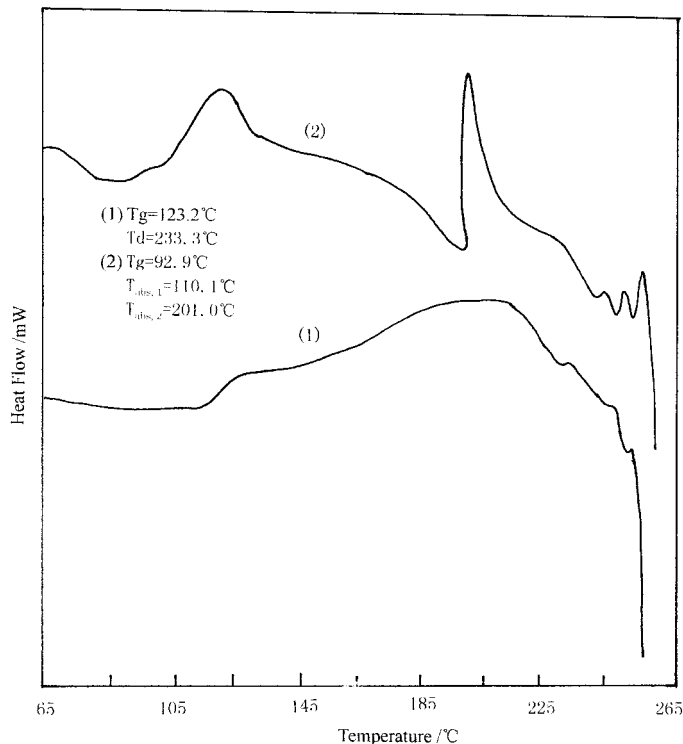


Figure 7 DSC of MPNC and matrix. Synthesized conditions—(A) MPNC sample: power voltage, 3.6 V; predrying time of SCF at ambient temperature, 24 h; ratio of molar side —Cl groups on PVC to molar copper ions, 1.6:1; copperized column as cathode. (B) PVC sample was prepared by dissolving PVC powder in THF and drying at 80°C under a vacuum for 4 h.

ported elsewhere.^{30–32} MPNC has an eminent characteristic of close bonding between the metal cluster surface and the polymer host. Further study on MPNC is needed to understand the NCR mechanisms.

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REFERENCES

- Cahn, R. W. *Nature* 1992, 359, 591.
- Li, Y.-D.; Duan, X.-F.; Qian, Y.-T.; Yang, L.; Ji, M.-R.; Cheng, W.-L. *J Am Chem Soc* 1997, 119, 7869.
- Gonsalves, K. E.; Strutt, P. R.; Xiao, T. D.; Klumens, P. G. *J Mater Sci* 1992, 27, 3231.
- Mahamuni, S.; Bendre, B. S.; Leppert, V. J.; Smith, C. A.; Cooke, D.; Risbud, S. H.; Lee, H. W. H. *Nanomet Struct Mater* 1996, 7, 659.
- Schulz, D. L.; Pehnt, M.; Curtis, C. J.; Ginley, D. S. *Mater Sci Forum* 1996, 169, 223–227.
- Kundu, T. K.; Chakravotry, D. *J Mater Res* 1994, 9, 2480.
- Roy, S.; Chatterjee, A.; Chakravotry, D. *J Mater Res* 1993, 8, 689.
- Gillbert, S. E.; Cavalleri, O.; Kern, K. *J Phys Chem* 1996, 100, 12123.
- Golden, J. H.; Deng, H.; DiSalvo, F. J.; Frechet, J. M. J.; Thompson, P. M. *Science* 1995, 268, 1463.
- Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P. *Science* 1995, 267, 1629.
- Gao, M.; Zhang, X.; Yang, B.; Li, F.; Shen, J. *Thin Solid Films* 1996, 242, 284–285.
- Golden, J. H.; DiSalvo, F. J.; Frechet, J. M.; J. Silcox, J.; Thomas, M.; Elman, J. *Science* 1996, 273, 782.
- Tang, J.; Chu, X.; Gao, X.; Zhao, W. *J Appl Polym Sci* 1996, 61, 1773.
- Tang, J.; Hu, K.; Fu, S.; Qi, H.; Cui, W.; Jia, Z.; Li, K.; Pang, H.; Wang, F. *J Appl Polym Sci* 1998, 69, 1159.
- Schultz, D. L.; Pehnt, M.; Curtis, C. J.; Ginley, D. S. *Materials Science Forum* 1996, 225–227, 169.

16. Sankaran, V.; Yue, J.; Cohen, R. E.; Schrock, R. R.; Silbey, R. *J Chem Mater* 1993, 5, 1133.
17. Francis, C. G.; Huber, H.; Ozin, G. A. *Inorg Chem* 1980, 19, 219.
18. Joint Committee on Powder Diffraction Standards (JCPDS): Powder Diffraction File [sets 1–5 (reversed)]: Inorganic volume, No. PD 1s–5iRB; pp 583, 664.
19. Hiemenz, P. C. *Polymer Chemistry: The Basic Concepts*; Marcel Dekker: New York, 1984; pp 48–67.
20. Sohn, R. H.; Cohen, R. E. *Acta Polym* 1996, 47, 340–343.
21. Translated (from Japanese) by Fang, S. B.; Wang, Y. P.; Wang, L.; Ye, C.; Chen, S. J.; Cao, W. X.; Li, F. J. *Gao Fen Zi Luo He Wu De Dian Zi Gong Neng*; Beijing University: Beijing, 1992; p 108.
22. Okieimen, F. E.; Ebhoaye, J. E. *Polym J* 1992, 28, 1423.
23. Troev, K.; Kisova, T.; Grozeva, A.; Borisov, G. *Polym J* 1993, 29, 1499.
24. Allan, J. R.; Binnie, B. *Polym J* 1991, 27, 1035.
25. Day, M.; Conney, J. D.; Mackinnon, M. *Polym Degrad Stab* 1995, 48, 341.
26. Khairou, K. S. *Polym Degrad Stab* 1994, 46, 315.
27. Jouse-Lius, S.; Hughes-Dillon, M. K. *Polym Degrad Stab* 1994, 46, 241.
28. Allan, J. R.; Baillie, G. M.; Bowley, H. J.; Gerrard, D. L. *Eur Polym J* 1988, 24, 1149.
29. Bershtein, V. A.; Egorov, V. M. *Differential Scanning Calorimetry of Polymers—Physics, Chemistry, Analysis, Technology*; Ellis Horwood: Chichester, 1994.
30. Wang, D.-H. *Thin Solid Films* 1996, 288, 254–255.
31. De, G.; Epifani, M.; Licciulli, A. *J Non-Crystal Solids* 1996, 201, 250–255.
32. Clay, R. T.; Cohen, R. E. *Supramol Sci* 1995, 2, 183–191.