Radiation synthesis of the nano-scale materials

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Abstract Some recent research jobs on fabricating the nano-scale materials via γ-irradiation in our laboratory are simply summarized in this paper. The main contents contain four aspects: (1) the preparation of metal alloy - powders; (2) the fabrication of polymer -metal nano-composites in aqueous solution, micro-emulsion and emulsion systems; (3) the synthesis of metal sulfide nano-particles and (4) the preparation of the ordered nano-structure materials. The corresponding preparation processes are also simply described.

Key words radiation synthesis nano-scale materials alloy-powders polymer - metal nanoparticles ordered nano-structure materials

It is well known that the radiolysis of water by γ-ray initially generates many products[1]:

$$H_2O \sim\sim\rightarrow e_{aq}^-, H\cdot, \cdot OH, H_2, H_2O_2, H_3O^+$$

In these products, the reduction potential of e_{aq}^- is as low as -2.77v. Theoretically, it can reduce all metals' ions except alkali metal and alkali-earth metal ions, and some higher valence non-metal elements (such as sulfur) to the lowest valence state. It is owing to above reason that radiation synthesis method of the nano-scale materials has been developed. This method has many virtues, for example, that the reaction condition is mild — room temperature and atmosphere pressure; preparation technology and manipulation process are simple; producing time is short and the yield is high. So much attention has been paid to it.

Our laboratory has been researching radiation synthesis of the nano-scale materials. At present, our jobs which have been finished and will be completed mainly contain metal alloy-powders[2-3], nano-composites[4-6], metal sulfides nano-particles[7], sorts of ordered nano-structure materials and so on.

1. the preparation of metal alloy-powders

Ultrafine alloy powders are important in many application fields such as

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catalysts[8-11], electrodes[12-13], pastes of different types and electric applications[9], so there have been many researches in their preparation. The γ-ray irradiation method is one of many preparing routes. Employing it, the faber-like Nickel - Silver and the spheric-shaped Copper - Palladium alloy-powders have successfully been prepared in our laboratory. By and large, the preparation process can be described as follows:

The solutions were formed by dissolving appropriate amounts analytical grade metal salts into distilled water, adding $NH_3 \cdot H_2O$ as a complex agent up to about pH = 10. Polyvinyl alcohol (or sodium dodecyl benzene sulfonate (SDBS)) was chosen as a surfactant and isopropanol as a scavenger for oxidative free radicals. All solutions were deaerated by bubbling with pure nitrogen, then irradiated in the field of a 2.59×10^{15}Bq ^{60}Co γ-ray source at a dose rate of 50 Gy/min. The precipitates obtained from the irradiated mixed solutions were washed with distilled water, ammonia aqueous solution and alcohol several times, then dried to powders.

XRD patterns of the samples show that the size of Ni - Ag alloy powders is about 20nm and of Cu - Pd alloy powders 10nm(see fig.1. (a), (b)). TEM images of the samples are shown in Fig.2, from which morphologies of the samples are clearly seen.

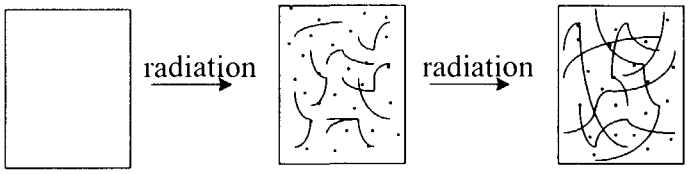
2. the fabrication of Polymer - metal nano-composites

Nano-composites with special electronic and optical properties are the materials in which the dimension of dispersed matter ranges from 1nm to 100nm. With respect to their different supporters, the nano-composites are usually divided into two kinds, namely inorganic and organic supporter system. Our laboratory mainly study the fabrication of organic supporter nano-composites. Up to now, we have fabricated several kinds of polymer - silver nano-composites via γ-irradiation in aqueous solution, micro-emulsion and emulsion systems.

2.1 Polyacrylamide - silver nano-composites were prepared in aqueous solution. γ-irradiation was employed to initiate both the polymerization of monomers and the reduction of silver ions. So the polymeric host and the dispersed phase were formed in the same step. But comparatively speaking, the polymerization of acrylamide monomers is quicker than the reduction and aggregation of silver ions. The earlier formed polyacrylamide chains lead to increase the viscosity of the system, which limit the further aggregation of silver particles and make them well dispersed in polymer matrix(see fig.3). However, it is also found that the existence of hydroxide radical scavenger (isopropanol) in system has a great influence on the properties of nano-composites. The silver particles of a system without isopropanol are sparsely dispersed in the polymer matrix and 50% of them are 7 - 12nm in diameter (see fig.3.a). When isopropanol is added to the system, the concentration of silver particles increases. Comparing with the former, the silver particles of the latter have a different

size distribution. It seems that there are two distribution peaks in TEM images. Many silver particles are 10 -15nm in diameter, but there are many more particles with diameters of about 1 - 5nm (see fig.3.b). At the same time, the experiment also reveals that the isopropanol influences the properties of polymer matrix because of some factors such as the apparent chain transfer of isopropanol.

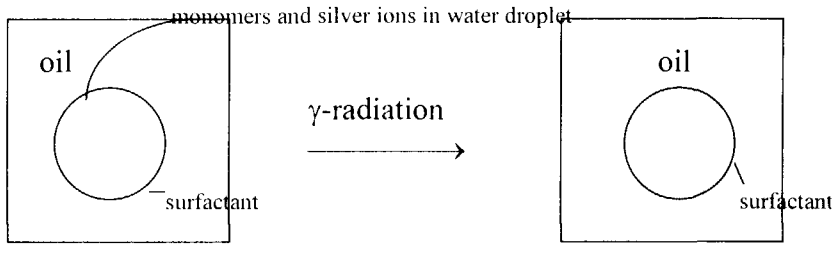
The synthetic process can be simply explained with the following graphs:



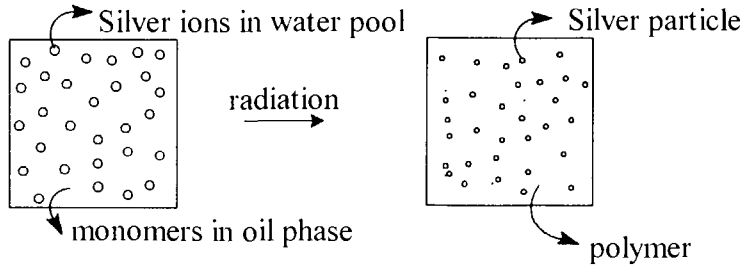
2.2 Polymer - silver nano-composites have been synthesized in micro-emulsion and different kinds of nano-composites are obtained when we adjust the composition of micro-emulsion. (1) When aqueous soluble monomers are introduced into water pools in W/O micro-emulsion, nano-composites with silver nano-particles in aqueous soluble polymer matrix are obtained; (2) When oil soluble monomers are introduced into continuous oil phase and silver ions in water pools, nano-composites with silver nano-particles in non-aqueous soluble polymer matrix are obtained; (3) When monomers are dispersed in both oil phase and aqueous phase while silver ions in water pools, the final products are stable polymer composite micro-spheres containing silver nano-particles; (4) Polymer micro-spheres immobilized with silver nano-particles have also been prepared by irradiating the O/W micro-emulsion, in which monomer droplets are dispersed in continuous aqueous phase.

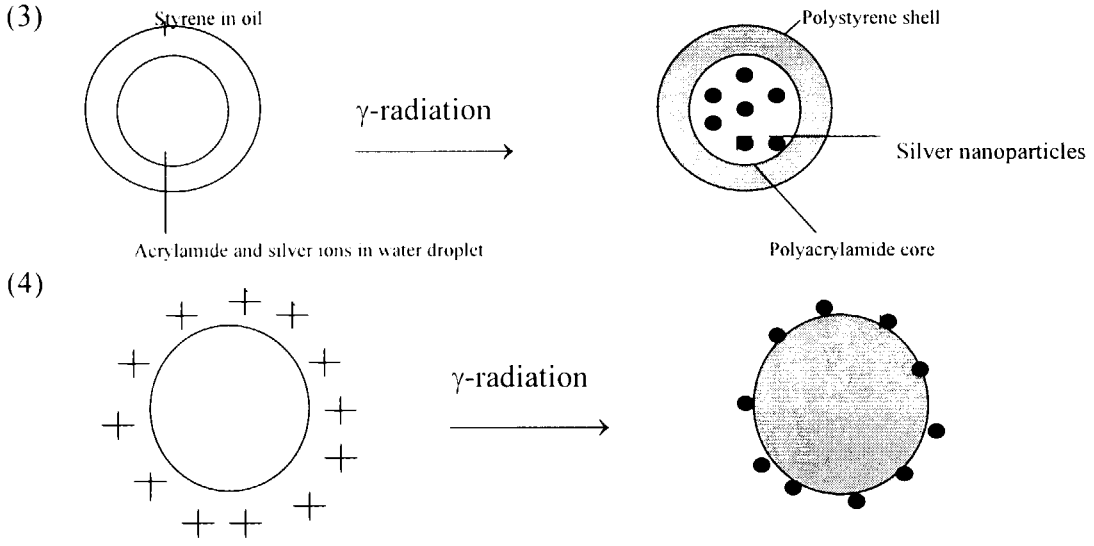
The formed processes of polymer - silver nano-composites in above four conditions can be graphed respectively as follows:

(1)



(2)





The XRD patterns and TEM micrographs of the products are shown in fig.4.

2.3 Emulsion systems have been employed to prepare nano-composites with silver particles in non-aqueous soluble polymer matrix, adding some aqueous soluble monomers to improve the dispersion and stabilization of silver nano-particles in polymer matrix. Generally speaking, there are two routes to fabricate nano-particles in emulsion systems with γ-irradiation. One is two steps synthesis: At first, monomers polymerize under γ-irradiation, and then inorganic salt is added and irradiated. The virtues of this method are that molecular weight of polymer can be adjusted and, owing to the formation of polymer, the system will immobilize more than before polymerization, which leads to the emulsion not being destroyed when inorganic salt is introduced. But more steps is its shortcoming. Another is one step synthesis: namely, O/W emulsion containing monomers and silver ions is irradiated directly with γ-ray. In this way, both the polymerization of monomers and the reduction of metal ions are induced by γ-ray at the same time. But it is difficult to obtain polymer with appropriate molecular weight and nano-particles with appropriate diameters.

Using the two steps synthesized route, we have obtained poly-(styrene-co-acrylate-co-butyl acrylate)-silver, poly-(styrene-co-methylacrylate-co-butyl acrylate)-silver etc. nano-composites. Their TEM images are shown in fig.5. We have also obtained poly-(styrene-co-acrylate-co-acrylonitrile)-silver nano-composites through one step synthesized route. A interesting fractal phenomenon of silver nano-particles is observed by TEM (see fig.6). However, up to now, there is not a good model to explain it.

3. the synthesis of metal sulfide nano-particles

Usually, metal sulfide nano-crystals have many unique properties and special applications, in particular, group II-VI such as cadmium sulfide are a kind of important semiconductor nano-materials. So much interest is focused on their

preparation. To synthesize metal sulfide nano-particles, we utilize sodium thiosulfate ($Na_2S_2O_3$) or mercapto ethanol as the reservoir of S^{2-} ions. A series of changes will occur when their aqueous solution are irradiated via γ-ray.

$H_2O \sim\sim\rightarrow H\cdot,\ \cdot OH, e_{aq}^-, H_2O_2, H_3O^+,$ ... ①

$S_2O_3^{2-} + e_{aq}^- \rightarrow \cdot S^- + SO_3^{2-}$ ..... ②

$\cdot S^- + e_{aq}^- \rightarrow S^{2-}$ .....③

$\cdot S^- + \cdot H \rightarrow S^{2-} + H^+$ .....④

$\cdot S^- + \cdot OH \rightarrow S + OH^-$ .....⑤

After isopropanol is added into the solution, the oxidative free radicals such as $\cdot OH$ are scavenged.

$\cdot OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2COH\cdot$

The reductive atmosphere of the system is maintained and the yield of nano-particles is improved. When metal cations exist in the solution, the sulfide particles are formed by precipitating reaction.

$n\ M^{2+} + n\ S^{2-} \rightarrow (MS)_n$ (M = Cd, Zn, Pb . . .)

In order to prevent the small sulfide particles from coming into close contact and undergoing further aggregation, a certain amount of surfactant sodium dodecyl sulfate (SDS) is also needed in the system.

The further studies show that some factors such as the absorbed dose, the concentration of the surfactant and the reductant can influence the size of products. Fig.7(a), (b) shows the XRD pattern and TEM image of CdS nano-particles, respectively.

In addition, we first combined γ-ray radiation with hydrothermal treatment to have successfully prepared Nickel disulfide nano-crystal[14].

4. the preparation of the ordered nano-structure materials

The low dimensional nano-scale materials such as nano-rods, nano-wires and nano-tubes are attracting much interest, due to their unique physical and chemical properties and potential important applications. There have been many reports of preparing kinds of the ordered nano-structure materials. But seen from literatures, a synthetic template is often needed. These templates comprise carbon nano-tubes and the nano-channels in nuclear track polycarbonate membranes or porous alumina. Furthermore, certain rodlike cationic surfactant micelles have also been employed as templates for fabricating rodlike nano-particles. There is no doubt that the template methods provide a convenient route to synthesize the low dimensional nano-structure materials, but the obtainment of these templates is not very easy.

Recently, we have successfully solved above problem through utilizing carbamide as the synthetic template. Not only the procedure of manipulation is very simple, but also the reaction condition is quite mild (room temperature and constant

pressure). This method, as we know, is first used to prepare the ordered nano-scale materials in the world. At present, we have prepared cadmium sulfide nano-rods[15] and silver nano-ribbons[16]. Their TEM micro-graphs and electron diffraction patterns and XRD pattern of CdS nano-rods are shown in fig.8. The preparation process can be simply described as follows:

After the reactants were dissolved in distilled water, amounts of carbamide was added into the solutions at relatively high temperature and then was crystallized rapidly at room temperature. Finally, the crystal contained the reactants was irradiated by γ-ray. After carbamide was dissolved with distilled water, the products were obtained.

A possible formation process can be speculated. When carbamide crystallized from the solutions at room temperature , due to the presence of the defects, a little of the solutions was embedded in carbamide matrix. After γ-radiation, the yielded particles further aggregated and grew. But owing to the confinement of the defects, they were obliged to reorganize. Because the defects appeared random and meandering, they could only grow expitaxially in accordance with the shapes and sizes of the defects. Thus, the low dimensional nano-scale materials with sorts of shapes and sizes were formed.

Moreover, we have also successfully synthesized α-FeO(OH) and γ-Fe_2O_3 nano-rods without using any templates in water system, CdS nano-wires in non-aqueous system, respectively.

The above jobs have been completed or are being finished in our laboratory. Now we are searching a way to prepare new nano-structure materials under γ-radiation condition.

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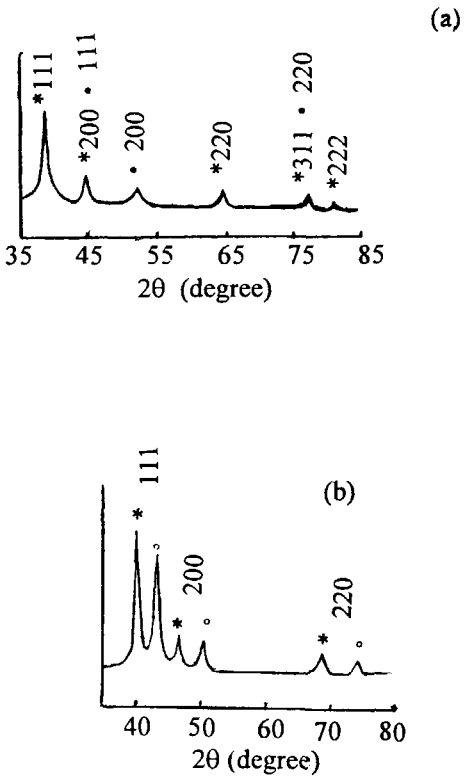


Figure1 XRD patterns of the samples. (a) Ni - Ag alloy powders (*Ag, • Ni); (b) Cu - Pd alloy powders(*Pd, ◦ Cu).

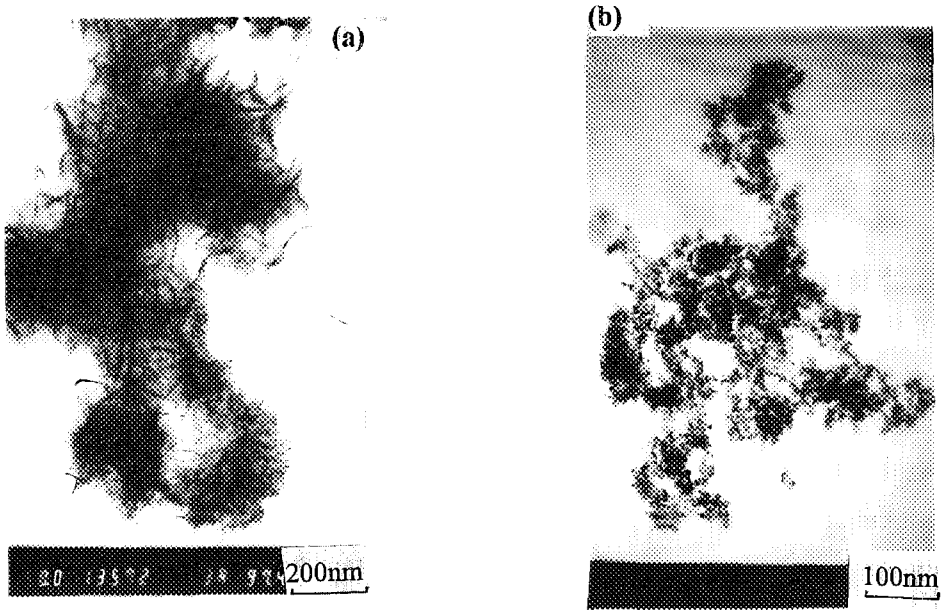


Figure2 TEM images of the samples. (a) Ni - Ag; (b) Cu - Pd alloy powders.

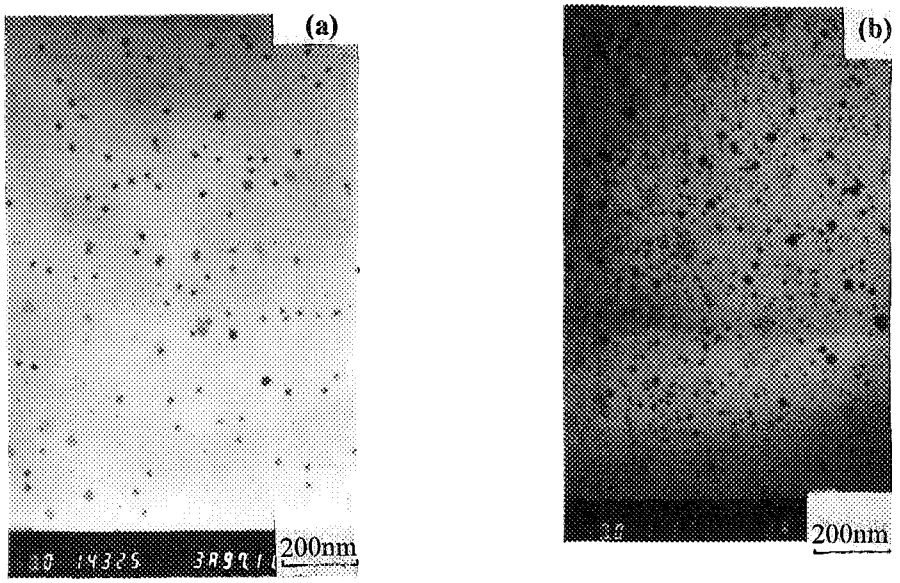


Figure3 TEM images of polyacrylamide - silver nanocomposites prepared in aqueous solution via γ-irradiation. (a) without isopropanol; (b) containing isopropanol.

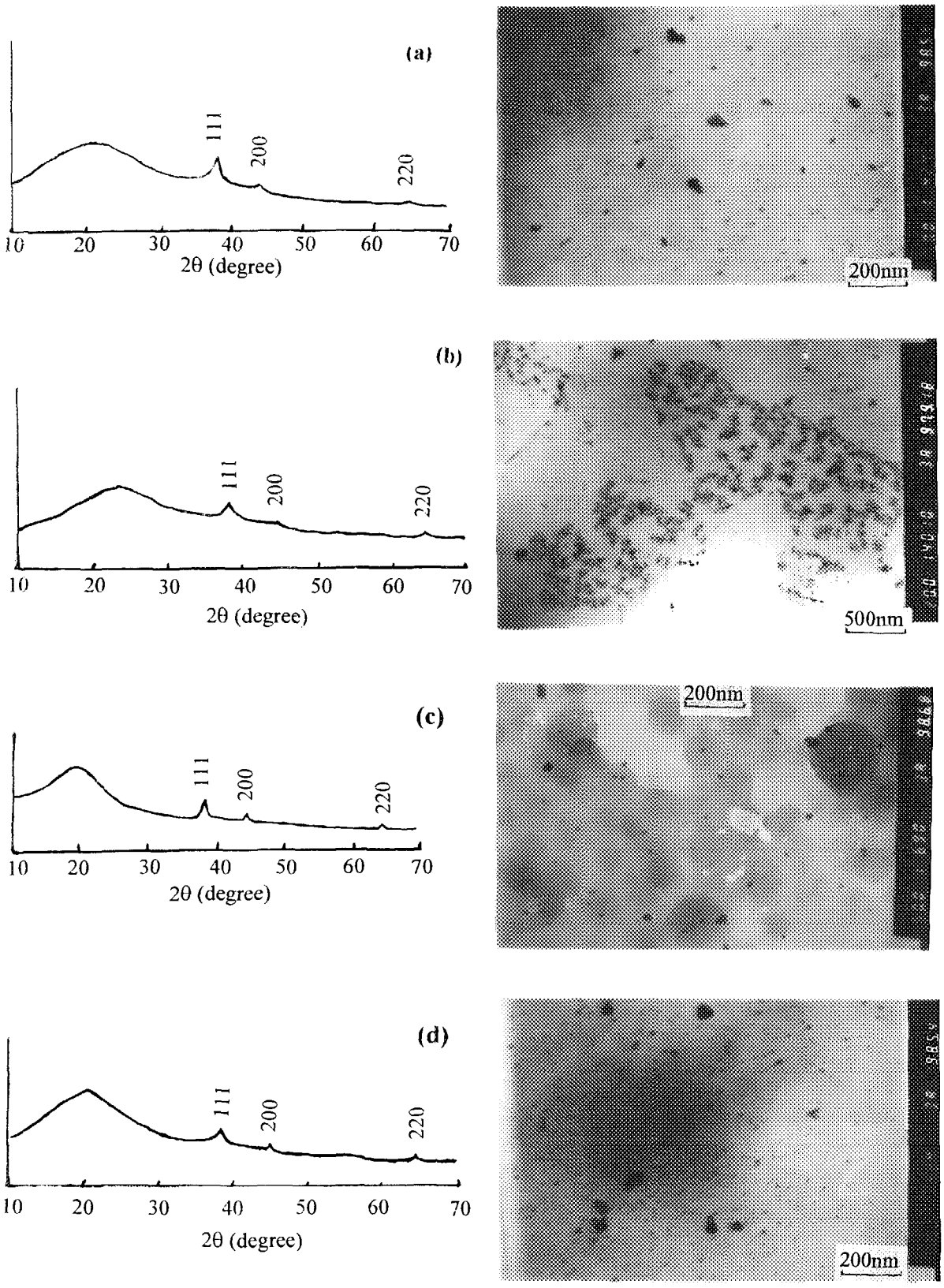


Figure4 the XRD patterns and TEM micrographs of the products fabricated in micro-emulsion systems. (a) polyacrylamide-silver nanocomposites; (b) poly-(butyl acrylate-co-styrene)-silver nanocomposites; (c) poly(styrene-co-acrylamide)-silver nano-spheres; (d) poly(styrene-co-methyl methylacrylate)-silver nano-spheres.

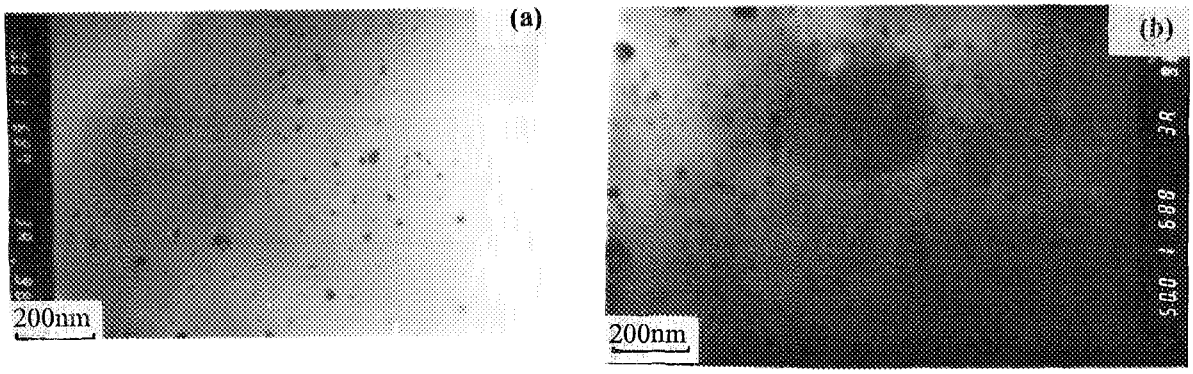


Figure5 the TEM images of the products synthesized by the two steps route in emulsion systems. (a) poly-(styrene-co-acrylate-co-butyl acrylate) - silver nano-composites; (b) poly(styrene-co-methylacrylate-co-butyl acrylate)-silver nano-composites.

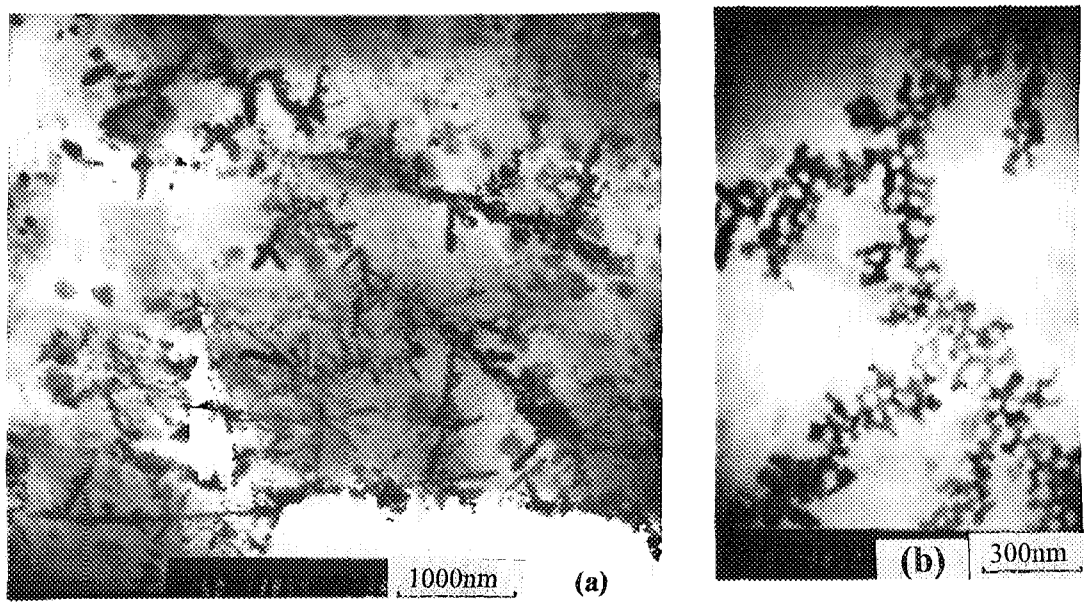


Figure6 the TEM images of poly(styrene-co-acrylate-co-acrylonitrile)-silver nano-composites. (a) branch-like fractal; (b) net-like fractal.

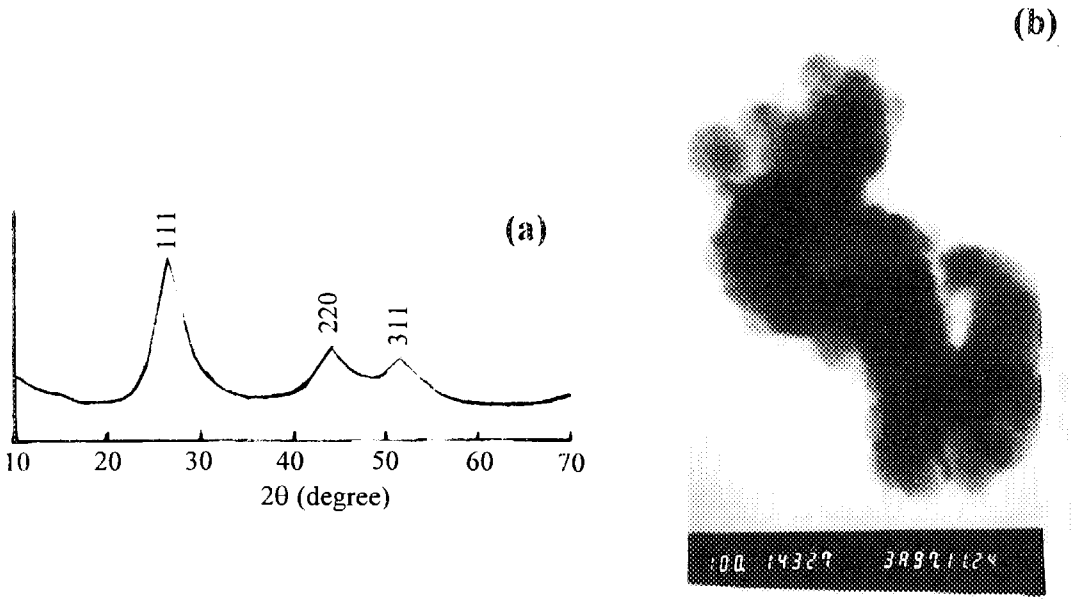
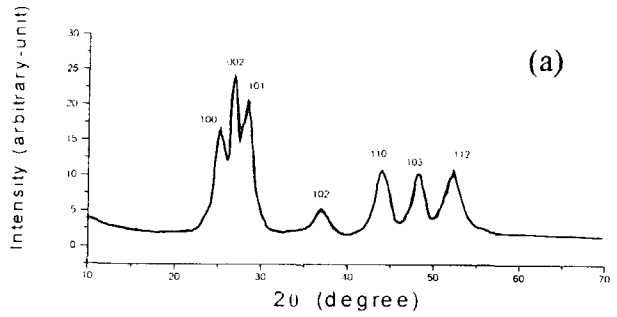
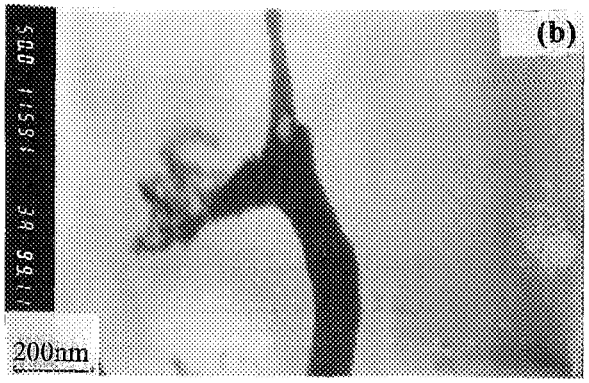
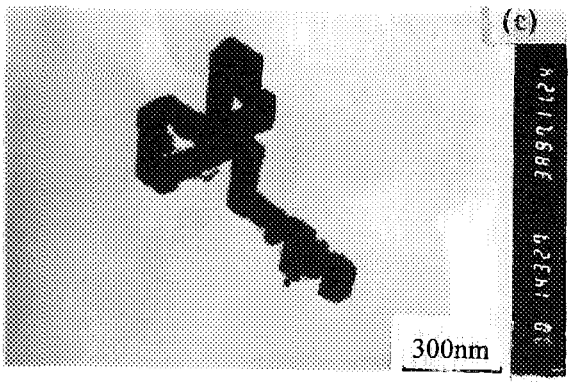
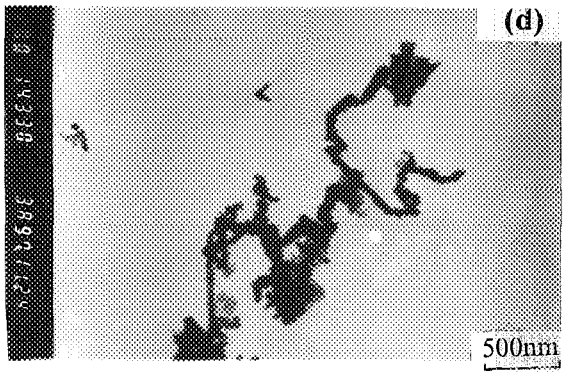


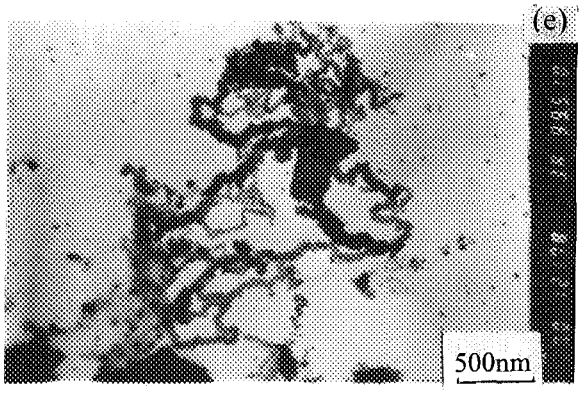
Figure7　the XRD pattern(a) and TEM micrograph (b) of CdS nanoparticles.

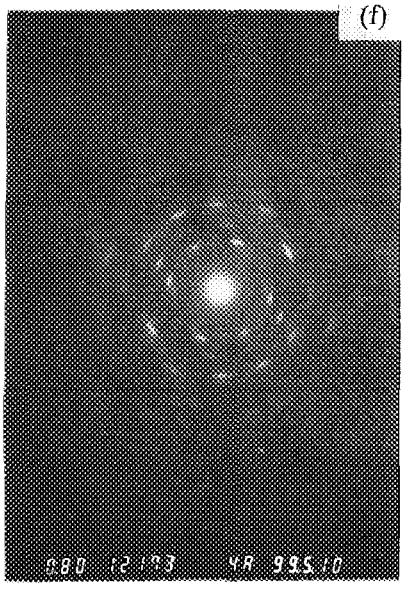












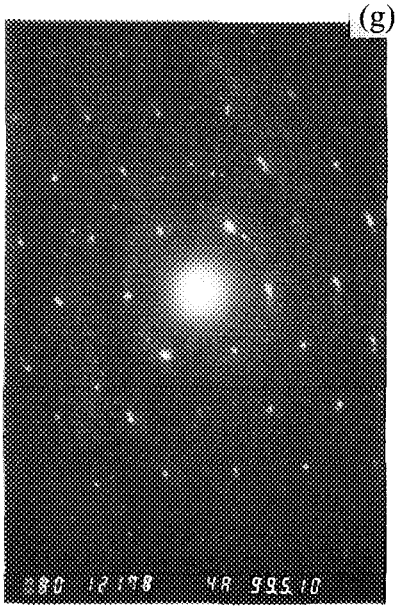


Figure8 (a) the XRD pattern of CdS nanorods; TEM images of the samples: (b) CdS nanorods; (c), (d), (e) Silver nanoribbons; the electron diffraction patterns of the samples: (f) CdS nanorods, (g) Ag nanoribbons.