

RADIOLYTIC SYNTHESSES OF NANOPARTICLES AND INORGANIC-POLYMER HYBRID MICROGELS

Q. Chen, J. Shi, R. Zhao, X. Shen, CHINA, PEOPLE'S REPUBLIC OF

Summary

In the second year of the project, we have gotten progress mainly in two directions. Firstly, for the first time, Prussian blue (PB) nanoparticles (NPs) were successfully synthesized by the partly radiolytic reduction of Fe^{3+} and $\text{Fe}(\text{CN})_6^{3-}$ in the presence of poly(N-vinyl pyrrolidone) (PVP) under N_2 atmospheres at room temperature. With the increase of the concentration of PVP, the size and the size distribution of the synthesized quasi-spherical PB NPs decreased obviously, leading to a hypsochromic shift on their peak position of the characteristic absorption. In the experiment, we further found that the smaller ones have a larger capacity to Cs^+ , suggesting that the application of PB NPs in curing thallotoxicosis may decrease the usage of PB for the patient to great extent. Secondly, through a series of preliminary experiments, we got a clear picture about the one-step radiolytic preparation of inorganic-poly(methacrylic acid-co-methyl methacrylate) hybrid microgels by surfactant-free emulsion polymerization. Besides, unpurified N-carbamothioylmethacrylamide was synthesized via the methacrylation of thiourea. These created favorable conditions for the one-step synthesis of metal sulfide-poly(methacrylic acid-co-methyl methacrylate) hybrid microgels by γ -irradiation and surfactant-free emulsion polymerization.

1. RADIOLYTIC SYNTHESSES OF INORGANIC NANOPARTICLES AND NANOSTRUCTURES IN AQUEOUS SOLUTIONS

1.1. Introduction

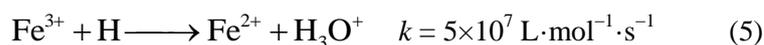
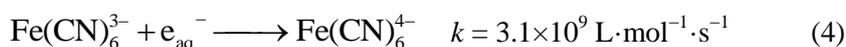
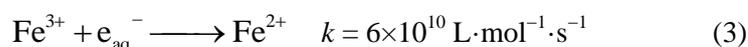
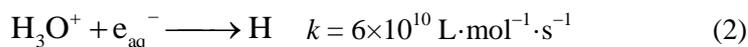
In the realm of nanoscience and nanotechnology, the largest activity has been focused on the synthesis and application of new nanoparticles (NPs) with different sizes and shapes [1-5]. Recently, the synthesis of NPs for ion-exchange began to attract much attention [6-9]. Similar to other properties, the ion-exchange performance of NPs is also affected by their morphologies. So far, the present results indicated that only a few special morphologies of some NPs (such as nanofibers, porous and layered structures) have higher exchange capacity to some heavy metal (*i.e.*, Hg^{2+} , Pb^{2+}), alkali metal and alkaline earth metal (*i.e.*, Cs^+ , Sr^{2+} , Ba^{2+}) ions. However, to the best of our knowledge, there is no report about the size effect of NPs on the exchange performance. It is believed that the systematic exploration on the NPs for ion-exchange will benefit their application in industry as well as in the field of biomedicine.

Among the numerous methods of preparing NPs, ionizing radiation (such as γ -irradiation, electron beam irradiation and so on) is powerful, since it can conveniently produce a series of species with tunable redox potentials, not be achievable by other means, in a wide range of temperature [10-13]. By far, besides few report about metal halide and nonmetal NPs [14-17], great efforts have been focused on the syntheses of metal, core-shell metal or alloy, and metal chalcogenide NPs in aqueous solution and organic solvent [10-13,18-19]. In the past several years, we tried our best not only to extend the application realm of ionizing radiation in the preparation of NPs, but also to explore the possible usage of the obtained NPs in the field of biomedicine.

1.2. Syntheses of Prussian blue nanoparticles for cesium ion-exchange

As is well known, ferric ferrocyanide, i.e., Prussian blue (PB), is not only an old blue dye, but also an efficient toxicide for thallotoxicosis. If the nano-sized PB particles have larger exchange capacity and faster exchange rate, the usage of PB for the patient will decrease to great extent. Nevertheless, the similar issue did not appear in the literature. This year, for the first time, the radiolytic synthesis of PB NPs was realized by us. Then, we paid more attention to the above-mentioned subject.

Under N_2 atmosphere, part of Fe^{3+} and $Fe(CN)_6^{3-}$ ions in the aqueous solution ($pH = 2.8$) were simultaneously reduced to Fe^{2+} and $Fe(CN)_6^{4-}$ ions by the radiolytically generated hydrated electrons (e_{aq}^-) and H atoms (Eqs. 1-6).



Then, PB NPs were generated by precipitating the obtained $Fe(CN)_6^{4-}$ ions with the residual Fe^{3+} ions. With respect to the Fe^{2+} ions, they were precipitated by the residual $Fe(CN)_6^{3-}$ ions, leading to the formation of thenard's blue NPs. Because PB and thenard's blue have the same structure, pure PB NPs were successfully obtained, which was confirmed by their X-ray diffraction pattern and X-ray photoelectron spectrum.

To obtain monodispersed PB NPs, several kinds of protective agents were tested. Meanwhile, poly(*N*-vinyl pyrrolidone) (PVP) was the most effective. The added PVP can eliminate the radiolytically generated oxidative $\cdot OH$ radicals and produce a reductive circumstance, favoring the generation of PB NPs. Besides, PVP can effectively protect the generated PB NPs from aggregation and growth. With the increase of the concentration of PVP, the size and the size distribution of the synthesized PB NPs decreased obviously (Figure 1 and Table 1).

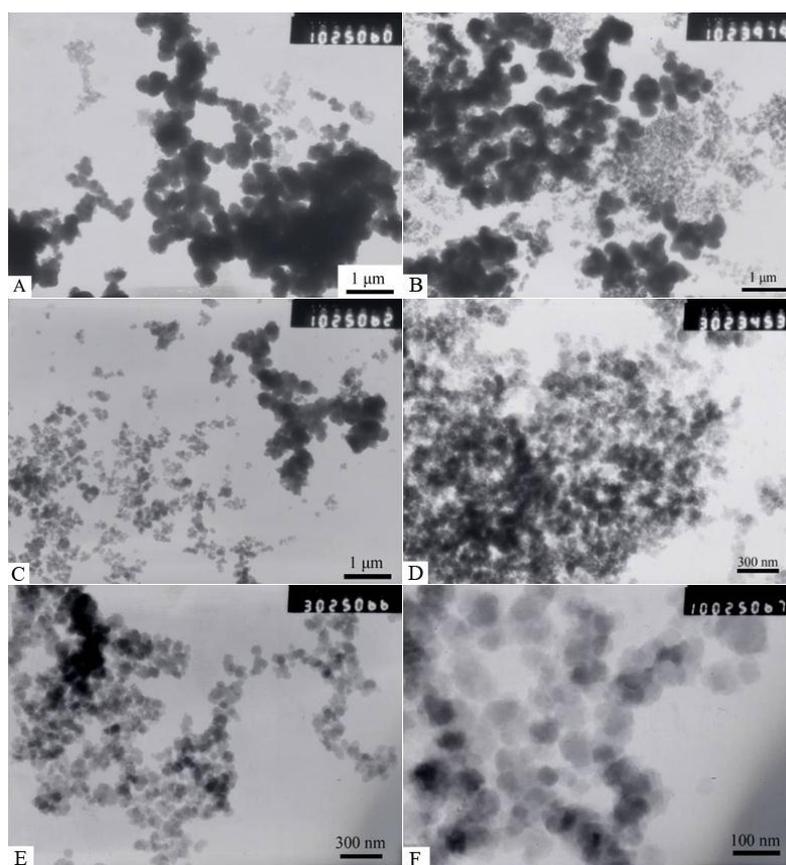


FIG. 1. TEM images of the samples synthesized at the different concentration of PVP (from A to F, [PVP] = 11.1, 22.2, 33.3, 55.6, 77.8, 77.8 mg·L⁻¹). The irradiation time and the dose rate are fixed at 1000 min and 10 Gy·min⁻¹, respectively.

As an old blue dye, the color of PB comes from the electron transfer between Fe (II) and Fe (III) in PB, *i.e.*, Fe^{III}(t_{2g}³e_g²)-CN-Fe^{II}(t_{2g}⁶) and Fe^{II}(t_{2g}⁴e_g²)-CN-Fe^{III}(t_{2g}⁵). As to their UV-vis spectra, the peak position of the characteristic absorption is always larger than 700 nm [20-22]. However, as far as we know, there is no report about the size effect on the optical properties of PB NPs. Here, with the decrease of the size and the size distribution of the synthesized PB NPs, their peak position of the characteristic absorption has a hypsochromic shift from larger than 900 nm to 735 nm, which presents an obvious size effect.

TABLE 1. EFFECT OF THE CONCENTRATION OF PVP ON THE SIZE, THE PEAK POSITION OF THE CHARACTERISTIC ABSORPTION AND THE ION-EXCHANGE CAPACITY OF THE OBTAINED PRUSSIAN BLUE NANOPARTICLES

[PVP]/ mg·L ⁻¹	11.1	22.2	33.3	44.4	55.6	66.7	77.8	88.9
ϕ /nm	50~200	80~200	80~170	80~150	80~120	70~100	70~100	~70
λ_{\max} /nm	>900	880	830	805	795	763	750	735
Q /mmol·g ⁻¹	–	0.285	–	0.299	–	0.389	–	0.426

Because of the hypertoxicity of TI⁺ and the similar properties between Cs⁺ and TI⁺, in our experiment, Cs⁺ was used as a simulacrum of TI⁺ to investigate the ion-exchange performance of the obtained PB NPs. It was found that they have a quicker exchange rate. In detail, the

equilibration time is about 60 min. With the decrease of the size and the size distribution of the synthesized PB NPs, their exchange capacity has a remarkable increase from $0.285 \text{ mmol}\cdot\text{g}^{-1}$ to $0.426 \text{ mmol}\cdot\text{g}^{-1}$ (Table 1), which also presents an obvious size effect. Moreover, the ion-exchange between Cs^+ and PB NPs is in accordance with the isothermal equation of Freundlich. This may be ascribed to the larger surface area of the smaller PB NPs and the exchange mainly take place on the surface of PB NPs. Therefore, the application of PB NPs in curing thallotoxicosis may decrease the usage of PB for the patient to great extent.

This part of work has been prepared as a manuscript, which will be submitted as soon as possible.

1.3. Radiolytic syntheses of mesoporous BaSO_4 microspheres

Method 1

In our previous work, “solid” BaSO_4 microspheres, mainly consisting of quasi-spherical NPs, have been synthesized by precipitating Ba^{2+} ions with SO_4^{2-} ions, which were generated from the reduction of $\text{K}_2\text{S}_2\text{O}_8$ in the presence of EDTA at an absorbed dose of 6 kGy under N_2 atmosphere by γ -irradiation [23]. According to the results of N_2 adsorption-desorption isotherm experiment, the “solid” BaSO_4 microspheres synthesized at an absorbed dose of 5 kGy under N_2 atmosphere are mesoporous and the diameter of the pores is about 4 nm, which is not easy to be found by SEM (Figures 2A and 2B). While the absorbed dose increases to 20 kGy, most of the synthesized BaSO_4 microspheres have an obvious mesoporous structure (Figure 2C) and the pore size is in the range of 20–60 nm (Figure 2D). This is the first report about the synthesis of mesoporous BaSO_4 microspheres with a larger pore size. The results of fragment analysis show that the former is constructed by quasi-spherical NPs and few irregular nanorods (Figure 3D), while the latter mainly consist of irregular nanorods and there is a small angle between the building blocks, leading to the radial arrangement of the nanorods (Figure 3A-3C). The generation of BaSO_4 has been confirmed by XRD, XPS and SAED (selected area electron diffraction) analysis.

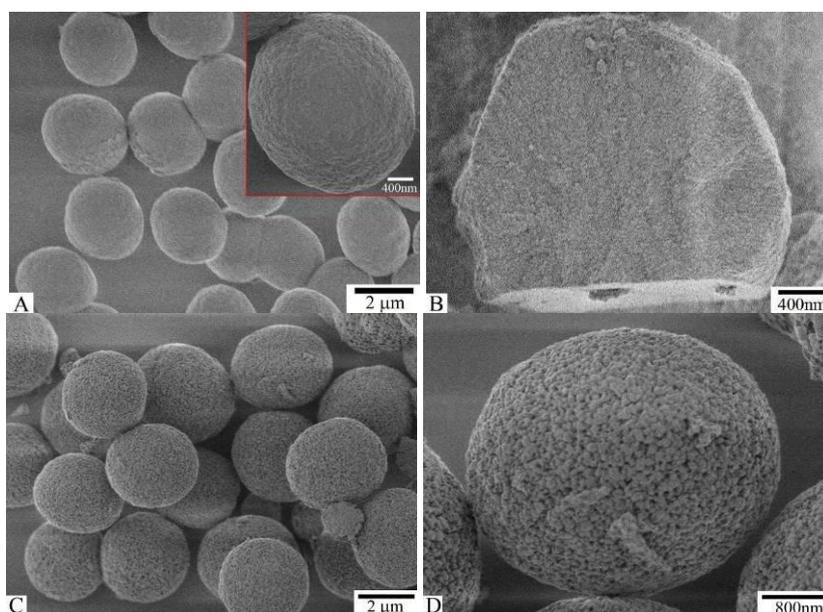


FIG. 2. SEM images of the samples synthesized with different absorbed doses: (A and B) 5 kGy, (C and D) 20 kGy.

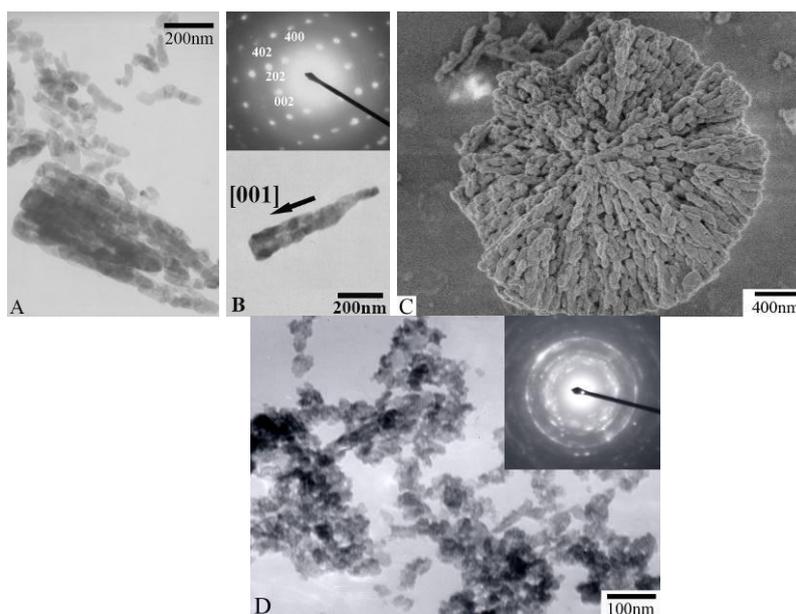
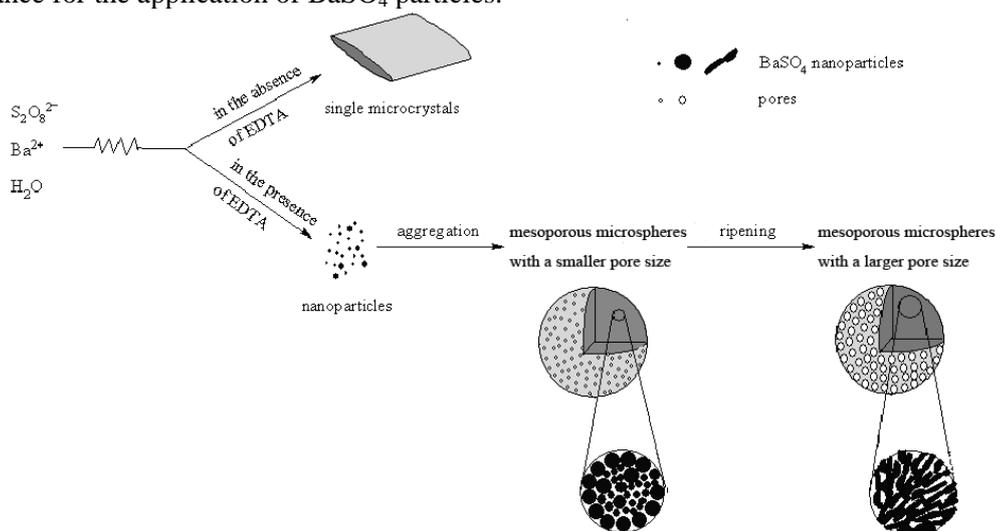


FIG. 3. TEM (A, B, D) and SEM (C) images of the fragments in the samples synthesized with different absorbed doses: (A –C): 20 kGy, (D): 5 kGy. The inset shows the SAED pattern of the corresponding product.

It is confirmed that the mesoporous microspheres with a larger pore size evolved from the mesoporous microspheres with a smaller pore size, which are generated at the early stage of irradiation course and are mainly constructed by quasi-spherical NPs, through Ostwald ripening (Scheme 1). In the process, some species may preferentially adsorb on the surfaces parallel to the [001] axes of BaSO₄ NPs, resulting in the formation of nanorods. It is the radial arrangement and the irregular shape that cause the generation of the mesoporous structure with larger pore size. Moreover, the controlled release of SO₄²⁻ and thus the slow generation rate of BaSO₄ may result in the in-situ formation of monolayer of BaSO₄ microspheres on the glass, which is of great importance for the application of BaSO₄ particles.



Scheme 1. Growth mechanism of mesoporous BaSO₄ microspheres with a larger pore size.

This is the work finished in the first year. This year, part of them has been published in *Crystal Growth & Design* as an communication. As to the specific species leading to the morphology transformation of BaSO₄ NPs, the preliminary experiment suggest that this may be the result of the coactions of S₂O₈²⁻ and H₃O⁺. The detail mechanism is still under investigation.

Method 2

Under N₂O atmosphere, most of the synthesized BaSO₄ microspheres have an obvious mesoporous structure (Figure 4A) and the pore size is in the range of 20–60 nm (Figure 4B). The mesoporous BaSO₄ microspheres with a larger pore size mainly consist of irregular nanorods, too.

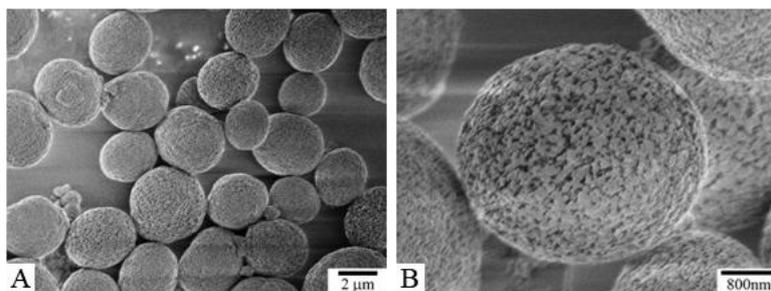
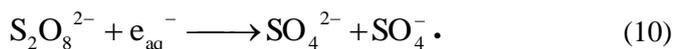
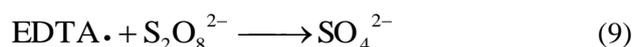
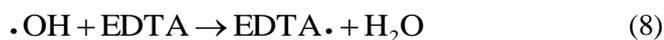


FIG. 4. SEM images of the BaSO₄ microspheres synthesized under N₂O atmospheres by γ -irradiation at an absorbed dose of 6 kGy.

Possible mechanism: e_{aq}⁻, one of the radiolytic product of water, is transformed to \cdot OH (Eq. 7) under N₂O atmosphere, which then is eliminated by EDTA, leading to the generation of EDTA radical (Eq. 8); it may be



the EDTA radicals that play a key role in the reduction of S₂O₈²⁻ (Eq. 9). While under N₂ atmosphere, e_{aq}⁻ is the main reductive species (Eq. 10). Because the reduction potential of e_{aq}⁻ is -2.9 V, much lower than that of EDTA radicals, the reduction rate of S₂O₈²⁻ under N₂ atmosphere is much faster than that under N₂O atmosphere. The slower reduction rate favors the formation of nanorod. This is the work finished in the first year, too.

As the above-mentioned description, Ostwald ripening play an important role in the formation of mesoporous BaSO₄ microspheres with a larger pore size. To eliminate the disturbance from Ostwald ripening, a contrast experiment at a higher dose rate and within a shorter time is necessary. However, for the lower dose rate of the ⁶⁰Co source in our institute, the related work is delayed, which will be altered at the end of this year.

Applications

Because BaSO₄ is inert in many chemical reactions and a large pore size favors the mass exchange, the mesoporous BaSO₄ microspheres with a larger pore size may act as promising candidates for catalyst carrier, adsorbent and so on. In the plan of this year, we are going to explore the immobilization of horseradish peroxidase in the mesoporous BaSO₄ microspheres with different pore size and the following catalysis effect on the reaction between H₂O₂ and *o*-phenylenediamine. Nevertheless, in our experiment, the immobilization capacity of horseradish peroxidase in the mesoporous BaSO₄ microspheres is too small to catalyze the planned reaction. Therefore, we will turn to explore the application of the mesoporous BaSO₄ microspheres in the field of ion-exchange in the next year.

1.4. Controllable radiolytic reduction of Cu²⁺ by β-cyclodextrin

Because ionizing radiation can decompose cyclodextrins (CDs), the safe absorbed dose was determined to be 10 kGy at the dose rate of 41.9 Gy/min by using pyrene as a fluorescent probe. Within the safe absorbed dose, the increase in the concentration of β-CD could transform the reduction product of Cu(NO₃)₂ from Cu₂O to Cu. When the concentration of β-CD increased to 8.0 mmol/L, the reduction product of Cu(NO₃)₂ became pure Cu NPs. During the irradiation course, β-CD is able to scavenge hydroxyl radical, which favors the generation of Cu. Moreover, the Cu NPs may be stabilized in a hydrophobic circumstance, such as the core of the micellar-type CD aggregates.

When the concentration of β-CD was 8.0 mmol/L, the reduction product of CuSO₄ was Cu₂O. This may be ascribed to the reason that NO₃⁻ can form inclusion complex with CD, while SO₄²⁻ cannot.

This is the work finished in the first year, which was published in this year in *Acta Physico-Chimica Sinica* as an invited research article for the Centennial Celebration of Chemical Research and Education at Peking University. In this year, we planned to radiolytically synthesize Ag NPs protected by β-CD for antimicrobial test. Unfortunately, only black Ag₂O NPs were obtained. As for the mechanism and the solution scheme, it is still in studying.

2. PREPARATION OF INORGANIC-POLYMER HYBRID MICROGELS BY γ-IRRADIATION AND SURFACTANT-FREE EMULSION POLYMERIZATION

2.1. Introduction

As a member of inorganic-polymer nanocomposite microspheres, hybrid microgels have been used extensively in the fields of coatings, colloid crystals, catalysis, diagnostics and so forth [24-27]. In order to synthesize the nanocomposite microspheres, a variety of methods have been employed, such as ion exchange [26,28], photo-thermal patterning [29], block polymer micelles [30] and surface-graft processing [31]. In these methods, the synthesis of polymer and the preparation of inorganic NPs are operated individually. Thus, inorganic NPs are difficult to be well dispersed in the polymer microspheres. In addition, microemulsions [32-34] and micelles [35] are often used to prepare nanocomposite microspheres, too. Since the surfactants are difficult to be removed completely, the application of the products is limited, especially in biomedical applications [36-37]. The combination of γ-irradiation and surfactant-free emulsion polymerization can simultaneously realize the formation of microgels, reduction of inorganic ions and sterilization in the absence of surfactants, which is able to overcome the above problems and meets the request of biomedical applications. Nevertheless, because the choice of monomers is limited, the development of this method is slowly.

In our previous work, 4-vinylpyridine (4-VP), with the feasible coordination with metal ions [38-39], as well as its easy formation of microgel [40], has been applied to the preparation of a hybrid microgel through the simultaneous formation of Ag NPs and poly(4-vinylpyridine) (P4VP) microgel by γ -irradiation and surfactant-free emulsion polymerization in a single step [41-42]. It was found that the Ag NPs were well dispersed within the polymer microspheres [41-42]. However, P4VP is not biocompatible polymer. Moreover, the single commercial monomer, which can be used as the succedaneum of 4-VP, is scarce. To overcome this difficulty and obtain microgels suitable to biomedicine, we try to use several kinds of monomers to substitute 4-VP.

2.2. Research progress

In the preliminary work, poly(methacrylic acid-*co*-methyl methacrylate) (poly(MAA-*co*-MMA)) microgels was gotten *via* the copolymerization of methacrylic acid (MAA) and methyl methacrylate (MMA) by γ -irradiation and surfactant-free emulsion polymerization. Furthermore, NaOH was added into the mixed solution of MAA and MMA to neutralize part of MAA. Then, a suitable amount of AgNO₃ and isopropanol were added. After being irradiated under N₂ atmosphere, a brown and translucent microgel dispersion was obtained, which was stable for two months at least. In its UV-vis spectrum, there was only a single peak at *ca.* 410 nm, related to the surface plasma (SP) band of Ag NPs. Moreover, the symmetrical peak suggested that the circumstance around the Ag NPs was similar to great extent. The further characterization on the hybrid microgel is in process.

However, this system was not suitable to synthesize CdS-poly(MAA-*co*-MMA) when CdCl₂ and Na₂S₂O₃ were used as cadmium and sulfur sources, respectively. Because the coordination ability of S₂O₃²⁻ to Cd²⁺ is much stronger than that of methacrylate anion, there were two kinds of CdS NPs (Φ : *ca.* 2 nm), *i.e.*, one existed in poly(MAA-*co*-MMA) microgel (Φ : 100-130 nm), the other distributed outside (Figure 5). Therefore, the selection of a suitable sulfur source and a monomer with a stronger coordination ability to Cd²⁺ is the most important.

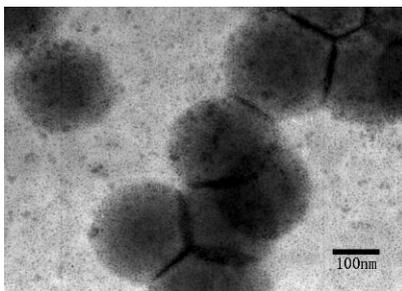
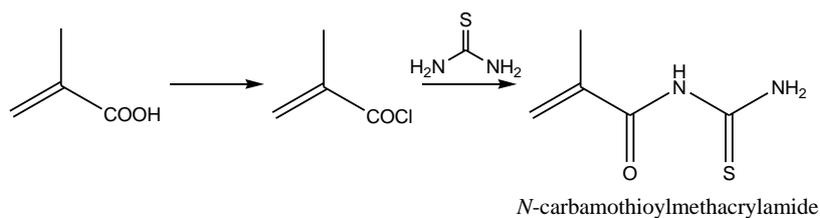


FIG. 5. TEM image of the CdS NPs and CdS-poly(MAA-*co*-MMA) hybrid microgel prepared by γ -radiation and surfactant-free emulsion polymerization in a single step.

It was known that thiourea can coordinate with many metal ions (such as Zn²⁺, Cd²⁺) and can generate S²⁻ by γ -radiolysis, which leads to the generation of metal sulfide NPs [43]. Therefore, we try to modify thiourea by methacryloyl group (Scheme 2). So far, the unpurified methacrylation product were obtained. After purification, the substituted thiourea will copolymerize with MAA and MMA *via* γ -irradiation and surfactant-free emulsion polymerization to synthesize CdS-poly(MAA-*co*-MMA) hybrid microgels.



Scheme 2

3. PUBLICATIONS

In this year, we published the following three papers, in which an acknowledgement of the contribution of the IAEA was included.

[1] CHEN, Q.D., SHEN, X.H., "Formation of mesoporous BaSO₄ microspheres with a larger pore size via Ostwald ripening at room temperature", *Cryst. Growth Des.* 10 (2010) 3838.

[2] CHEN, Q.D., SHEN, X.H., GAO, H.C., "Radiolytic syntheses of nanoparticles in supramolecular assemblies", *Adv. Colloid Interface Sci.* 159 (2010) 32. (Invited review)

[3] YANG, S.G., CHEN, Q.D., SHI, J.F., SHEN, X.H., "Controllable radiolytic reduction of Cu²⁺ in aqueous solution by β-cyclodextrin", *Acta Phys.-Chim. Sin.* 26 (2010) 805. (in Chinese)

REFERENCES

[1] BURDA, C., CHEN, X.B., NARAYANAN, R., EL-SAYED, M.A., "Chemistry and properties of nanocrystals of different shapes", *Chem. Rev.* 105 (2005) 1025.

[2] ROUCOUX, A., SCHULZ, J., PATIN, H., "Reduced transition metal colloids: A novel family of reusable catalysts?", *Chem. Rev.* 102 (2002) 3757.

[3] SUN, Y.G., XIA, Y.N., "Shape-controlled synthesis of gold and silver nanoparticles", *Science* 298 (2002) 2176.

[4] TIAN, N., ZHOU, Z.Y., SUN, S.G., DING, Y., WANG, Z.L., "Synthesis of tetrahedral platinum nanocrystals with high-index facets and high electro-oxidation activity", *Science* 316 (2007) 732.

[5] LIU, L.P., ZHUANG, Z.B., XIE, T., WANG, Y.G., LI, J., PENG, Q., LI, Y.D., "Shape Control of CdSe Nanocrystals with Zinc Blende Structure", *J. Am. Chem. Soc.* 131 (2009) 16423.

[6] MANOS, M.J., DING, N., KANATZIDIS, M.G., "Layered metal sulfides: Exceptionally selective agents for radioactive strontium removal", *Proc. Natl. Acad. Sci. U. S. A.* 105 (2008) 3696.

[7] YANG, D.J., ZHENG, Z.F., ZHU, H.Y., LIU, H.W., GAO, X.P., "Titanate nanofibers as intelligent absorbents for the removal of radioactive ions from water", *Adv. Mater.* 20 (2008) 2777.

- [8] MANOS, M.J., KANATZIDIS, M.G., "Highly Efficient and Rapid Cs⁺ Uptake by the Layered Metal Sulfide K₂Mn_xSn_{3-x}S₆ (KMS-1)", *J. Am. Chem. Soc.* 131 (2009) 6599.
- [9] DING, N., KANATZIDIS, M.G., "Permeable layers with large windows in [(CH₃CH₂CH₂)₂NH₂]₅In₅Sb₆S₁₉·1.45 H₂O: High ion-exchange capacity, size discrimination, and selectivity for Cs⁺", *Chem. Mater.* 19 (2007) 3867.
- [10] HENGLEIN, A., "Physicochemical Properties of Small Metal Particles in Solution - Microelectrode Reactions, Chemisorption, Composite Metal Particles, and the Atom-to-Metal Transition", *J. Phys. Chem.* 97 (1993) 5457.
- [11] HODAK, J.H., HENGLEIN, A., HARTLAND, G.V., "Photophysics of nanometer sized metal particles: Electron-phonon coupling and coherent excitation of breathing vibrational modes", *J. Phys. Chem. B* 104 (2000) 9954.
- [12] BELLONI, J., MOSTAFAVI, M., REMITA, H., MARIGNIER, J.L., DELCOURT, M.O., "Radiation-induced synthesis of mono- and multi-metallic clusters and nanocolloids", *New J. Chem.* 22 (1998) 1239.
- [13] BELLONI, J., "Nucleation, growth and properties of nanoclusters studied by radiation chemistry - Application to catalysis", *Catal. Today* 113 (2006) 141.
- [14] ZHU, Y.J., QIAN, Y.T., CAO, Y.F., "gamma-radiation synthesis of nanocrystalline powders of copper(I)halides", *Mater. Sci. Eng. B-Solid State Mater. Adv. Technol.* 57 (1999) 247.
- [15] ZHU, Y.J., QIAN, Y.T., HAI, H., ZHANG, M.W., "Preparation of ultrafine tellurium powders by the gamma-radiation method at room temperature", *J. Mater. Sci. Lett.* 15 (1996) 1700.
- [16] ZHU, Y.J., QIAN, Y.T., HAI, H.A., ZHANG, M.W., "Preparation of nanometer-size selenium powders of uniform particle size by gamma-irradiation", *Mater. Lett.* 28 (1996) 119.
- [17] ZHU, Y.J., QIAN, Y., "Preparation of nanometer-size amorphous powders of arsenic by gamma-irradiation at room temperature", *Mater. Sci. Eng. B-Solid State Mater. Adv. Technol.* 47 (1997) 184.
- [18] HULLAVARAD, N.V., HULLAVARAD, S.S., KARULKAR, P.C., "Cadmium Sulphide (CdS) Nanotechnology: Synthesis and Applications", *J. Nanosci. Nanotechnol.* 8 (2008) 3272.
- [19] NI, Y.H., GE, X.W., XU, X.L., CHEN, J.F., ZHANG, Z.C., "Developments in Preparation of Nano-scale Materials", *J. Inorg. Mater.* 15 (2000) 9.
- [20] TAGUCHI, M., YAMADA, K., SUZUKI, K., SATO, O., EINAGA, Y., "Photoswitchable magnetic nanoparticles of Prussian blue with amphiphilic azobenzene", *Chem. Mater.* 17 (2005) 4554.
- [21] YAMADA, M., OHNISHI, N., WATANABE, M., HINO, Y., "Prussian blue nanoparticles protected by the water-soluble pi-conjugated polymer PEDOT-S: synthesis and multiple-color pH-sensing with a redox reaction", *Chem. Commun.* (2009) 7203.
- [22] BUSTOS, E., MANRIQUEZ, J., OROZCO, G., GODINEZ, L.A., "Preparation, characterization, and electrocatalytic activity of surface anchored, Prussian blue containing Starburst PAMAM dendrimers on gold electrodes", *Langmuir* 21 (2005) 3013.

- [23] CHEN, Q.D., BAO, H.Y., SHEN, X.H., "Radiolytic synthesis of BaSO₄ microspheres", *Radiat. Phys. Chem.* 77 (2008) 974.
- [24] SCHARTL, W., "Crosslinked spherical nanoparticles with core-shell topology", *Adv. Mater.* 12 (2000) 1899.
- [25] CARUSO, F., "Nanoengineering of particle surfaces", *Adv. Mater.* 13 (2001) 11.
- [26] XU, S.Q., ZHANG, J.G., PAQUET, C., LIN, Y.K., KUMACHEVA, E., "From hybrid microgels to photonic crystals", *Adv. Funct. Mater.* 13 (2003) 468.
- [27] KARG, M., HELLWEG, T., "Smart inorganic/organic hybrid microgels: Synthesis and characterisation", *J. Mater. Chem.* 19 (2009) 8714.
- [28] ANTONIETTI, M., GROHN, F., HARTMANN, J., BRONSTEIN, L., "Nonclassical shapes of noble-metal colloids by synthesis in microgel nanoreactors", *Angew. Chem.-Int. Edit. Engl.* 36 (1997) 2080.
- [29] JONES, C.D., LYON, L.A., "Photothermal patterning of microgel/gold nanoparticle composite colloidal crystals", *J. Am. Chem. Soc.* 125 (2003) 460.
- [30] MOFFITT, M., VALI, H., EISENBERG, A., "Spherical assemblies of semiconductor nanoparticles in water-soluble block copolymer aggregates", *Chem. Mater.* 10 (1998) 1021.
- [31] CHEN, C.W., CHEN, M.Q., SERIZAWA, T., AKASHI, M., "In-situ formation of silver nanoparticles on poly(N-isopropylacrylamide)-coated polystyrene microspheres", *Adv. Mater.* 10 (1998) 1122.
- [32] NI, Y.H., GE, X.W., LIU, H.R., ZHANG, Z.C., YE, Q., "In situ synthesis and characterization of spherical CdS/polyacrylamide nanocomposites by gamma-irradiation in W/O microemulsions", *Chem. Lett.* (2001) 924.
- [33] WANG, W., ASHER, S.A., "Photochemical incorporation of silver quantum dots in monodisperse silica colloids for photonic crystal applications", *J. Am. Chem. Soc.* 123 (2001) 12528.
- [34] WU, D.Z., GE, X.W., ZHANG, Z.C., WANG, M.Z., ZHANG, S.L., "Novel one-step route for synthesizing CdS/polystyrene nanocomposite hollow spheres", *Langmuir* 20 (2004) 5192.
- [35] ROOS, C., SCHMIDT, M., EBENHOCH, J., BAUMANN, F., DEUBZER, B., WEIS, J., "Design and synthesis of molecular reactors for the preparation of topologically trapped gold clusters", *Adv. Mater.* 11 (1999) 761.
- [36] PELTON, R., "Temperature-sensitive aqueous microgels", *Adv. Colloid Interface Sci.* 85 (2000) 1.
- [37] SAUNDERS, B.R., VINCENT, B., "Microgel particles as model colloids: theory, properties and applications", *Adv. Colloid Interface Sci.* 80 (1999) 1.
- [38] BRONSTEIN, L.H., SIDOROV, S.N., VALETSKY, P.M., HARTMANN, J., COLFEN, H., ANTONIETTI, M., "Induced micellization by interaction of poly(2-vinylpyridine)-block-

poly(ethylene oxide) with metal compounds. Micelle characteristics and metal nanoparticle formation", *Langmuir* 15 (1999) 6256.

[39] MALYNYCH, S., LUZINOV, I., CHUMANOV, G., "Poly(vinyl pyridine) as a universal surface modifier for immobilization of nanoparticles", *J. Phys. Chem. B* 106 (2002) 1280.

[40] CHEN, Q.D., SHEN, X.H., GAO, H.C., "Synthesis of poly(N,N'-methylenebisacrylamide-co-4-vinylpyridine) microgels by gamma-ray irradiation", *Acta Polym. Sin.* (2005) 60.

[41] CHEN, Q.D., SHEN, X.H., GAO, H.C., "One-step synthesis of silver-poly(4-vinylpyridine) hybrid microgels by gamma-irradiation and surfactant-free emulsion polymerization", *Acta Polym. Sin.* (2006) 722.

[42] CHEN, Q.D., SHEN, X.H., GAO, H.C., "One-step synthesis of silver-poly(4-vinylpyridine) hybrid microgels by gamma-irradiation and surfactant-free emulsion polymerisation. The photoluminescence characteristics", *Colloid Surf. A-Physicochem. Eng. Asp.* 275 (2006) 45.

[43] NI, Y.H., GE, X.W., LIU, H.R., ZHANG, Z.C., YE, Q., WANG, F., "gamma-irradiation route to prepare silver sulfide nanocrystals", *Chem. J. Chin. Univ.-Chin.* 23 (2002) 176.