

A Novel Method for the Preparation of Core-Shell Nanoparticles and Hollow Polymer Nanospheres

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ABSTRACT: A one-step method to prepare core-shell nanoparticles and thus hollow nanospheres is reported. The process for the formation of core and shell took place during reaction. Once the core formed, it was covered with the shell substance produced *in situ*, and thus, the shell hindered the continued growth of the core. Based on this method, we readily obtained core-shell nanoparticles by choosing AgCl, CuS, or Fe(III) diethyldithiocarbamate (FeDEC)₃ as model core substances and the cogel from gelatin and gum arabic as the shell substance. High-resolution transmission electron microscopy (HRTEM) directly revealed the core-shell structure. TEM results showed the average particle sizes were

under 100 nm, depending on the core substance and the concentration of substances producing cores. After removal of the core materials, hollow nanospheres resulted, which were directly observed by TEM. The observation further verified the core-shell structure. UV spectrophotometry also gave signals of coated structure and revealed high core content (51.1%) and nearly perfect coating (91.6%). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2594–2600, 2004

Key words: gelatin; gum arabic; core-shell structure; nanoparticle; hollow nanosphere

INTRODUCTION

Core-shell nanoparticles (CS-NPs), often made up of a solid core surrounded by a well-defined shell layer, are known to exhibit unique and advanced properties over single-component nanoparticles, making them attractive for use in a wide range of applications, and are therefore of extensive scientific and technological interest. In addition, such a structure has advantages in the prevention of particle aggregation, in the protection of core materials from chemical corrosion, in the isolation of active components, in the creation of the controlled release of core materials, and in other advanced properties, etc.

Recent efforts to fabricate CS-NP relied on a number of approaches. Inorganic and hybrid shells on particles have been commonly prepared either by controlled surface precipitation of inorganic molecular precursors or by direct surface reaction that makes use of specific functional groups on the cores to induce coating. Step-by-step precipitation¹ or ion exchange^{2,3} provides routes for the preparation of core-shell nanosized semiconductors with broad and advanced prop-

erties. Through surface oxidization,⁴ or through reduction of metal ion in dendrimer or micelle, such as by NaBH₄,^{5–9} coated metal powder was obtained, which can exist in open air. Alternatively, polymer-coated nanoparticles can be readily incorporated into thin films or polymers, giving unusual properties. Means for the creation of polymer-coated nanoparticles include polymerization at the particle surface,^{10–12} heterocoagulation polymerization,¹³ and emulsion polymerization,¹⁰ besides the direct absorption of polymer.¹⁰ CS-NPs can also be obtained by using coupling agents on the colloidal particles produced in advance as a primer for the growth of secondary shells around the core particles.^{14,15}

The creation of hollow nanospheres or nanocavities has attracted attention in recent years because of its broad range of applications. For example, it is used as template reactor to synthesize size-controllable nanoparticles or CS-NP; as delivery vehicle for the removal of contaminated waste and for the controlled release of substances such as drugs, cosmetics, dyes, and inks; or as a carrier of catalyst. Such nanocavities were commonly obtained from the precursor CS-NP by removal of the core materials by using a variety of chemical and physical methods, such as calcination or solvent etching, where the core was used as a sacrificial template to produce a range of hollow capsules.^{11,12,16–18}

However, to date, all techniques applied to fabricate the core-shell structure involved at least two steps: the

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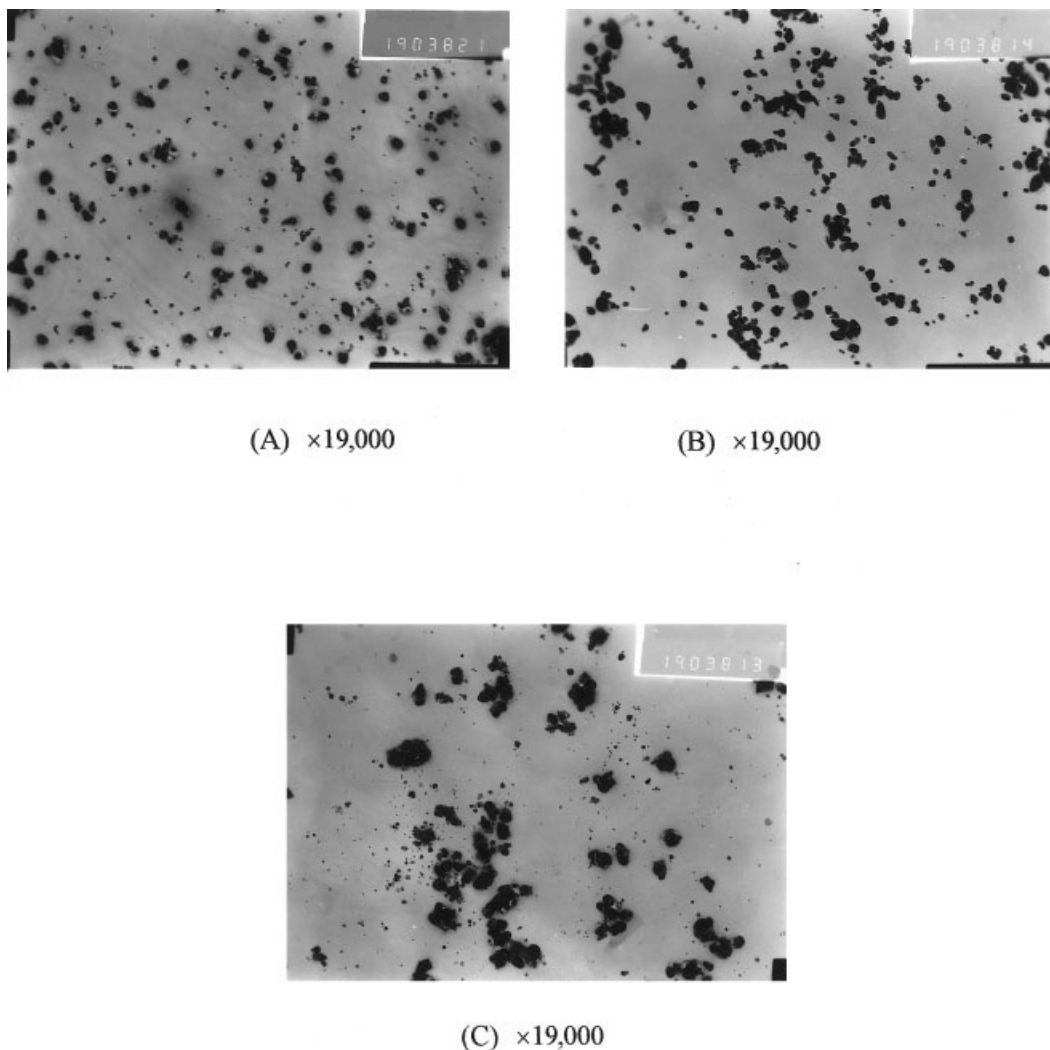


Figure 1 TEM of AgCl crystal granule coated with cogel from the coacervation of gelatin-gum arabic. NaCl or AgNO₃ concentrations before reaction (mol/L): (A) 0.04; (B) 0.2; (C) 0.4.

synthesis of core particles in advance and the coating process by the shell material produced in the subsequent step. An important challenge is how to avoid the occurrence of aggregation of core particles prior to coating in these techniques.

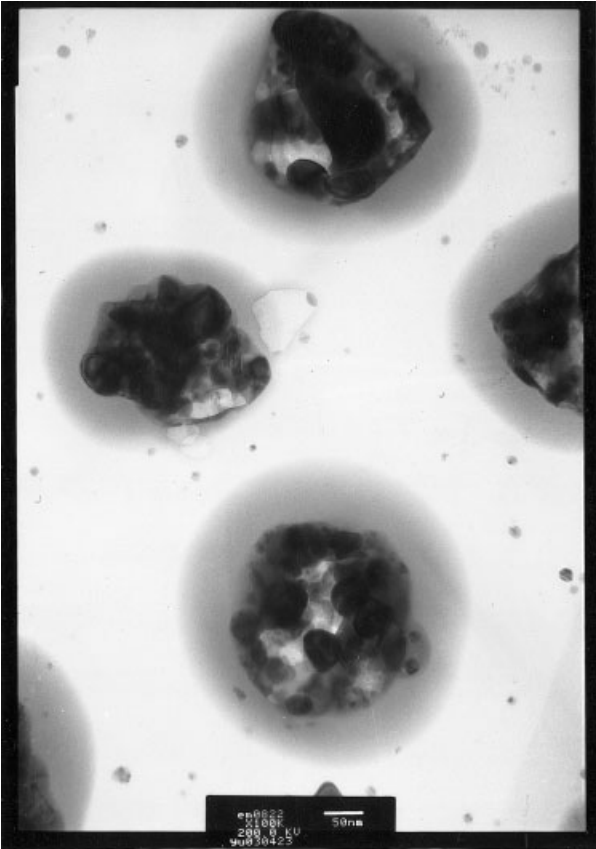
The approach presented here is fundamentally different. Instead, we report a one-step method for the preparation of CS-NPs. The process for formation of core and shell took place simultaneously in a reaction system. Once the core substance formed, the shell substance produced *in situ* hindered the continued growth of larger, bulkier crystal for core. A core-shell structure was formed. This strategy has distinct advantages: the whole reaction process is simple and can be performed at room temperature and ambient pressure in addition to avoiding the occurrence of aggregation of core substance efficiently. Removal of core materials is much easier, without employing the calcination at higher temperature¹⁹ or the degradation for the polymer core templates.²⁰

EXPERIMENTAL

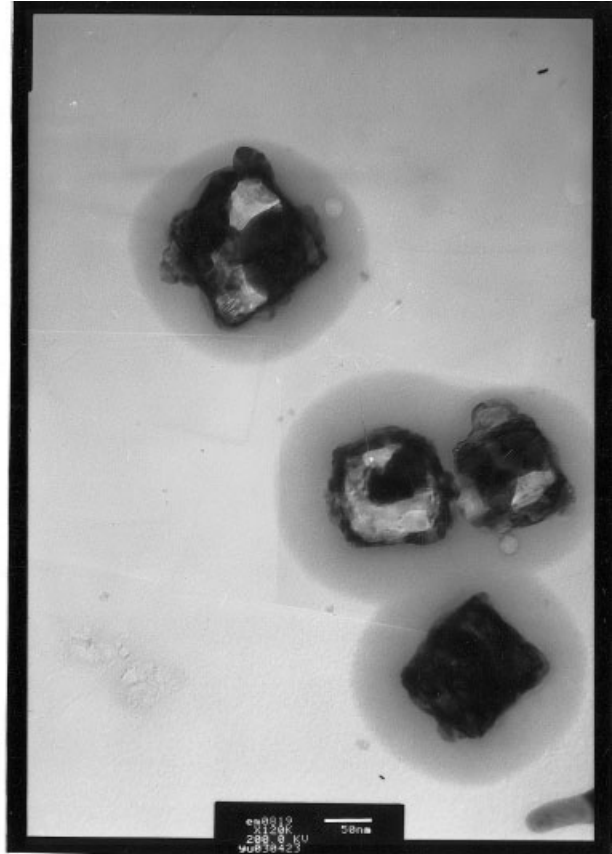
Gelatin produced from calfskin and gum arabic were purchased from Aldrich Chemical Co. The isoelectric point of the gelatin was measured at 4.45. All other reagents were analytic and used without treatment.

Photographs in Figure 1 and Figures 3–6 were taken on a JEM-100CXII-type electron microscope at an accelerating voltage of 100 kV in a copper grid coated with a thin carbon film. Photographs in Figure 2 were taken on a JEM 2010-type electron microscope at an accelerating voltage of 200 kV in a copper grid coated with a thin carbon film.

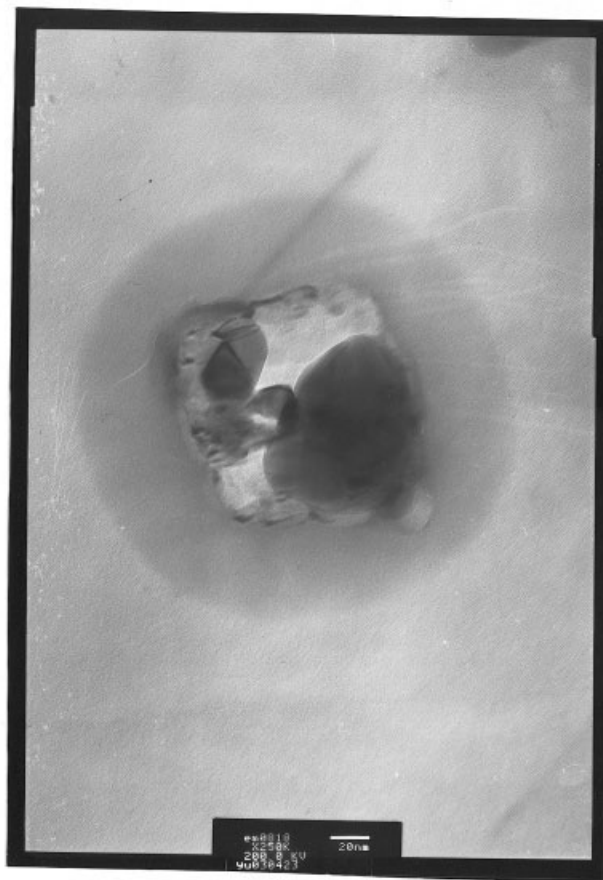
Synthesis and characterization typically included 5 g gum arabic in 150 mL 0.04 mol/L AgNO₃ solution dropped into 5 g of gelatin in 150 mL 0.04 mol/L NaCl solution at 40°C. Both of the solutions were adjusted to pH = 3.9 by acetic acid solution prior to mixing. After dropping, the system was stirred for 30 min, cooled to 5°C at a rate of 1°C/



(A) $\times 100,000$



(B) $\times 120,000$



(C) $\times 250,000$

Figure 2 HRTEM of (B) in Figure 1.

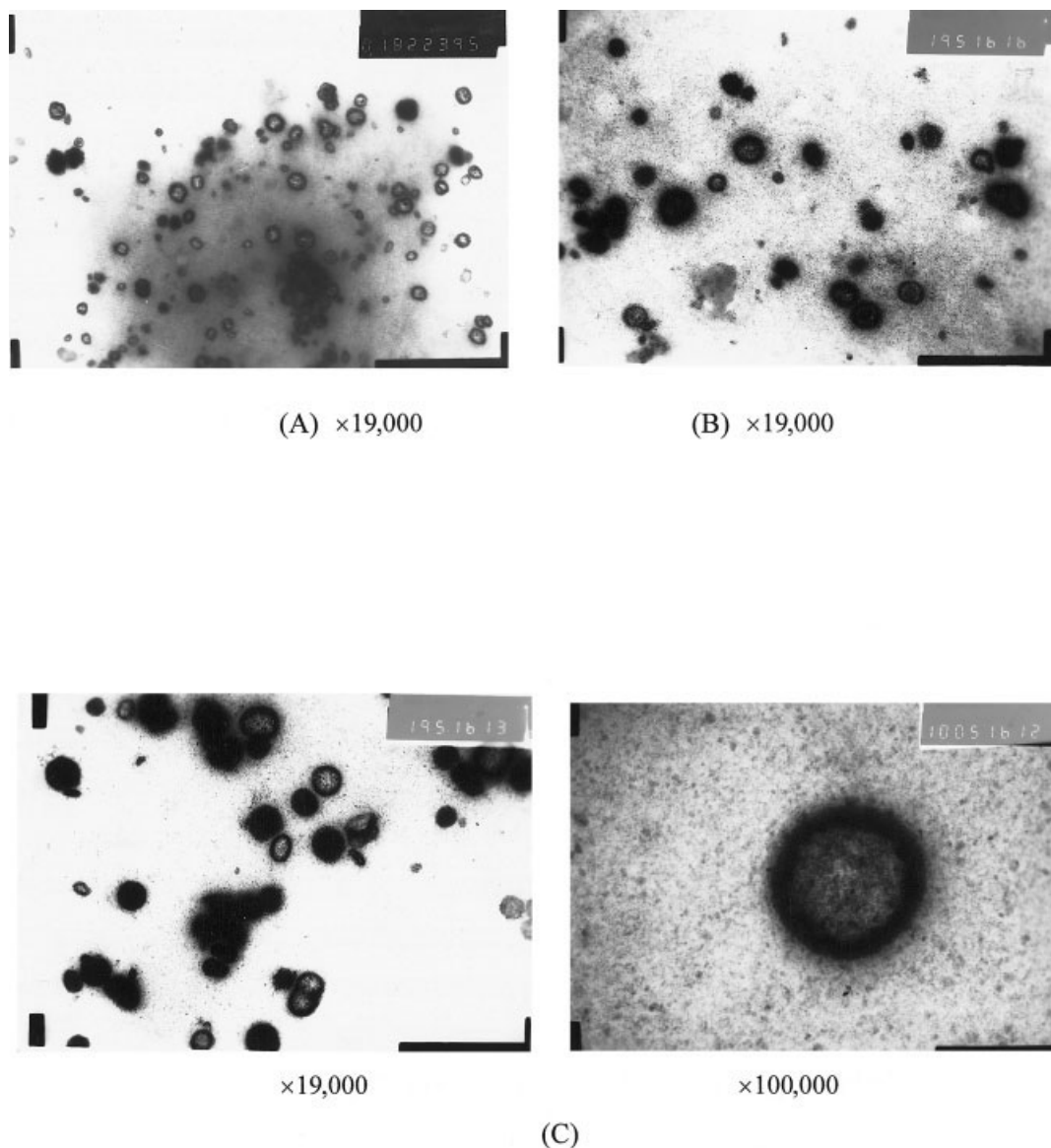


Figure 3 TEM of hollow nanospheres. (A), (B), and (C) correspond to the (A), (B), and (C) in Figure 1 by removal of the core material, respectively.

min, and then cured for 30 min by addition of formaldehyde. After adjusting pH to 9 with sodium hydroxide solution, the mixture was stirred for 30 min again and then heated to 50°C at a rate of 1°C/min and held for 30 min. The resulting slurry was dialyzed to the extent that no chloride ion could be detected by AgNO_3 solution and then observed under TEM. Spray drying of the slurry gave powders. The coated percentage and even the core material amount were then determined by spectrophotometry. Dispersing the powders in a solvent of core substance and monitoring the absorptivity versus time, we calculated the coated percentage according to a measured relationship of a known amount of the core substance versus absorptivity.

RESULTS AND DISCUSSION

Gelatin protein, containing $-\text{COO}^-$ and $-\text{NH}_3^+$ groups, carries a more positive charge from $-\text{NH}_3^+$ when pH is below its isoelectric point. Gum arabic is a negative-charged macromolecule containing lots of $-\text{COO}^-$. Therefore, gelatin and gum arabic solution, under suitable pH, can be coacervated to form cogel. Typically, we performed the reaction of AgNO_3 and NaCl and the coacervation reaction of gelatin and gum arabic in the same reaction system. Once AgCl was formed, the cogel produced *in situ* covered the surface of AgCl crystal granule and hindered its growth. A core-shell structure was fabricated.

Theoretically, the closer the formation rates of core and shell matched, the smaller the final particle size is and the more complete the coating is. Thus, once the core particle is formed, the coacervation reaction producing shell had better begin. Otherwise, either the core particle aggregates or the cogel accumulates: core-shell structure cannot result. So, the formation rates of core and shell are key factors in complete coating and the particle size. Choosing different model materials as cores is a convenient way to adjust the core formation rate.

By choosing AgCl as the model core material, the irregular shape of particles was observed under TEM at $\times 19,000$ (Fig. 1). To make clear the fine structure of the resulted particles, high-resolution TEM (HRTEM) was applied. When the magnification was set at $\times 120,000$ or $\times 250,000$, we found the core structure of irregular morphology surrounded by a global or ellipsoidal corona (Fig. 2). The diffraction pattern of core crystal was observed. In addition, the size of the core crystal in Figure 2 was very close to the particle size in Figure 1. Obviously, the particles of irregular morphology observed at lower magnification came from the core crystal structure of AgCl and the shell layer came from the gelatin-gum arabic cogel. These observations provided direct evidence of core-shell structure.

The average particle size was 80 nm at 0.04 mol/L of NaCl or AgNO₃ based on the observation in Figure 1. Enhancing the concentrations of NaCl or AgNO₃ caused the core materials to form more quickly and hence aggregate more severely. So, the average particle size increased and its distribution gradually became wide (Fig. 1).

Such co-gel-coated AgX is perhaps meaningful and useful for photosensitive film because the smaller particle size of AgX provides photographs of higher resolution power.

After the resulting slurry-containing AgCl particle was treated by adding aqueous ammonia to extract AgCl through formation of Ag(NH₃)⁺ and was then washed with water to neutral pH, the remaining material was observed under TEM, as shown in Figure 3. The photographs demonstrated obvious nanosized global cavity structure. These observations were also direct evidence of the core-shell structure. Figures 2 and 3 show that the shell thickness was approximately equal to the core particle radius and the coating was perfect.

Nanosized CuS,²¹ CdS,²² and ZnS²³ have been synthesized by many other methods owing to their semi-conductance. Coated CuS nanoparticles can also be fabricated by substituting Na₂S for NaCl and CuSO₄ for AgNO₃ in the present approach. The formation rate of core may be varied and thus the resulting particle size may be different. As shown by TEM, the resulting CuS particles were 10–20 nm in size (Fig. 4),

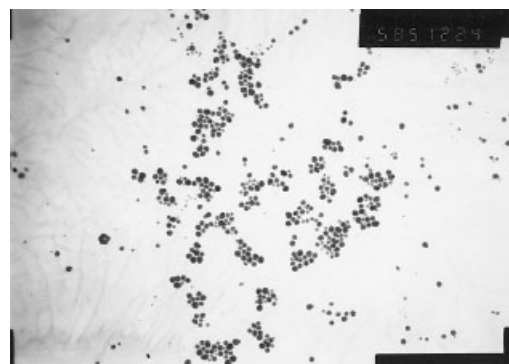
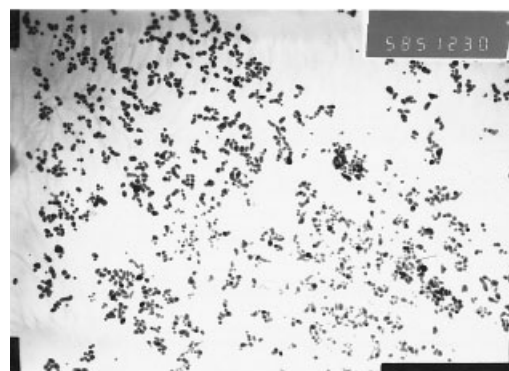
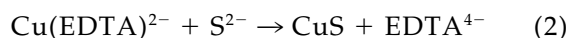
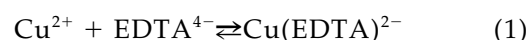
(A) $\times 58,000$ (B) $\times 58,000$

Figure 4 TEM of CuS crystal granule coated with cogel from the coacervation of gelatin-gum arabic. Na₂S or CuSO₄ concentrations before reaction (mol/L): (A) 0.04; (B) 0.08.

much less than that with AgCl as core material. In addition, the concentrations of CuSO₄ or Na₂S also had an effect on particle size: the particle size was very small when the concentrations of CuSO₄ or Na₂S were low, for instance, at 0.04 or 0.08 mol/L, but no obvious particles were observed at over 0.2 mol/L of CuSO₄ or Na₂S.

To further investigate the effect of the production rate of core material on the resulted particle size, we added sodium ethylene diamine tetraacetic acid (EDTA) to gum-arabic solution containing CuSO₄. The addition of EDTA changed the formation path of CuS as follows:



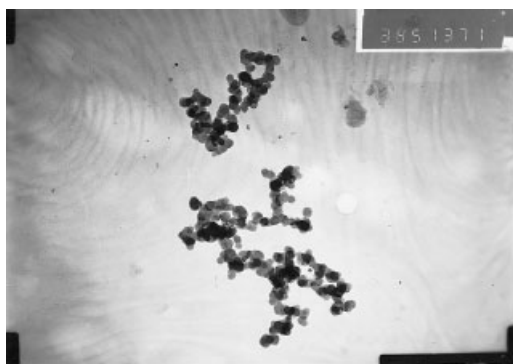
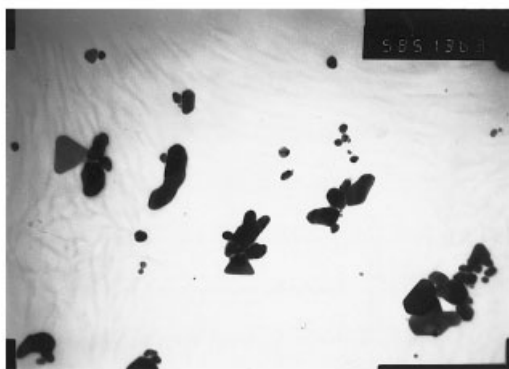
(A) $\times 58,000$ (B) $\times 58,000$

Figure 5 TEM of CuS crystal granule coated with cogel from the coacervation of gelatin-gum arabic at 0.04 mol/L of Na_2S or CuSO_4 before reaction. (A) and (B) 0.25 and 0.75M ratio of EDTA/Cu, respectively.

The formation rate of CuS was limited by the provision of copper ion based on the equilibrium process of eq. (1). Besides, the release of EDTA^{4-} , referring to eq. (2), changed the local environment; for example, the pH around just formed the CuS particle. The local pH change decelerated the coacervation reaction of gelatin and gum arabic and as a result, CuS had more of a chance to aggregate to form larger particle sizes. TEM shows that the size was about 20 nm at 0.25M ratio of EDTA to Cu^{2+} , and the size increased to 50 nm at 0.75 of the molar ratio, compared with 10–20 nm without adding EDTA (Fig. 5).

Fe(III) diethyldithiocarbamate [$\text{Fe}(\text{DEC})_3$] is a well-known kind of photodegradant and can be simply synthesized by the reaction of FeCl_3 and diethyldithiocarbamate sodium (NaDEC) in aqueous solution. Considering that nanoparticle $\text{Fe}(\text{DEC})_3$ may show additional special photocatalysis and that the coated

photodegradant may be used to control photodegradation of polymers, we synthesized coated $\text{Fe}(\text{DEC})_3$ nanoparticles by substituting NaDEC for NaCl and FeCl_3 for AgNO_3 . The size of the resulting particles was 40–80 nm under the experimental conditions (Fig. 6), much smaller as compared to the usual methods.²⁴ The core-shell structure was further verified by UV spectrophotometry. Experiments show that the inner material was released in acetone, a solvent of $\text{Fe}(\text{DEC})_3$, according to a linear relationship of absorptivity against the square root of the material release time ($t^{1/2}$). The coated percentage of particles can thus be calculated from this relationship because the absorptivity at $t = 0$ is related to the uncoated or partially coated particles. In this way, we found that the

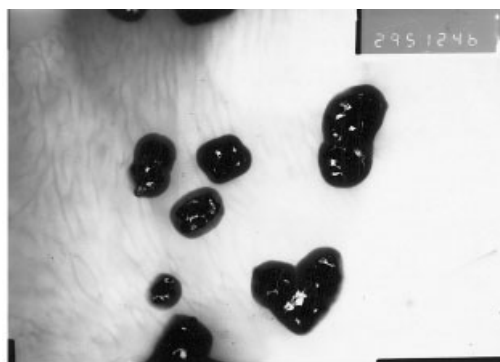
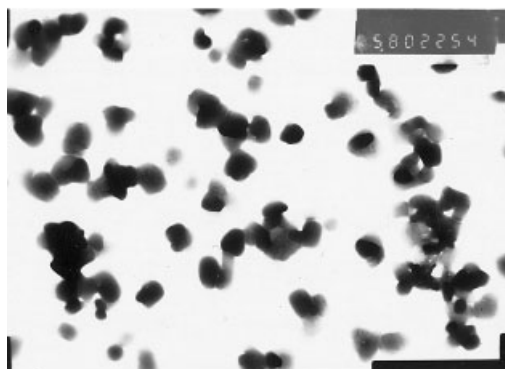
(A) $\times 29,000$ (B) $\times 58,000$

Figure 6 TEM of $\text{Fe}(\text{DEC})_3$ crystal granule coated with cogel from the coacervation of gelatin-gum arabic. NaDEC concentrations before reaction: 0.06 and 0.02 mol/L, respectively.

coated percentage was about 91.6%. Compared with the coated percentage (60%) in literature,²⁵ the coated percentage in our experiments was much higher. The core weight percentage was decided also by means of the measured linearity of absorptivity against a known amount of Fe(DEC)₃. The results show that the core weight percentage was 51.1%, which is quite high and is very meaningful to nanoparticle applications.

In summary, a novel and convenient method to synthesize CS-NP was developed, giving small size, high core content, and nearly perfect coating. By removing the core template of the CS-NP, a hollow polymer nanosphere resulted.

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