Template-free method to prepare polymer nanocapsules embedded with noble metal nanoparticles

Yongyi Gao,[ab] Xiaobin Ding,*[a] Zhaohui Zheng,[a] Xu Cheng[a] and Yuxing Peng*[a]

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In this paper, polymer nanocapsules embedded with noble metal nanoparticles and showing a good catalytic activity were prepared by a novel and convenient method.

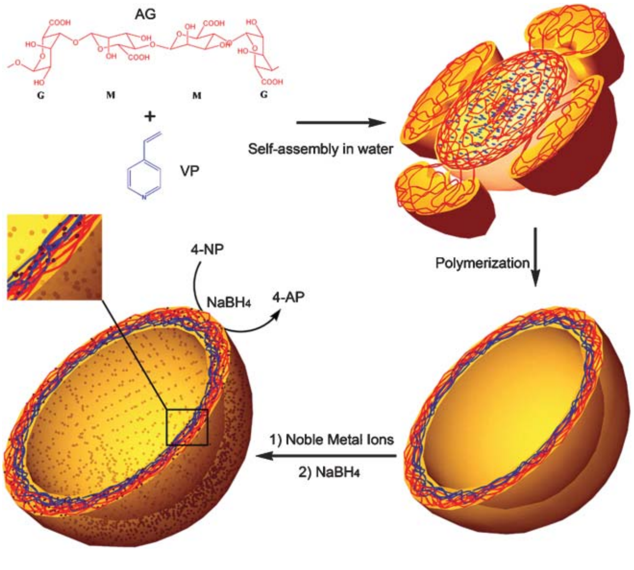
Metal nanoparticles exhibit different properties as compared with their bulk materials.[1] The versatility of physical and chemical properties of metal nanoparticles render them as promising materials in fields ranging from optoelectronics[2] and sensors[3] to catalysis[4] and medicine. However, such nanoparticles require a suitable support to prevent them undergoing aggregation during the reaction to be catalyzed. Polymer–nanoparticle composites are promising candidates for the purpose of exploiting or enhancing the unique properties of the nanoparticles while the polymer matrix can control host–guest interactions to ensure the well-defined spatial distribution of nanoparticles. The immobilization of metal nanoparticles in a polymeric matrix such as block copolymer micelles,[5] dendrimers,[6] latex particles,[7] and microgels[8] provides a convenient approach for applications taking place at low temperatures and in an aqueous environment.

Recently, polymer microcapsules have been used to prepare metal nanoparticles because encapsulation of metal nanoparticles inside the capsule or in the capsule wall can lead to the creation of novel catalyst systems.[9] Compared with polymer microspheres or micelles, microcapsules with a hollow-inner structure can encapsulate large quantities of guest molecules or large-sized guests within the "empty" core domain. They are also mechanically more stable than polymer vesicles, which lack the covalent or ionic interactions responsible for the formation of the structural changes in nanocapsules. Core–shell micelles or vesicles of block copolymers in selective solvents and layer-by-layer (LBL) deposition of polyelectrolytes onto a template core are the most common methods to prepare microcapsules.[10]

However, most of the previous studies have been focused on metal-nanoparticle-adsorbing microcapsules in the submicrometer to micrometer range, usually prepared through the LBL method.[9] In this paper, we report a novel and practicable method, shown in Scheme 1, to prepare polymer nanocapsules embedded with noble metal nanoparticles. Compared with other methods of fabricating nanocapsules, this method is performed in aqueous solution without any organic solvent or template cores. Namely, it is unnecessary with this technique to prepare any uniform spherical templates, regular amphiphilic polymers, complex dendrimers or hyperbranched polymers beforehand, and repeated absorption and washing processes are also not required.

Alginic acid (AG), which bears carboxyl groups, was chosen as the anionic polymer and synthesized by adding acid to sodium alginate solution. 4-Vinyl pyridine (VP), which bears basic groups, was chosen as the cationic monomer. AG on its own does not dissolve and VP is only slightly soluble in water at neutral pH, but when AG and VP are added to water at a stoichiometric ratio of 1 : 1 ([acid]/[pyridine]) they do dissolve. The alteration from hydrophobic to hydrophilic is caused by deprotonation of AG and protonation of VP. Then they become closely attracted to one another through electrostatic forces. Fig. 1(a,b) shows that the structure of AG–VP in aqueous solution prior to polymerization is flower-like. The average diameter of these structures was 276 ± 74.2 nm (PDI = 0.009), and the zeta-potential was -35.1 mV.

Alginate nanocapsules were prepared through polymerization, which was initiated by potassium persulfate at 80 °C and allowed to proceed for 90 min. The TEM pictures of as-synthesized nanocapsules are shown in Fig. 1(c,d). The average diameter of nanocapsules is 129 ± 34 nm (PDI = 0.073), smaller than the flower-like micelles. This is because during the polymerization, single VP molecules turn into long-chain macromolecules one after another. And after that chains of AG and poly-4-vinyl pyridine (PVP) enwind with each other, which leads to the restriction of their movement. A zeta potential of -53.6 mV was determined, the minus in which indicated AG to be mainly distributed in the outer wall of the nanocapsules, and the higher absolute value



Scheme 1 A proposed scheme for the formation of nanocapsules.

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[a] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, P. R. China. E-mail: xbding@cioc.ac.cn; Fax: 86 28 85233426; Tel: 86 28 85233426
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100049, P. R. China. Fax: 86 28 85233426; Tel: 86 28 85233426

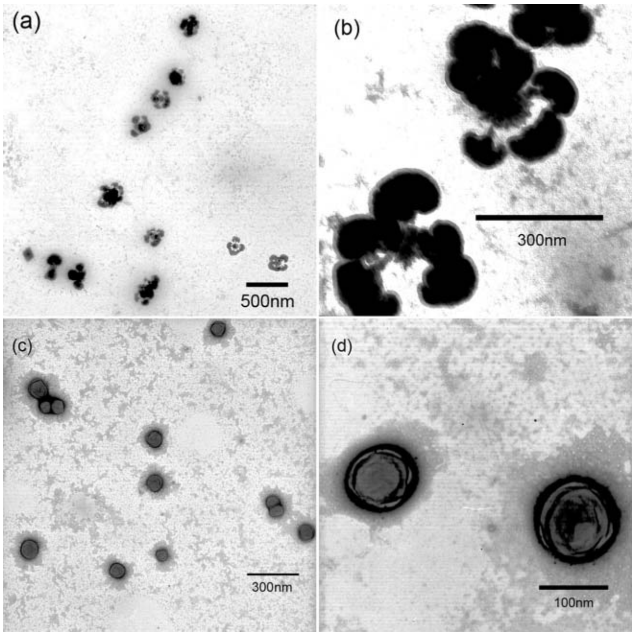

Fig. 1 TEM micrograph of flower-like micelles (a,b) and polymer nanocspsules (c,d). Before the observation, the sample was stained by phosphotungstic acid.

indicating that spherical capsules rather than flower-like micelles had the more stable conformation.[11]

AG and PVP are both able to adsorb and separate metal ions.[12] The coordinated complex of nanocapsules and noble metal ions was prepared by adding K_2PtCl_6, $KAuCl_4$, K_2PdCl_4, and $AgNO_3$ into alginate nanocapsules solution respectively, followed by continuous stirring for 12 h. Subsequently, the noble metal ions embedded on the dispersed nanocapsules were reduced by a sodium borohydride solution with continuous stirring. Fig. 2 shows representative TEM images of nanocapsules with noble metal nanoparticles, and the insert image shows a higher magnification micrograph. As we know, polymer nanocapsules

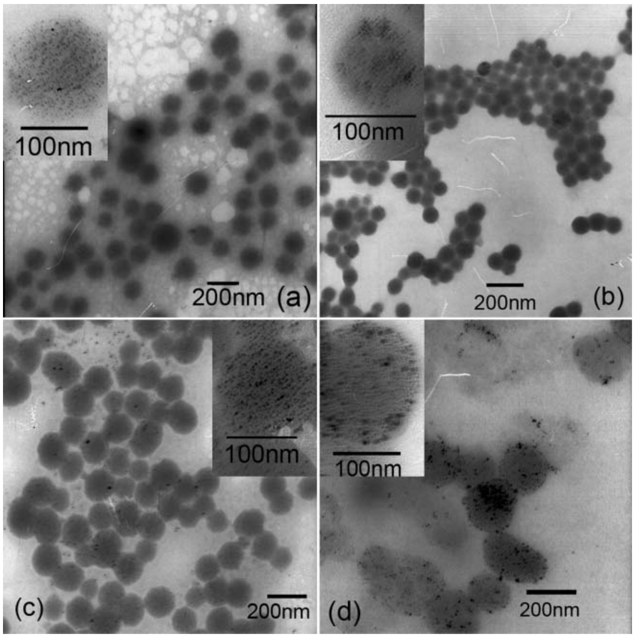

Fig. 2 TEM micrograph of polymer nanocapsules embedded with Au (a), Pt (b), Pd (c) and Ag (d) nanoparticles. The insert is a higher magnification micrograph and the bar in it is 100 nm.

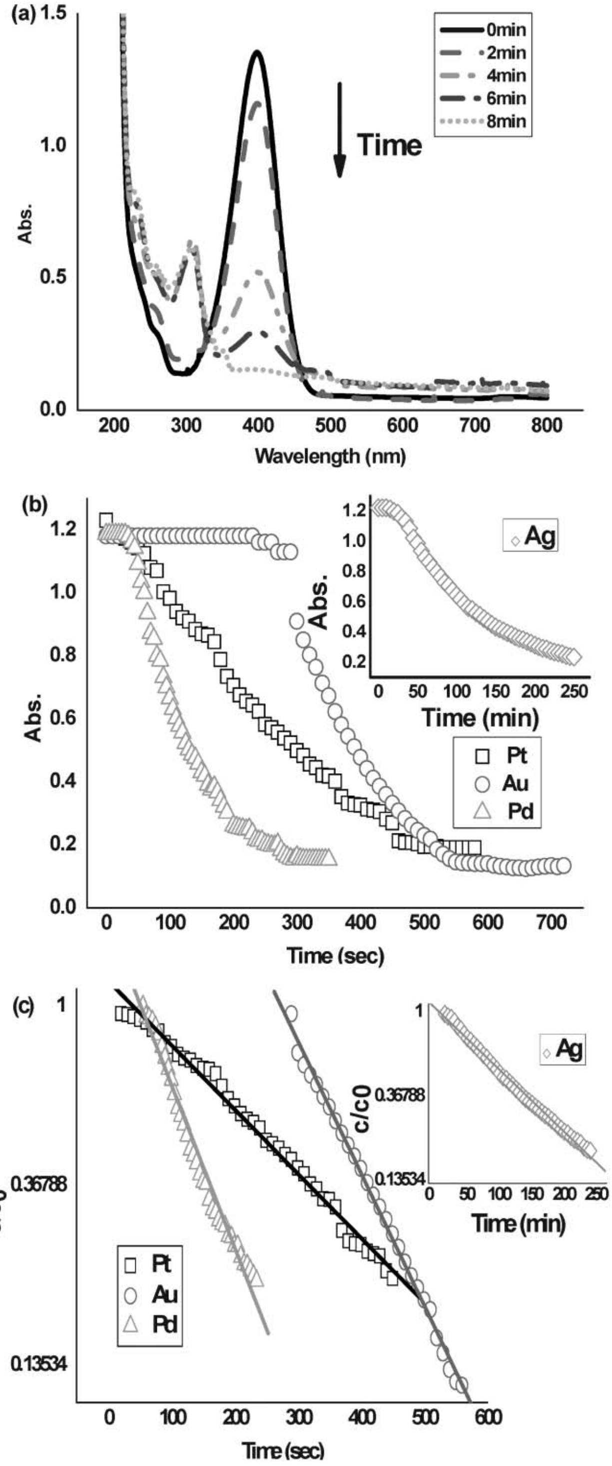

Fig. 3 (a) Typical UV-VIS spectra of conversion of 4-NP to 4-AP in the present of polymer nanocapsules embedded with Pt nanoparticles. (b) Plot of absorbance *versus* time and (c) Plot of $\ln(c/c_0)$ *versus* time for the reduction of 4-NP. The concentrations of the reactants were as follows: [4-NP] = 0.67 mmol L^{-1}, [$NaBH_4$] = 0.067 mol L^{-1} and [noble metal] = 1.30 μmol L^{-1}, with T = 288 K.

which do not adsorb metal nanoparticles cannot be observed in the absence of staining agents. However, in Fig. 2, all samples can be observed distinctly under the same conditions, which confirms that metal nanoparticles are present in the nanocapsules. The spherical nanocapsules with homogeneous color indicate a uniform distribution of noble metal nanoparticles in the nanocapsules. $[PtCl_6]^{2-}$, $[AuCl_4]^{-}$, $[PdCl_4]^{2-}$ which bear minus charge preferred to complex with PVP in the inner wall of the nanocapsules. In like manner, Ag^+ preferred to complex with AG next to the outer surface of the nanocapsules. They all were reduced *in-situ* and embedded in the wall of the nanocapsules. After treatment for 6 h with ultrasound (20 kHz, 50 W), the nanocapsules were still stable and the noble nanoparticles had not escaped from the nanocapsules.

Having discussed the synthesis and structure of the nanocapsules with noble metal nanoparticles, we now turn to the catalytic properties of these nanocapsules. As a model reaction, we used the reduction of 4-nitrophenol (4-NP) by $NaBH_4$ to 4-aminophenol (4-AP). When the polymer nanocapsules embedded with noble metal nanoparticles were added into the mixture of 4-NP and $NaBH_4$, the yellow color of solution faded gradually. Such decolorization was reflected in the absorption spectra shown in Fig. 3a. The peak at 400 nm gradually diminished as the reaction proceeded and the yellow color disappeared completely after 8 min. Additional experiments demonstrated that no reduction takes place without the catalyst. It is therefore evident that the conversion is solely due to the presence of the nanocapsules.

The reaction does not start immediately but only after an "activation" time (Fig. 3b). The existence of the "activation" time can be attributed to entanglement of polyelectrolyte chains in the nanocapsule wall slowing the diffusion of reactants towards the noble metal nanoparticles. And the "activation" time was different depending on the noble metal nanoparticles embedded within the nanocapsules, which may be due to the different activating abilities of the noble metal nanoparticles in the reaction mixtures. Fig. 3c shows a linear correlation with time, that is, $\ln(c/c_0)$ *versus* time plot. The reaction constants of nanocapsule with Pt, Au, Pd and Ag nanoparticles are $3.58 \times 10^{-3}\ s^{-1}$, $7.36 \times 10^{-3}\ s^{-1}$, $8.83 \times 10^{-3}\ s^{-1}$ and $1.23 \times 10^{-4}\ s^{-1}$ respectively.

In summary, we have presented a practicable and convenient route to prepare polymer nanocapsules embedded with noble metal nanoparticles, which is performed in aqueous solution without any template cores, compared with other complicated and tedious methods. This method has been reported for the preparation of chitosan hollow nanospheres and alginate nanospheres,[13] and its universality is testified again by our research. The good catalytic activity of the nanocapsule is proved in the reduction reaction of 4-NP in an aqueous solution.

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