Communication

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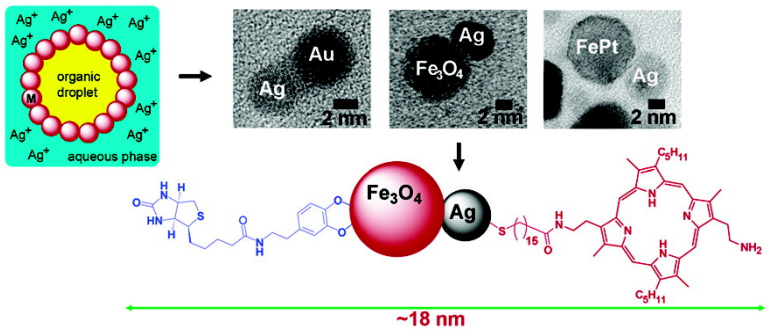

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Heterodimers of Nanoparticles: Formation at a Liquid−Liquid Interface and Particle-Specific Surface Modification by Functional Molecules

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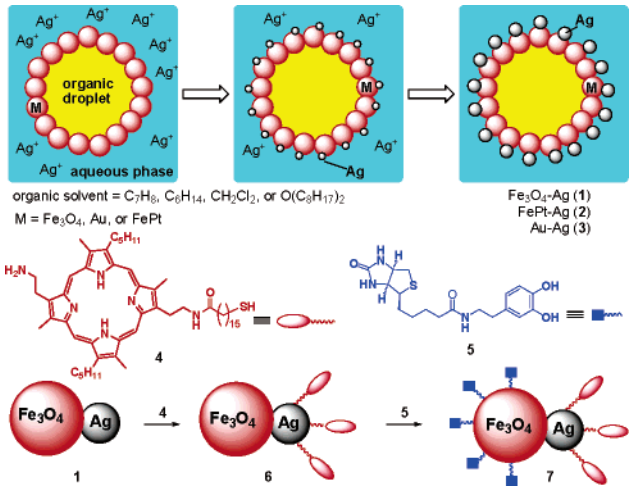
This communication describes a simple methodology to create heterodimers of nanoparticles and to demonstrate particle-specific functionalization of such nanostructures. The rapid development of applications of nanomaterials, ranging from electro-optics to biology,[1,2] demands sophisticated controls over their inherent properties, which usually rely on the composition and shape of nanomaterials,[3] as well as their appropriate surface modifications. While the prescription of starting materials easily provides a precise composition of a nanostructure,[4] shape-controlled chemical synthesis of nanomaterials has only achieved limited success.[5] Despite the increased number of reports on the synthesis of shape-controlled nanostructures, there are few reports on the synthesis of heterostructures that are smaller than 20 nm.[6] Here, we report a new method to create heterodimeric nanostructures at an ambient condition. On the basis of a fundamental property of nanoparticles, that is, nanoparticles self-assemble at a liquid−liquid interface to form "colloidosomes",[7] a heterogeneous reaction takes place on the exposed surface of the nanoparticles that form the colloidosomes and produces the heterodimers of two distinct nanospheres. To demonstrate their unique properties, we used two different kinds of functional molecules covalently bonding to the two spheres of heterodimers in a particle-specific fashion. Besides demonstrating a chemical reaction directly on the colloidosomes, this work offers a convenient methodology to engineer different arrays of functional molecules in a dimension of less than 20 nm, which has not been explored previously. These kinds of nanostructures may lead to useful biological applications; for example, such functionalized heterodimers may act as a versatile platform for labeling, mapping, and studying several receptors simultaneously since it is quite common for receptors to be several nanometers apart on the cell surfaces.

The synthetic route for making the heterodimers is easy and straightforward. After the as-prepared nanoparticles of Fe_3O_4 [8] were dissolved in a proper organic solvent (e.g., dichlorobenzene, dichloromethane, hexane, or dioctyl ether), a solution of the nanoparticles was added into an aqueous solution of silver nitrate. Ultrasonic emulsification afforded a stable emulsion of the two solutions. After a 30 min reaction period, centrifugation separated the organic layer, which contained the well-dispersed heterodimers (**1**). As illustrated in Scheme 1, we suggest that the following mechanism is responsible for generating the heterodimers. Ultrasonication provides the necessary energy to mix the organic phase and the aqueous phase to form the microemulsion which is stabilized by the nanoparticles that self-assemble at the liquid−liquid interface.[7] The imperfect coverage or labile nature of the surfactant molecules on the surface of the nanoparticles allows few Fe(II) sites to act as the catalytic center for the reduction of Ag^+ and the seeding of the Ag nanoparticle. Once the nucleation sites of the silver are formed, the subsequent reduction of Ag^+ proceeds only at the pre-existing nucleation sites until the reaction stops. After

Scheme 1



the reaction stopped, we obtained the heterodimers from the organic phase, suggesting that the surfactants cover the surface of the Ag sphere. Two factors prevent the formation of silver shells on the nanoparticles: (i) partial exposure of the nanoparticles to the aqueous phase and (ii) self-catalyzed reduction of the Ag^+ and the nucleation of silver.[9] Therefore, the heterodimers with gradually increased Ag spheres should be observed throughout the reduction process.

To confirm our assumption, we used transmission electron microscopy (TEM) to follow the process illustrated in Scheme 1. As shown in Figure 1A, the Fe_3O_4 nanoparticles have a diameter of 8 nm before the reaction. At the intermediate stage, the silver spheres of the Fe_3O_4−Ag heterodimers enlarge to 3 nm (Figure 1B); the overall lengths of the final heterodimers are about 13.5 nm, in which the diameter of Fe_3O_4 remains at 8 nm, and that of Ag grows to 5.5 nm (Figure 1C). These results provide direct evidence to the proposed mechanism of the formation of a Ag sphere. X-ray fluorescence (XRF) and selected area electron diffraction (SAED) measurements of **1** confirm the existence of silver.[10] The ratio of Fe_3O_4 to silver is about 1.43:1 (according to XRF), which matches with the observed sizes of each part of the heterodimer. In addition, high-resolution TEM (Figure 1D) of **1** indicates that the silver part is crystalline despite the fact that its crystal lattices exhibit random orientation. To demonstrate the generality of this procedure, we used other nanoparticles to form colloidosomes for making other heterodimers. When FePt nanoparticles[11] (8 nm) or Au nanocrystals[12] (5 nm) were used, we also obtained the corresponding FePt−Ag (**2**) or Au−Ag (**3**) heterodimers (Figure 1E,F). This procedure also affords the heterodimer of Fe_3O_4−Au (**8**),[9] whose magnetic properties can further facilitate the applications of gold nanoparticles.[2] One clear advantage of this process is that the sizes of the heterodimer can be easily controlled

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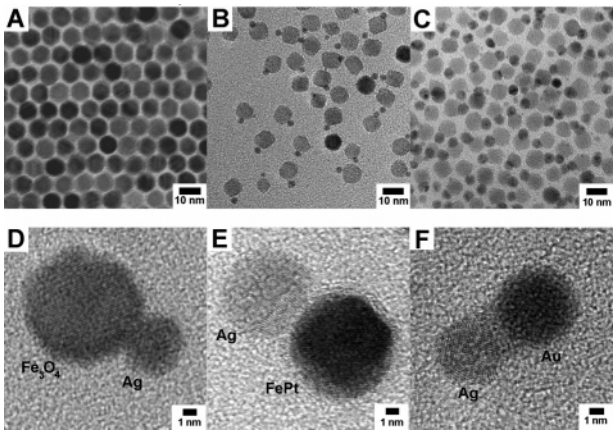

Figure 1. TEM images of (A) the as-prepared Fe_3O_4 nanoparticles; the Fe_3O_4−Ag heterodimers after (B) 10 min reaction and (C) after reaction stopped at 30 min. HRTEM of (D) **1**, (E) **2**, and (F) **3**.

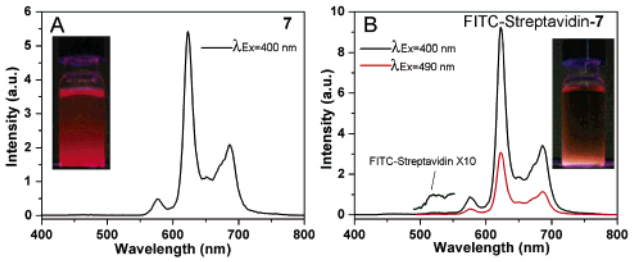

Figure 2. Fluorescent spectra of (A) **7** and (B) **7** binding to streptavidin-FITC. (Inset: the corresponding fluorescent images were obtained using a UV lamp with the wavelength centered at 365 nm.)

by the reaction time (which controls the sizes of Ag nanoparticles) and the sizes of the first nanoparticles.

The substantial difference in surface chemistry of the two spheres in **1** allows different functional molecules to attach to the heterodimer in a particle-specific way via ligand exchange. To explore this possibility, we synthesized compound **4** using the monoamidation of di(2-aminoethyl)porphyrin[13] with $HS(CH_2)_{15}COOH$ and **5** by reacting biotin with protected dopamine. When **4** reacted with Fe_3O_4 nanoparticles, the resulting nanoparticles failed to give the characteristic fluorescence from the porphyrin moiety, suggesting that **4** cannot bind to the Fe_3O_4 spheres in **1**. Therefore, we used **1** to react with **4** in THF for 10 min under sonication to give **6**, which subsequently reacted with **5** in water for another 10 min sonication to yield water-soluble **7**. With the assistance of a small magnet, **7** was thoroughly washed with deionized water. The fluorescent image and spectrum of **7** (Figure 2A) clearly prove that the molecules of **4** reside on **7**. After treating **7** with FITC-labeled streptavidin and the removal of excess FITC-streptavidin,[10] the resulting fluorescent image (Figure 2B), changing from red to orange-red, suggests that **4** and **5** exist on **7**. When being excited at both 400 and 490 nm, the conjugate of FITC-streptavidin-**7** exhibits only weak FITC emissions at 520 nm (due to the efficient energy transfer[14] between FITC and **4**), also proving that **4** and **5** exist on **7**. The XPS and ToF−SIMS experiments further confirm the presence of **4** and **5** on **7**.[10] On the basis of weight analysis and UV−vis spectra, we estimate that, on average, ∼27 molecules of **4** attach to the Ag sphere and ∼2135 molecules of **5** to the Fe_3O_4 sphere.[10]

Thus, we have demonstrated a simple, efficient, and general method to form heterodimeric nanostructures based on the reactions on the colloidosome. This procedure not only controls the sizes and compositions of nanoparticle heterodimers but also allows functional molecules to be attached on specific parts of the heterodimers. This work offers easy access to multifunctional heterodimers (such as **7**) that are hydrophilic, fluorescent, responsive to magnetic forces, and able to bind to specific receptors. We envision that such heterodimers will be useful nanomaterials for biomedical applications, such as protein binding, molecular imaging, and pathogen detections.[15]

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Supporting Information Available: SAED of **1**, **2**, **3**, and the starting materials. UV−vis, XRD, XRF, XPS, and ToF−SIMS analysis. TEM and EDP of **8**. This material is available free of charge via the Internet at http://pub.acs.org.

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