Nanoparticle Assemblies

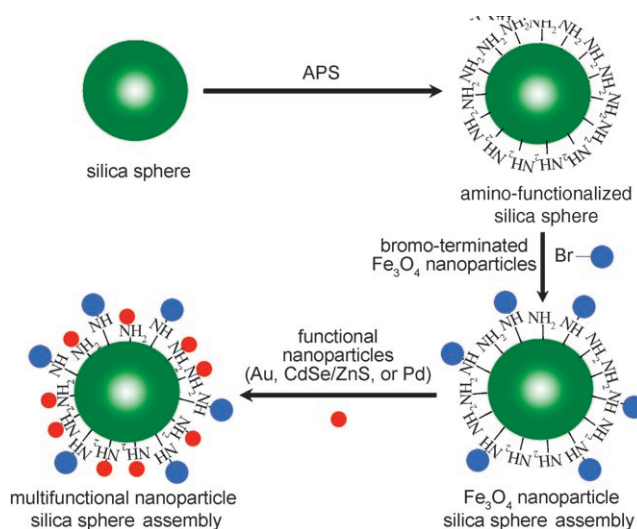# Generalized Fabrication of Multifunctional Nanoparticle Assemblies on Silica Spheres**

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Uniformly sized colloidal nanoparticles have attracted a great deal of attention, not only for their fundamental scientific interest, which is derived from their size-dependent properties, but also for their many technological applications, which include biomedical imaging and functional building blocks for nanoscale devices.[1] Many types of nanoparticles have been assembled on the surfaces of various spherical supports, such as Stöber silica and polymer latex spheres, by various methods including layer-by-layer (LbL) techniques using oppositely charged polyelectrolytes,[2] methods based on direct electrostatic interactions between nanoparticles and supports,[3] and techniques based on the coordination of the nanoparticles on amino- or thiol-functionalized silica spheres.[4] Magnetic nanoparticles[5] have been applied as magnetically separable

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catalysts, contrast-enhancement agents for magnetic resonance imaging (MRI), magnetic carriers for drug-delivery systems, biosensors, and bioseparation.[6]

Controlled assembly of magnetic nanoparticles on the desired supports is important for these applications. There have been several reports on the assembly of magnetic nanoparticles on spherical templates by the LbL technique.[2d–g] For example, alternating layers of polyelectrolytes and magnetite nanoparticles, synthesized in an aqueous phase, were assembled on polystyrene latex spheres. Nanoparticles synthesized in an organic phase are generally more crystalline and uniform than those prepared in the aqueous phase. Recently, FePt alloy nanoparticles[7] and magnetite nanoparticles,[8] synthesized in an organic phase, were assembled on silica spheres by electrostatic interaction. However, it was necessary for these nanoparticles, initially synthesized in an organic phase, to be transformed into water-dispersible nanoparticles, because the assembly procedures were performed in the aqueous phase. Herein we report on a new procedure to assemble hydrophobic magnetite (Fe_3O_4) nanoparticles through covalent bonding on silica spheres by means of a nucleophilic substitution reaction in organic media. We also fabricated multifunctional nanoparticle/silica sphere assemblies by subsequent assembly of nanoparticles of Au, CdSe/ZnS, or Pd on the magnetite nanoparticle-bearing silica spheres. The synthesized multifunctional silica spheres exhibited a combination of magnetism and surface plasmon resonance (Au), luminescence (CdSe/ZnS), or catalysis (Pd).

The general synthetic procedure for multifunctional nanoparticle/silica sphere assemblies is shown in Scheme 1 (see also the Experimental Section). Uniformly sized silica spheres were prepared by the Stöber method.[9] For the assembly of the nanoparticles, the surfaces of the silica spheres were functionalized with amino groups by treatment with (3-aminopropyl)trimethoxysilane (APS). Monodisperse nanoparticles of Fe_3O_4,[5h] Au,[10] CdSe/ZnS,[11] and Pd[12] were synthesized by procedures described previously. To assemble Fe_3O_4 nanoparticles on the silica spheres, the capping oleic

Scheme 1. Synthetic procedure to obtain multifunctional nanoparticle/silica sphere assemblies.

acid ligands of the Fe_3O_4 nanoparticles were exchanged with 2-bromo-2-methylpropionic acid (BMPA).[13] The BMPA-stabilized Fe_3O_4 nanoparticles were assembled on the surfaces of the amino-functionalized silica spheres. The resulting Fe_3O_4 nanoparticle/silica sphere assemblies were designated as Mag-SiO_2. Subsequently, functional nanoparticles of Au, CdSe/ZnS, or Pd were additionally assembled on Mag-SiO_2 to give multifunctional assemblies designated as Mag-SiO_2-Au, Mag-SiO_2-CdSe/ZnS, and Mag-SiO_2-Pd, respectively.

A field-emission scanning electron microscopy (FE-SEM) image of Mag-SiO_2 (Figure 1a) showes that uniform 14-nm

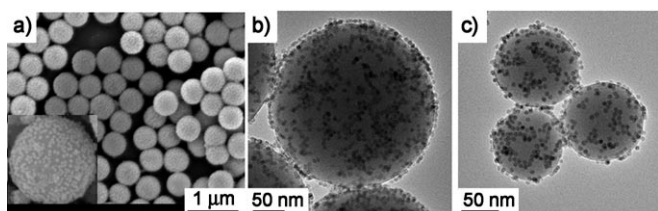***Figure 1.*** SEM and TEM images of Mag-SiO_2. a) FE-SEM image of 500-nm silica spheres assembled with 14-nm Fe_3O_4 nanoparticles (inset: high-magnification FE-SEM image). b) TEM image of 300-nm silica spheres assembled with 7-nm Fe_3O_4 nanoparticles. c) TEM image of 100-nm silica spheres assembled with 7-nm Fe_3O_4 nanoparticles.

Fe_3O_4 nanoparticles were well assembled on the surfaces of the 500-nm silica spheres. Figure 1b and c shows transmission electron microscopy (TEM) images of 7-nm Fe_3O_4 nanoparticles assembled on 300- and 100-nm silica spheres, respectively. The BMPA-stabilized Fe_3O_4 nanoparticles were covalently bonded onto the surfaces of the amino-functionalized silica spheres by a direct nucleophilic substitution reaction between the terminal Br groups of the ligands and NH_2 groups on the silica spheres in THF.[14] This constitutes a new and simple method of assembling magnetite nanoparticles synthesized in organic media on silica spheres by direct covalent bonding, as opposed to the more complicated LbL method, which is conducted in the aqueous phase by using the electrostatic interaction between magnetic nanoparticles and polyelectrolytes. When the original oleic acid stabilized Fe_3O_4 nanoparticles were used instead of BMPA-stabilized ones in assembling Fe_3O_4 nanoparticles on the silica spheres, the number of magnetite nanoparticles attached to the silica spheres was substantially reduced.

By using Mag-SiO_2 as support, various multifunctional composite nanoparticle assemblies were fabricated by coordinating functional nanoparticles of Au, CdSe/ZnS, or Pd to the residual surface amino groups. It is well known that alkyl amines such as hexadecylamine and oleylamine, which are often used as stabilizing ligands for nanoparticles of noble metals and semiconductors, bind to the metal atoms on the surfaces of the nanoparticles through the lone-pair electrons on the nitrogen atom.[11, 12] Similarly, the lone-pair electrons in the amino groups of the amino-modified silica spheres seem to bind to the metal atoms (Au in Au nanoparticles, Zn in the case of CdSe/ZnS core/shell nanoparticles, and Pd in Pd nanoparticles). For example, when we assembled Pd nanoparticles on both amino-modified silica spheres and pristine

unmodified silica spheres, the number of Pd nanoparticles assembled on the former was much higher than that on the latter. Figure 2a shows a TEM image of Mag-SiO_2-Au, in which gold nanoparticles 1–3 nm in size and 7-nm Fe_3O_4
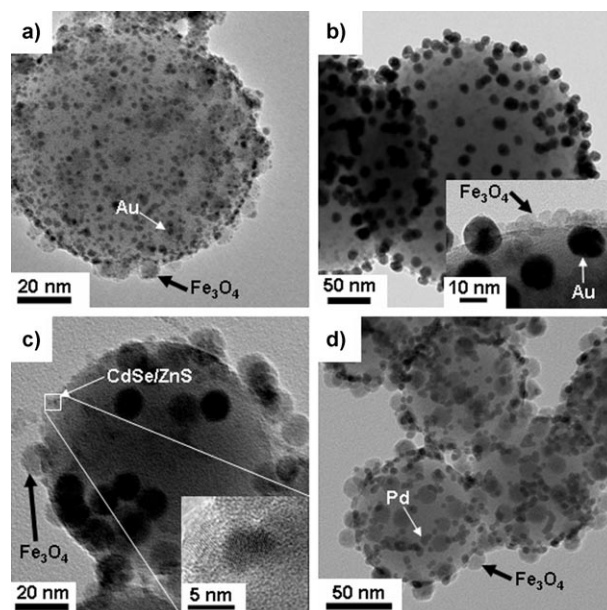

Figure 2. a) TEM image of Mag-SiO_2-Au, in which gold nanoparticles 1–3 nm in size and 7-nm Fe_3O_4 nanoparticles were assembled on 100-nm silica spheres. b) TEM image of Mag-SiO_2-Au, in which 13-nm Au nanoparticles and 7-nm Fe_3O_4 nanoparticles were assembled on 300-nm silica spheres. c) TEM image of Mag-SiO_2-CdSe/ZnS, in which 4.5-nm CdSe/ZnS quantum dots and 14-nm Fe_3O_4 nanoparticles were assembled on 100-nm silica spheres. d) TEM image of Mag-SiO_2-Pd, in which 5-nm Pd nanoparticles and 14-nm Fe_3O_4 nanoparticles were simultaneously assembled on 100-nm silica spheres.

nanoparticles were assembled on 100-nm silica spheres. Larger Au nanoparticles (13 nm) were also assembled on 300-nm silica spheres with 7-nm magnetite nanoparticles (Figure 2b). The TEM and high-resolution TEM (HRTEM) images of Mag-SiO_2-CdSe/ZnS showed that these composite nanoparticle assemblies consist of highly crystalline 4.5-nm CdSe/ZnS quantum dots coexisting with 14-nm Fe_3O_4 nanoparticles on the surfaces of 100-nm silica spheres (Figure 2c). Assembly of 14-nm Fe_3O_4 nanoparticles and 5-nm Pd nanoparticles on 100-nm silica spheres produced Mag-SiO_2-Pd (Figure 2d).

The properties of these multifunctional nanoparticle assemblies are depicted in Figure 3. For applications involving magnetic delivery or separation, superparamagnetic properties are more desirable than ferromagnetism, because there should be no residual magnetism after the magnetic field is removed. The field-dependent magnetization curve of the Mag-SiO_2 sample of Figure 1a at 300 K showes no hysteresis (Figure 3a), that is, Mag-SiO_2 exhibits superparamagnetic behavior derived from the well-assembled magnetite nanoparticles on the silica spheres. The UV/Vis spectrum of the Mag-SiO_2-Au of Figure 2b shows the characteristic surface plasmon band at 530 nm (solid line in Figure 3b). On the other hand, the supernatant solution after removal of Mag-
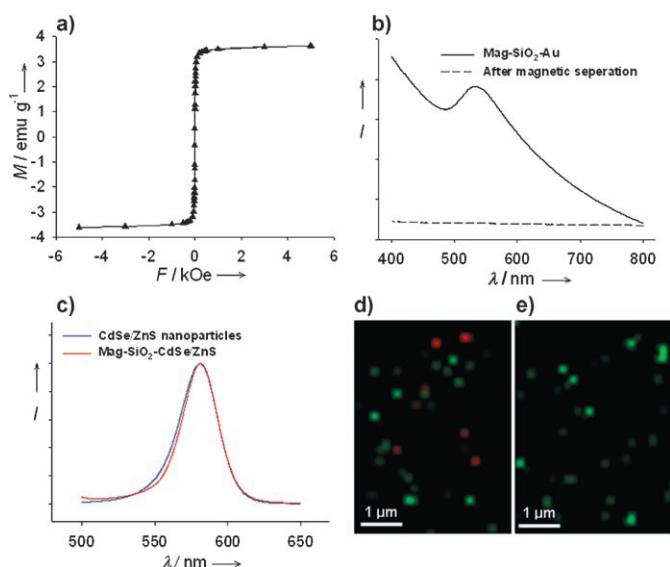
Figure 3. a) Field-dependent magnetization at 300 K of the Mag-SiO$_2$ sample of Figure 1 a. b) UV/Vis absorption spectra of a suspension of the Mag-SiO$_2$-Au sample of Figure 2 b before (solid line) and after (dotted line) removal of Mag-SiO$_2$-Au by magnetic separation. c) Photoluminescence spectra ($\lambda_{ex} = 450$ nm) of pristine CdSe/ZnS nanoparticles (blue line) and the Mag-SiO$_2$-CdSe/ZnS sample of Figure 2 c (red line). d, e) Confocal micrographs obtained from a mixed suspension of red-emitting Mag-SiO$_2$-CdSe/ZnS and green-emitting SiO$_2$-CdSe/ZnS before and after removal of red-emitting Mag-SiO$_2$-CdSe/ZnS by using a magnet, respectively.

SiO$_2$-Au with a magnet showed no absorption peak (dotted line in Figure 3b) and thus demonstrated the magnetic-separation characteristics of the silica spheres. The Mag-SiO$_2$-CdSe/ZnS spheres of Figure 2c exhibited an emission peak at a position slightly red-shifted from that of the pristine CdSe/ZnS nanoparticles (Figure 3c).

To demonstrate the combined magnetic and luminescent properties of Mag-SiO$_2$-CdSe/ZnS simultaneously, we prepared red-emitting Mag-SiO$_2$-CdSe/ZnS (Fe$_3$O$_4$ nanoparticles and red-emitting CdSe/ZnS nanoparticles assembled on silica spheres) and green-emitting SiO$_2$-CdSe/ZnS (green-emitting CdSe/ZnS nanoparticles assembled on silica spheres without Fe$_3$O$_4$ nanoparticles). Then, the two samples were mixed in chloroform and magnetic separation was performed. The confocal micrograph of the mixed solution (Figure 3d) showed that red and green dots were coexistent, whereas only green dots remained after magnetic separation (Figure 3e), that is, red-emitting Mag-SiO$_2$-CdSe/ZnS was completely removed from the mixture. This combination of magnetic and optical properties should enable the Mag-SiO$_2$-CdSe/ZnS nanoparticle assemblies to be used simultaneously for biolabeling and MRI.

To investigate the catalytic activity of Mag-SiO$_2$-Pd, a Sonogashira coupling reaction was performed. After completion of the coupling reaction, Mag-SiO$_2$-Pd could easily be separated from the reaction mixture by using a magnet. The reaction solution was dark before magnetic separation (Figure 4a), whereas black Mag-SiO$_2$-Pd was attracted to the magnet and a yellowish solution remained after magnetic separation (Figure 4b). High catalytic activities for aryl
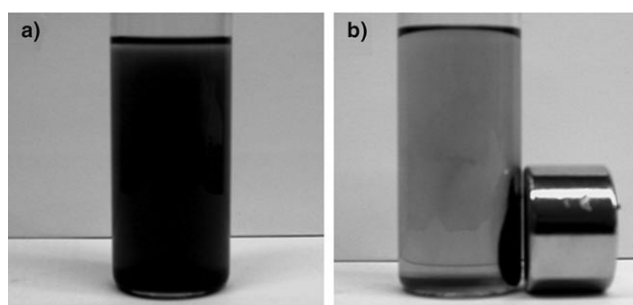

Figure 4. Photographs of reaction mixtures a) before and b) after magnetic separation of Mag-SiO$_2$-Pd used in reaction (1).

iodides and aryl bromides were shown by Mag-SiO$_2$-Pd (Table 1). To investigate the stability of the silica spheres during the catalytic reactions, we performed recycling experiments.

Table 1: Test of catalytic activity of Mag-SiO$_2$-Pd in the Sonogashira coupling reaction (1).[a]
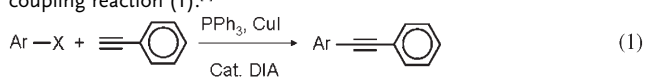
Entry	X	Ar	Catalyst (mol %)[b]	Yield [%][c]
1	I	4-acetylphenyl	Mag-SiO$_2$-Pd (3)	95.0
2	I	2-thienyl	Mag-SiO$_2$-Pd (3)	99.3
3	I	2-thienyl	recovered from entry 2 (3)	98.1
4	I	phenyl	Mag-SiO$_2$-Pd (3)	100
5	Br	2-thienyl	Mag-SiO$_2$-Pd (5)	99.5
6	Br	2-thienyl	recovered from entry 5 (5)	98.2
7	Br	2-thienyl	recovered from entry 6 (5)	88.1
8	Br	2-thienyl	recovered from entry 7 (5)	75.7
9	Br	2-thienyl	recovered from entry 8 (5)	16.9

[a] DIA = diisopropylamine; reaction conditions: 85 °C, 18 h. [b] Catalyst concentration based on Pd. [c] Yield of isolated product.

As summarized in Table 1 (entries 5–9), Mag-SiO$_2$-Pd was recycled four times for coupling 2-bromothiophene. Recently, Nacci et al. reported that the yield of Suzuki and Stille coupling reactions with Pd nanoparticles gradually decreased as recycling proceeded.[15] Our recycling experiments showed a similar trend. The catalytic activity of Mag-SiO$_2$-Pd for the Sonogashira coupling was maintained above 75 % yield until the third recycling. However, the yield steeply decreased to 17 % in the fourth recycling reaction. The TEM image of the recovered Mag-SiO$_2$-Pd after the first reaction showed that not only Fe$_3$O$_4$ nanoparticles but also Pd nanoparticles were firmly attached to the silica spheres. In contrast, the TEM image after the fourth recycling experiment revealed that most of Pd nanoparticles were detached from the silica spheres, whereas many Fe$_3$O$_4$ nanoparticles were still firmly attached to the silica spheres. These results demonstrate that the decrease in yield of the catalytic coupling reactions resulted from detachment of Pd nanoparticles from the silica spheres.

In summary, we have reported a simple, reproducible, and general method of preparing multifunctional nanoparticle assemblies on silica spheres. Magnetite nanoparticles synthe-

sized in an organic phase were covalently bonded on silica spheres, and subsequently nanoparticles of Au, CdSe/ZnS, or Pd were assembled. These multifunctional nanoparticle/silica sphere assemblies are likely to find many catalytic and biomedical applications derived from their combination of magnetic properties with surface plasmon resonance, luminescence, or catalysis.

Experimental Section

Synthesis of amino-functionalized Stöber silica spheres: Uniform 100-, 300-, and 500-nm silica spheres were synthesized by the Stöber method.[9] The surfaces of the silica spheres were functionalized with amino groups by treatment with APS in refluxing ethanol.

Ligand exchange of Fe_3O_4 nanoparticles synthesized in an organic phase: Monodisperse Fe_3O_4 nanoparticles (14- and 7-nm) capped with oleic acid were synthesized in an organic phase by procedures described previously.[5h] 50 mg of the as-synthesized nanoparticles were dispersed in 3 mL of chloroform and the resulting solution was added to 30 mL of BMPA in chloroform (0.1 M solution).[13] After stirring the solution at room temperature for 48 h, the nanoparticles were precipitated by adding an excess of ethanol. The precipitated nanoparticles were retrieved by centrifugation.

Synthesis of Mag-SiO$_2$: The BMPA-stabilized magnetite nanoparticles dispersed in 3 mL of THF were added to a solution containing 0.1 g of amino-functionalized silica spheres dispersed in 20 mL of THF, and the resulting dispersion was heated to reflux for 3 h. The magnetite nanoparticle/silica sphere assemblies were isolated by three cycles of centrifugation, redispersion in THF, and magnetic separation.

Synthesis of Mag-SiO$_2$-Au: Citrate-stabilized gold nanoparticles with sizes of 1–3 and 13 nm were prepared by procedures described previously.[10] 10 mg of Mag-SiO$_2$ was dispersed in 30 mL of aqueous Au nanoparticle solution, and the resulting aqueous dispersion was stirred for 6 h at room temperature. The Mag-SiO$_2$-Au spheres were isolated by three cycles of centrifugation, redispersion in water, and magnetic separation.

Synthesis of Mag-SiO$_2$-CdSe/ZnS: CdSe/ZnS nanoparticles were prepared by a procedure described previously.[11] A dispersion of 20 mg of CdSe/ZnS nanoparticles in 3 mL of chloroform was mixed with 10 mg of Mag-SiO$_2$ in 10 mL of chloroform, and the resulting dispersion was stirred at room temperature for 6 h. The Mag-SiO$_2$-CdSe/ZnS spheres were isolated by three cycles of centrifugation, redispersion in chloroform, and magnetic separation.

Synthesis of Mag-SiO$_2$-Pd: 5-nm Pd nanoparticles were prepared by a procedure described previously.[12] A dispersion of 20 mg of Pd nanoparticles in 3 mL of chloroform was mixed with 10 mg of Mag-SiO$_2$ in 10 mL of chloroform, and the resulting dispersion was stirred at room temperature for 6 h. The Mag-SiO$_2$-Pd spheres were isolated by three cycles of centrifugation, redispersion in chloroform, and magnetic separation.

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