Synthesis of Fe_3O_4/PdO heterodimer nanocrystals in silica nanospheres and their controllable transformation into Fe_3O_4/Pd heterodimers and FePd nanocrystals†

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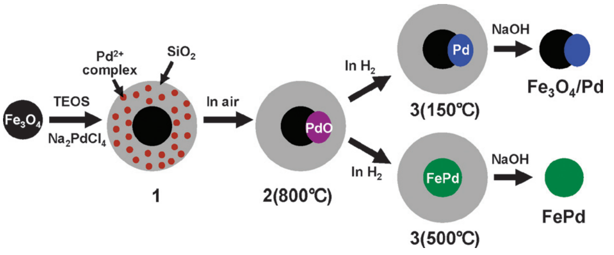
The thermal annealing of silica nanospheres encapsulating Fe_3O_4 nanocrystals and Pd^{2+} complexes led to the formation of heterodimers consisting of Fe_3O_4 and PdO nanoparticles encapsulated in a silica shell, allowing for their controllable transformation into either Fe_3O_4/Pd heterodimers or FePd alloy nanocrystals through a solid state reduction process.

An important direction in current nanochemistry is the synthesis and fabrication of hybrid nanocrystals containing two or more chemically different species.[1] The integration of different functionalities in individual nanocrystals can endow them with novel properties and unique applicability which cannot be achieved with single component nanocrystals.[2] The properties of hybrid nanocrystals can be dramatically changed by varying the distribution of the chemical species inside them.[3] In general, conventional chemical methods produce chemically disordered alloys or core-shell structures in which two distinct chemical species are isotropically distributed. In recent years, several hybrid nanocrystals with a phase-segregated heterostructure have been produced through an approach based on the lattice mismatch and immiscibility between two inorganic species.[4] For example, several heterodimers based on magnetic nanocrystals, including Au/Fe_3O_4, Ag/Fe_3O_4, CdS/FePt, and γ-Fe_2O_3/metal sulfides, were synthesized through subsequent crystal growth at the surface of the preformed seed nanocrystals.[5] While significant advances have been made in the preparation of hybrid nanocrystals, the control of the transformation between the different structures and the fine tuning of their properties still remains a significant challenge.

In this context, our research efforts have been devoted to the development of a novel method of fabricating hybrid nanocrystals containing a magnetic component. In this work, we synthesized anisotropically phase-segregated heterodimers consisting of Fe_3O_4 and PdO nanocrystals during the thermal annealing of silica nanospheres encapsulating Fe_3O_4 nanocrystals and Pd^{2+} complexes. Herein, we report the novel and facile synthesis of heterodimers of Fe_3O_4/PdO nanoparticles in silica nanospheres and their controllable transformation into either Fe_3O_4/Pd heterodimers or FePd alloy nanocrystals, which have the potential to be used as recyclable catalysts or magnetic storage media, by their subsequent reduction in a hydrogen atmosphere (Scheme 1).

The encapsulation of Fe_3O_4 nanocrystals and Pd^{2+} complexes inside the silica shell was conducted by the modification of the reverse microemulsion technique.[6] 8 nm sized Fe_3O_4 nanocrystals stabilized by oleic acid were prepared using the previously reported procedure.[7] The Fe_3O_4 nanocrystals were mixed with a cyclohexane solution of polyoxyethylenenonylphenyl ether (Igepal CO-520, containing 50 mol% hydrophilic groups). Then, an aqueous solution containing Na_2PdCl_4 was injected into the suspension, generating a microemulsion system containing Pd^{2+} complexes in the water droplets and Fe_3O_4 nanoparticles in the external organic phase. The formation of silica around the Fe_3O_4 nanocrystals was initiated by the successive addition of NH_4OH aqueous solution and tetraethyl orthosilicate (TEOS). When MeOH was added after 12 h, brown solids were precipitated out of the reaction suspension. The resulting solids were isolated by magnetic decantation and washed several times with EtOH. Transmission electron microscopy (TEM) analyses of the resulting solids revealed the formation of silica nanospheres, **1**, containing Fe_3O_4 nanocores and tiny aggregates of Pd^{2+} complexes homogeneously distributed over the silica matrix (Fig. 1a).

The nanospheres **1** were annealed in air at various temperatures. The X-ray diffraction (XRD) pattern of the annealed solids, **2**, showed the formation of a PdO phase, while preserving the crystalline phase of the cores in the form of Fe_3O_4 (ESI†). The TEM image of the nanospheres annealed at 400 °C, **2**(400 °C), showed the creation of small PdO nanoparticles



Scheme 1 Preparation and transformation of the nanospheres **1**.

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† Electronic supplementary information (ESI) available: Expermental procedures for the syntheses of **1**, **2**, and **3**, TEM images of Fe_3O_4 nanoparticles, XPS of **1**, EDS of Fe_3O_4/Pd heterodimers, XRDs of **1**, **2**, **3**, and Fe_3O_4 coated by silica, and TEM images of silica nanospheres synthesized in the absence of Fe_3O_4 nanoparticles. See DOI: 10.1039/b812690a

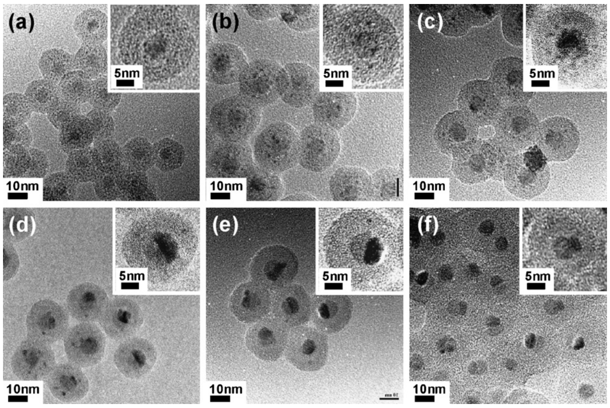

Fig. 1 TEM images of the silica nanospheres containing Fe_3O_4 nanocores and Pd^{2+} complexes before and after the annealing in air at different temperatures: (a) **1**, (b) **2**(400 °C), (c) **2**(500 °C), (d) **2**(600 °C), (e) **2**(700 °C), and (f) **2**(800 °C).

with an average size of 2 nm in a silica matrix (Fig. 1b). When the annealing was conducted at a higher temperature, PdO grains appeared to be attached to the Fe_3O_4 surface. Therefore, after annealing at 600 °C, the nanospheres, **2**(600 °C), were found to have both small grains of PdO attached to the Fe_3O_4 surface and individual small PdO nanoparticles distributed in a silica matrix (Fig. 1d). The nanospheres annealed at 800 °C, **2**(800 °C), showed the formation of PdO grains with average size of 6 nm attached to the surface of the Fe_3O_4, resulting in heterodimers consisting of Fe_3O_4 and PdO nanocrystals (Fig. 1f). As a control experiment, silica nanospheres containing Pd^{2+} complexes were prepared in the absence of Fe_3O_4 nanoparticles and treated at high temperature. When the nanospheres were annealed at 700 °C, it was observed that the majority of the PdO phase grew on the surface of the silica spheres to form patches having a relatively large size. It was also observed that a lower number of PdO nanoparticles formed in the silica matrix when the heat treatment was conducted at 700 °C, as compared to when the annealing was performed at 500 °C (ESI†). From these observations, it can be inferred that the formation of the Fe_3O_4/PdO heterodimer **2**(800 °C) is mainly due to the coalescence of the nanoparticles at high temperature. In our hypothesis, the PdO nanoparticles, generated during the decomposition of the Pd^{2+} complexes, would diffuse and combine at the Fe_3O_4 surface only at high temperature. The attachment of the PdO phase to Fe_3O_4 may be understood in terms of the more favourable interaction of PdO with the interface between Fe_3O_4 and silica compared with that between silica and air. When the nanospheres **2**(400 °C), containing PdO nanoparticles in a silica matrix, were subsequently treated at 800 °C for 5 h, the Fe_3O_4/PdO heterodimer was also generated, which supports our hypothesis based on the coalescence of the nanoparticles.

When the nanospheres containing the heterodimers were annealed under a flow of Ar + 4% H_2, it was revealed that the conversion of the nanostructure proceeded in different ways depending on the annealing temperature. Therefore, after the annealing of **2**(800 °C) at 150 °C, the PdO phase was reduced to a Pd phase without any significant changes in the size and shape of the grains, resulting in the formation of the Fe_3O_4/Pd heterodimer within the silica shell, **3**(150 °C) (Fig. 2a). The reduction of PdO to Pd was also detected by the changes in the XRD pattern after the annealing. When the reductive annealing was conducted at 500 °C, the Fe_3O_4/Pd heterodimer was transformed into spherical FePd alloy nanoparticles having a size of 7 nm, presumably *via* the reduction of both Fe_3O_4 and PdO phases and the interdiffusion between the reduced phases (Fig. 2c). The XRD pattern of the solid annealed at 500 °C, **3**(500 °C), showed the disappearance of the Fe_3O_4 peaks and the shift of the Pd peak to a slightly higher angle, indicating the formation of a disordered fcc FePd alloy phase (Fig. 2d).[8] When the silica nanospheres containing Fe_3O_4 nanoparticles, prepared without the addition of a Pd^{2+} complex, were successively annealed in air and in hydrogen atmosphere, the reduction of Fe_3O_4 was not observed. From this, it can be assumed that Pd of the Fe_3O_4/Pd heterodimer facilitates the reduction of the Fe_3O_4 phase resulting in a FePd alloy (ESI†). Recently, Teranish *et al.* reported the conversion of a Fe_3O_4/Pd heterodimer into FePd@α-Fe nanoparticles during a reductive annealing process.[9] And, Hyeon *et al.* also observed the transformation of the Fe/Pt heterodimers within a silica shell into FePt nanoparticles through the solid state reaction at high temperature.[10] Both **3**(500 °C) and **3**(150 °C) were superparamagnetic at room temperature, while they showed ferromagnetic behaviour at 5 K (Fig. 2e). The magnetic coercivity, derived from the hysteresis loop at 5 K, was found to be markedly enhanced for **3**(500 °C) containing the FePd phase, compared with that of **3**(150 °C) having the Fe_3O_4/Pd heterodimer. The magnetic coercivity values for **3**(150 °C) and **3**(500 °C) at 5 K were 290 and 720 Oe, respectively. The silica shell of **3** could be readily removed by etching with aqueous NaOH solution to afford inorganic nanoparticles without any coating on their surface. The TEM images of the resulting solids showed the highly crystalline nature of the nanocrystals and the preservation of the morphology of the Fe_3O_4/Pd heterodimer and FePd nanocrystals, even after the removal of the silica shell (Fig. 3).

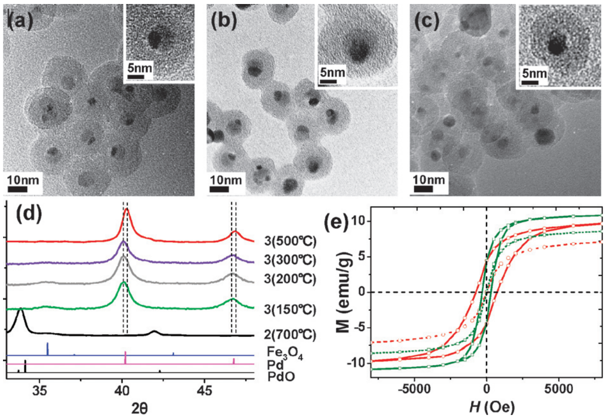

Fig. 2 TEM images of the silica nanospheres of (a) **3**(150 °C), (b) **3**(200 °C), and (c) **3**(500 °C), (d) XRD patterns of the silica nanospheres before and after heat treatment under reductive conditions, and (e) magnetic hysteresis loops of **3**(150 °C) (green lines) and **3**(500 °C) (red lines) at T = 5 K (dotted lines) and T = 300 K (solid lines).

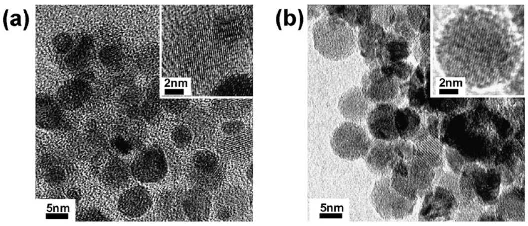

Fig. 3 TEM images of (a) the Fe_3O_4/Pd heterodimer and (b) the FePd nanocrystals obtained by removing silica shells from **3**(150 °C) and **3**(500 °C), respectively.

In conclusion, we demonstrated a novel method of synthesizing heterodimeric nanostructures of Fe_3O_4/PdO based on the transformation of the nanostructure within silica nanospheres. We also demonstrated their controllable transformation into either Fe_3O_4/Pd heterodimers or FePd alloy nanoparticles, having much potential usefulness, through the solid phase reduction process. In particular, the resulting nanoparticles combining the catalytic activity of Pd and the superparamagnetic properties of the magnetic component can be attractive materials for the development of recyclable nanocatalyst systems.[11] Our further research efforts will be directed toward this end.

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