Synthesis and detection the oxidization of Co cores of Co@SiO\textsubscript{2} core-shell nanoparticles by \textit{in situ} XRD and EXAFS

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Abstract

In this paper, the Co@SiO\textsubscript{2} core-shell nanoparticles were prepared by the sol-gel method. The oxidization of Co core nanoparticles was studied by the synchrotron radiation-based techniques including \textit{in situ} X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) up to 800°C in air and N\textsubscript{2} protection conditions, respectively. It was found that the oxidization of Co cores is undergoing three steps regardless of being in air or in N\textsubscript{2} protection condition. In the first step ranging from room temperature to 200°C, the Co cores were dominated by Co\textsubscript{0} state as well as small amount of Co\textsuperscript{2+} ions. When temperature was above 300°C, the interface between Co cores and SiO\textsubscript{2} shells was gradually oxidized into Co\textsuperscript{2+}, and the CoO layer was observed. As the temperature increasing to 800°C, the Co cores were oxidized to Co\textsubscript{3}O\textsubscript{4} or Co\textsubscript{3}O\textsubscript{4}/CoO. Nevertheless, the oxidization kinetics of Co cores is different for the Co@SiO\textsubscript{2} in air and N\textsubscript{2} gas conditions. Generally, the O\textsubscript{2} in the air could get through the SiO\textsubscript{2} shells easily onto the Co core surface and induce the oxidization of the Co cores due to the mesoporous nature of the SiO\textsubscript{2} shells. However, in N\textsubscript{2} gas condition, the O atoms can only be from the SiO\textsubscript{2} shells, so the diffusion effect of O atoms in the interface between Co core and SiO\textsubscript{2} shell plays a key role.

Keywords: Core-shell nanoparticles; Co@SiO\textsubscript{2}; \textit{in situ} XRD/XAFS; Synchrotron radiation techniques

Background

In the past years, nanomaterials have been attracted extensive interests due to their unique properties and potential applications in chemistry, physics, biology, and catalysis. For example, magnetic nanoparticles have potential applications in catalyst, resonance imaging, drug targeting, and bio-conjugation. However, the magnetic nanoparticles can be oxidized easily in atmosphere and thus limiting the applications of these nanomaterials [1-3].

Recently, a series of supported cobalt or cobalt oxide materials such as Co/Al\textsubscript{2}O\textsubscript{3}, Co/\kappa-Al\textsubscript{2}O\textsubscript{3}, Co/SiO\textsubscript{2}, and Co/TiO\textsubscript{2} have been studied for catalysis. The most famous application of the Co/SiO\textsubscript{2} and Co/Al\textsubscript{2}O\textsubscript{3} catalysts is for the Fischer-Tropsch synthesis [4-8]. W. Ma and T. Das investigated the influence of support type and cobalt cluster size on the kinetics of Fischer-Tropsch synthesis of Co/SiO\textsubscript{2} catalysts, and the kinetic results demonstrated that the Fischer-Tropsch reaction exhibited some structure sensitivity to the kinetic effect of water with respect to support type and Co cluster size [5,6]. A. M. Saib studied the surface oxidation behavior of the nanosized cobalt crystallites (4 to 5 nm) of Co/SiO\textsubscript{2}/Si(100) model catalyst using \textit{in situ} near-edge X-ray absorption fine structure (NEXAFS) under model Fischer-Tropsch synthesis conditions. No surface oxidation of cobalt was observed under these model FTS conditions over a wide temperature range, i.e., 150°C to 400°C [7]. The Co/SiO\textsubscript{2} materials can be used as catalyst for hydrogen generation as well [9]. In general, it has been reported that the Co\textsubscript{3}O\textsubscript{4} particles were more readily reduced to metallic cobalt in H\textsubscript{2} than the Co\textsuperscript{2+} species. After reduction at 480°C in H\textsubscript{2}, the CO hydrogenation activity in ten atmospheres of 3H\textsubscript{2}:1CO at 260°C with supported 5 wt% cobalt decreased as the order of Co/SiO\textsubscript{2} > Co/TiO\textsubscript{2} > Co/Al\textsubscript{2}O\textsubscript{3} > Co/\kappa-Al\textsubscript{2}O\textsubscript{3}. Therefore, the determination of the types of cobalt species present on each support and their
reduction properties was to the key points to explain the catalysts’ CO hydrogenation activities [10].

Different strategies have been proposed for the preparation of Co/oxide core-shell nanoparticles. X. J. Yin and X. Lu have synthesized the Co/SiO$_2$ core-shell nanoparticles using the novel aqueous solution method and improved sol-gel method combining with hydrogen reduction, and they also found that the saturation magnetization and coercivity varies with the SiO$_2$ content. The size and the saturation magnetization value of samples decreased with the increase of the SiO$_2$ content [11,12]. In order to protect the oxidation of magnetic nanoparticles, an inert shell onto the magnetic core nanoparticles could be an elegant approach. V. Salgueirino-Maceira et al. reported a sol-gel method to synthesize the Co nanoparticles which are coated with a protective silica layer and then using the standard Stöber (by adding the tetraethoxysilane (TEOS) into aqueous/ethanolic solution) method to obtain the Co@SiO$_2$ core-shell nanoparticles. They have also reported the first synthesis of unique silica-coated chains of 32-nm cobalt nanoparticles resembling nanoscale pearl necklaces in colloidal suspension under magnetic stirring. This phenomenon was attributed to the magnetic dipole-dipole interaction between neighbor particles [13,14]. Up to now, there are many magnetic core-shell materials which have been made including Fe$_3$O$_4$@SiO$_2$/Ag, Fe$_2$O$_4$@SiO$_2$, Fe$_3$O$_4$@SnO$_2$, Co@SiO$_2$, Pt@CoO, FePt@SiO$_2$, Fe$_3$O$_4$@Au, Fe$_2$O$_3$-CdSe@SiO$_2$, and Fe$_3$O$_4$/Fe$_2$O$_3$@SiO$_2$ [15-23]. For example, the Fe$_3$O$_4$@SiO$_2$ is a common magnetic core-shell nanoparticle. The core particle Fe$_3$O$_4$ can be used in resonance imaging, whereas the shell layer is mesoporous SiO$_2$, which can provide enough space for additive and can be used for loading particles to adsorb or isolate protein and antibody. Moreover, through the surface modification of the shell layer by adsorbing noble metal nanoparticles, the core-shell system can be used for catalyst, luminescence imaging, and photodynamic therapy [24].

However, the stability and thermal properties of Co@SiO$_2$ under high temperature have not been completely studied. In this paper, the in situ extended X-ray absorption fine structure (EXAFS) and X-ray diffraction (XRD) techniques are used to probe the properties of Co@SiO$_2$ core-shell nanoparticles with temperature up to 800°C.

**Methods**

**Chemical reagents**

Cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O), sodium borohydride (NaBH$_4$), sodium citrate dehydrate, and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., China. TEOS and 3-aminopropyltriethoxysilane (APS) were purchased from Sigma-Aldrich, St. Louis, MO, USA. All reagents were used as received. Deionized water was distilled by a Milli-Q water purification system (Millipore Corp., Bedford, MA, USA).

**Preparation of Co@SiO$_2$ core-shell nanoparticles**

Co@SiO$_2$ core-shell nanoparticles were prepared by V. Salgueirino-Maceira’s method [13,14]. Firstly, citrate stabilized Co nanoparticles were prepared from the conventional NaBH$_4$ reduction of CoCl$_2$·6H$_2$O. In a typical procedure, under vigorous stirring and N$_2$ protection, 0.2 mL of 0.4 M CoCl$_2$ solution was added quickly into 200 mL water which contains 4×10$^{-3}$ M NaBH$_4$ and 4×10$^{-4}$ M sodium citrate. The solution turned brown or black immediately after mixing. Secondly, 800 mL ethanol with 14.4 μL APS and 169 μL TEOS was added into the above solution after 1 min and then kept stirring at least 24 h to complete the reaction. Finally, the Co@SiO$_2$ core-shell nanoparticles were separated by centrifugation and dried in air for further investigation.

**Transmission electron microscopy**

Bright-field transmission electron microscopy (TEM) observation was performed on a JEM 1230 electron microscope (JEOL Ltd., Akishima-shi, Japan) operated at 80 kV. The specimens were prepared by dropping the Co@SiO$_2$ solution onto a carbon-coated TEM grid. After the specimens were dried in air, they were used for the TEM observation.

**Ultraviolet-visible absorption spectroscopy**

During the preparation of Co@SiO$_2$ nanoparticles, the color of the solution changing from colorless to brown was observed, indicating that the Co$^{2+}$ ions have been reduced to Co nanoparticles. Moreover, in the period of silica-coating procedure, the surrounding mediate of Co nanoparticles changed which could inflect the absorption cross section. So we used the Nicolet Evolution 300 spectrophotometer (Thermal Fisher Scientific, Waltham, MA, USA) to invest the ultraviolet-visible (UV-vis) absorption spectroscopy of the reaction solution. The wavelength range is 190 ~ 1,100 nm.

**Extended X-ray absorption fine structure measurements**

Transmission EXAFS measurements of Co K edge (7,709 eV) were performed at the beamline 4B9A of Beijing Synchrotron Radiation Facility (BSRF). The storage ring was operated at 2.5 GeV with current about 200 mA. The EXAFS signals in the energy range from 7,589 to 8,709 eV were collected with two ionization chambers filled with 100% N$_2$ gas. The incident X-ray was monochromatized with a double-crystal Si (111) monochromator to an energy resolution ($\Delta E/E$) of 2×10$^{-4}$. In order to take in situ EXAFS measurements, the Co@SiO$_2$ should mix with BN powder and was pressed into a pill of 10 mm in diameter and 1 mm in...
thickness \((d)\). By adjusting the ratio of Co@SiO\(_2\) and BN in the mixture, the absorption thickness \((\Delta \mu \cdot d)\) was optimized to one, where \(\Delta \mu\) is the difference of Co absorption coefficients after and before the Co K absorption edge (7,709 eV). Then, the pill was placed on the sample holder which can be inserted into the heating furnace. The temperature uncertainty can be controlled within ±0.1°C with an 818 temperature controller. During heating the sample, the heating rate was set to 10°C/min. The room temperature EXAFS spectrum was first collected, and subsequently, the high-temperature EXAFS spectra were orderly collected in the temperature range from 100°C to 800°C with a temperature interval of 100°C. Before EXAFS measurements at each target temperature, the sample was heat preserved at least 30 min to ensure the sample reaching a thermal equilibrium. In order to invest the influence of reaction atmosphere’s to Co oxidation process, we made the EXAFS measurements under air and N\(_2\) conditions.

**Results and discussion**

The TEM image of the Co@SiO\(_2\) core-shell nanoparticles is shown in Figure 1. Most of the Co@SiO\(_2\) nanoparticles with ~50 nm diameter contain multiple Co cores, but the Co cores are separated from each other. According to the TEM image, the average diameter of Co cores is evaluated to be about 20 nm. The obtained Co@SiO\(_2\) core-shell nanoparticles are different from the previous work [13,14] which may be due to the different reaction conditions, such as the rate of protect N\(_2\) gas and stirring rate.

**X-ray diffraction measurements**

*In situ* XRD of the Co@SiO\(_2\) core-shell nanoparticles was measured at the beamline 4B9A-XRD of BSRF using an image plate. The diffraction signals were collected after the EXAFS measurements at each target temperature. As same as the EXAFS, the temperature range is 25°C ~ 800°C.

![Figure 1 TEM image of the as-prepared Co@SiO\(_2\) core-shell nanoparticles.](image1)

![Figure 2 UV-vis spectra of solution during synthesis time.](image2)
Figure 2 shows the UV-vis spectroscopy during the reaction process. The initial CoCl$_2$ solution exhibits a high absorption peak at 510 nm (blue line), which is disappeared immediately after the addition of NaBH$_4$ solution. In the meantime, there are two weak absorption peaks at 230 and 280 nm which belong to the Co nanoparticles (yellow line). Based on these results, it reveals that the Co nanoparticles are synthesized immediately after the addition of NaBH$_4$ solution. The UV-vis spectroscopy of Co@SiO$_2$ core-shell nanoparticles after the addition of APS and TEOS (red line) was measured as well (cf. Figure 2). No significant change from the Co nanoparticles was observed, except the higher intensities of the absorption peaks. This is because that the SiO$_2$ shell could change the dielectric constant around Co cores and thus increases the absorption intensities.

In order to invest the structure changes during the heating process, combining in situ XRD and EXAFS techniques were performed. Figure 3 shows the results of the in situ XRD measurements. Figure 3a,b represents the measurements in air and N$_2$ atmosphere, respectively. In addition, the sample in Figure 3b is the mixture of Co@SiO$_2$ and BN powders. No diffraction peaks were observed in spite of being in air or N$_2$ atmosphere when the temperature was below 800°C, indicating that the Co@SiO$_2$ core-shell nanoparticles are maintained amorphously. However, when the temperature is above 800°C, SiO$_2$ and Co$_3$O$_4$ crystals were clearly observed (Figure 3). It is worth noting that the SiO$_2$ shells could not protect the Co cores from oxidizing to Co$_3$O$_4$, which can be demonstrated in the following EXAFS analysis.

To characterize the structure change of Co cores of the nanoparticles, in situ EXAFS technique was used to
probe the local atomic structures of Co in the Co@SiO$_2$ nanoparticles. In situ EXAFS spectra of the Co K edge were fitted with the following EXAFS function [25-27]:

$$
\chi(k) = \sum_j N_j S_j^2 F_j(k) e^{-2k^2\sigma_j^2} e^{-2R_j/k} \sin[2kR_j + \phi_j(k)]
$$

where $j$ refers to the $j$th coordination shell, $N_j$ is the coordination number of the $j$th shell, $S_j^2$ is the amplitude reduction factor, $F_j(k)$ is the element-specific backscattering amplitude, $R_j$ is the average distance between the absorbing atom and the backscattering atoms in the $j$th shell, $\lambda(k)$ is the mean free-path length of photoelectron, $\sigma_j^2$ is the Debye-Waller factor, and $\phi_j(k)$ is the phase shift experienced by the photoelectron in the scattering process.

The post-edge background was removed by using a derivative method [28,29]. For the Co@SiO$_2$ core-shell
nanoparticles in air condition, the Fourier transforms were performed in the $k$ range of 2.67 to 14.49 Å$^{-1}$, and the first Co-Co and Co-O shells were isolated by Fourier filter with $R$ range of about 1.10 to 2.70 Å. Figure 4 shows the Fourier-transformed $k^3$-weighted EXAFS spectra of Co@SiO$_2$ samples in air and N$_2$ conditions. The amplitudes and phase shifts of Co-Co and Co-O atom pairs were extracted from theory spectra of CoO which was calculated by FEFF 8.0 [26]. For fitting the EXAFS spectra, we consider the peak around 1.5 Å to Co-O bonds and the peak around 2.4 Å to Co-Co bonds respectively. Therefore, the Co-O and Co-Co scattering paths were used to fit the spectra. The amplitude and phase shift of Co-O atom pair were calculated with FEFF 8.0 code, and the amplitude and phase shift of Co-Co were extracted from Co-foil EXAFS measurement. From the Figure 4a, two peaks were observed during the heating process, and Co-O and Co-Co bonds could fit the spectra very well which were shown in Figure 5. It means that in air condition, the Co core nanoparticles were partially oxidized even at room temperature and then were gradually oxidized to Co$_3$O$_4$ with the temperature rising to 800°C. However, only one peak was indicated in the N$_2$ gas condition when the temperature was below 400°C (Figure 4b). With further increase in temperature, the second peak appeared. Consequently, in N$_2$ gas protection condition, the Co core nanoparticles could be oxidized to Co$_3$O$_4$ when the temperature was above 400°C, and below that temperature, the Co core nanoparticles are dominated by Co$^0$ state. Unfortunately, the EXAFS spectra of Co@SiO$_2$ nanoparticles could not be fitted well by Co-O and Co-Co scattering paths. Nevertheless, they showed the same trend as in the air condition.

Comparing the measurements in Figure 4a,b, we can make a conclusion that the Co@SiO$_2$ core-shell nanoparticles can be oxidized to Co$_3$O$_4$ in spite of the protection of SiO$_2$ shell. In other words, the SiO$_2$ shell cannot protect the Co nanoparticles from being oxidized to Co$_3$O$_4$, but they could exhibit different behaviors in the air and N$_2$ gas conditions. For the nanoparticles in air condition, the O$_2$ in air can get onto the Co cores easily because the SiO$_2$ shell is in mesoporous state. So even at room temperature, the Co core nanoparticles could be oxidized to CoO which were demonstrated by EXAFS and XANES measurements. In the first step, only the surface atoms of Co cores were oxidized by O$_2$. As the temperature increases up to 300°C, the organic ligands leave off the Co core surface, and the Co surface were oxidized to CoO. With further increase in temperature, the CoO layer increased, which was reflected from the $k$ space of XAFS spectra (Figure 5), and Figure 5a to h shows the fitting results of Co K edge $k^3$-weighted EXAFS spectra of Co@SiO$_2$ nanoparticles in air condition. Finally, the Co core nanoparticles were oxidized thoroughly to Co$_3$O$_4$ when temperature reaches 800°C. Figure 6 gives the diagrammatic sketch of this procedure.

![Figure 6 Schematic illustration of oxidization of Co cores of Co@SiO$_2$ nanoparticles in air condition.](image-url)
Figure 7 gives the diagrammatic sketch of the oxidation procedure in the N\textsubscript{2} gas protection condition. The oxidation of Co core is much different from that in air condition. No exotic O atoms come into the Co@SiO\textsubscript{2} during the heating process. Thus, the O atoms could only be from the SiO\textsubscript{2} shells. At low temperature, there is no or seldom Co-O bond existing in the system and the Co-Co bond is dominant. When the temperature was above 300°C, the diffusion effect of O at the Co core surface becomes obvious, and a Co-O band layer will be formed at the interface between Co cores and SiO\textsubscript{2} shells, which is demonstrated by XAFS in \( k \) space (cf. Figure 8b). With further increase in temperature, a lot of O atoms in SiO\textsubscript{2} shell could diffuse into the Co cores and resulting in the increase of the Co-O layer. In the Figure 4b, a peak around 1.5 Å appeared corresponding to the Co-O bond. The m-SiO\textsubscript{2} shell makes phase transition to \( \beta \)-SiO\textsubscript{2} around 600°C; it is well known that the O becomes active during the phase transition process, so the diffusion of O into Co core is much faster, and leading further oxidization of the Co core. According to Figures 4b and 8b, the Co nanoparticles are likely oxidized to CoO/Co\textsubscript{3}O\textsubscript{4} composite because the O and Si are in stoichiometric equal (Si:O = 1:2) in SiO\textsubscript{2} shell.

Figure 7 Schematic illustration of oxidation of Co cores of Co@SiO\textsubscript{2} nanoparticles in N\textsubscript{2} protection.

![Figure 7](image)

Figure 8 EXAFS \( k^2\chi(k) \) function of Co K edge of Co@SiO\textsubscript{2} nanoparticles in air (a) and in N\textsubscript{2} gas condition (b).

![Figure 8](image)
For fitting the EXAFS spectra of Co@SiO$_2$ in N$_2$ gas protection, the signal around 1.5 Å was also considered to be from the CoSi$_2$, but no reasonable fitting parameters can be obtained. However, the formation of CoSi$_2$ during the heating and annealing process could not be excluded, accounting into the trace amount of which cannot be identified by XAFS technique.

In order to describe the oxidation process precisely, the Co K-edge $k^3$-weighted Fourier transformed function was studied as shown in Figure 8. We can observe that in the range of $k = 3.0^{-6.0} \text{Å}^{-1}$, the oxidation procedure can be divided into three steps in spite of being in air and N$_2$ gas conditions. From room temperature to 200°C, the Co core is mostly in Co$^0$ and may exist some amount of Co$^{2+}$. As the temperature increases to 600°C, the Co core is oxidized to Co$^{2+}$ gradually. When temperature is higher than 800°C, the Co core is transformed into CoO$_2$ thoroughly (in air) or partially (in N$_2$ gas, CoO/CoO$_4$ complex).

Conclusions

In summary, the Co@SiO$_2$ core-shell nanoparticles were prepared, and in situ XRD and EXAFS techniques were used to detect the oxidation process of the Co core with temperature increases to 800°C in both air and N$_2$ gas conditions. We find that there are three steps during the heating program control temperature procedure in spite of being in air or in N$_2$ gas protection. In the first step from room temperature to 200°C, the Co cores are mainly in Co$^0$ state as well as some amount of Co$^{2+}$ ions. When temperature is above 300°C, the interface between Co core and SiO$_2$ shell is gradually oxidized into Co$^{2+}$, and the CoO layer appears. With temperature increases to 800°C, the Co cores are oxidized to CoO$_2$ or CoO$_4$/CoO. Nevertheless, the oxidation kinetics of Co cores is strongly influenced by gas condition. In the air condition, the O$_2$ in the air could get through easily onto the surface of the Co cores and induces the oxidation of the Co cores due to mesoporous nature of SiO$_2$ shells. In the case of N$_2$ gas condition, the O atoms could only come from the SiO$_2$ shells, so the diffusion of O atoms at the interface between Co core and SiO$_2$ shell is the main factor. Our current work could provide some hints to study the stability property of core-shell nanoparticles at high temperature.

Competing interests

The authors declare that they have no competing interests.

Authors’ contributions

KZ carried out the preparation samples and done the in situ XRD/XAFS experiments and drafted the manuscript. ZZ and YZ performed some parts of the experiments and discussed the manuscript. ZW helped to design the experiments and gave some adviseable idea for the manuscript. All authors read and approved the final manuscript.

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References

1. Jin Y, Choi J, Cheon J. Shape control of semiconductor and metal oxide nanocrystals through nonhydrolytic colloidal routes. Angew Chem Int Ed. 2006;45:3414–39.
2. Xia YN, Yang PD, Sun YG, Wu YY, Mayers B, Gates B, et al. One-dimensional nanostructures: synthesis, characterization, and applications. Adv Mater. 2003;15:353–59.
3. Xia YN, Xiong YJ, Lim B, Skrabalak SE. Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics? Angew Chem Int Ed. 2009;48:860–103.
4. Rofer-Depoorter CK. A comprehensive mechanism for the Fischer-Tropsch synthesis. Chem Rev. 1981;81:447–74.
5. Ma W, Jacobs G, Sparks DE, Gnanamani MK, Pendyala V, Yen CH, et al. Fischer-Tropsch synthesis support and cobalt cluster size effects on kinetics over CoAlO$_2$ and CoSiO$_2$ catalysts. Fuel. 2011;90:756–65.
6. Das TK, Conner WA, Li J, Jacobs G, Dry ME, Davis BH. Fischer-Tropsch synthesis kinetics and effect of water for a CoSiO$_2$ catalyst. Energy Fuel. 2005;19:1430–9.
7. Salb AM, Borgna A, VandeVoort J, VanBerge PJ, Nienhantsverdriet JW. In situ surface oxidation study of a planar Co/SiO$_2$/Si(100) model catalyst with nanosized cobalt crystallites under model Fischer-Tropsch synthesis conditions. J Phys Chem B. 2006;110:8657–64.
8. Venezia AM, Parola VL, Liotta LF, Pantaleo G, Luiggi M, Boutonnet M, et al. CoSiO$_2$ catalysts for Fischer-Tropsch synthesis: effect of Co loading and support modification by TiO$_2$. Catal Today. 2012;197:18–23.
9. Su C, Shih Y, Huang Y, Lu M. Synthesis and characterization of Co$_3$Si$_2$O$_4$ as catalyst catalyze hydrogen generation. Mater Lett. 2011;65:3212–5.
10. Castner DG, Watson PR, Chan NY. X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, and analytical electron microscopy studies of cobalt catalysts. 1. Characterization of calcined catalysts. J Phys Chem. 1989;93:3188–94.
11. Yin XJ, Peng K, Hu AP, Zhou LP, Chen JH, Du YW. Preparation and characterization of core-shell structured Co/SiO$_2$ nanosphere. J Alloys Compounds. 2009;479:372–5.
12. Lu X, Liang G, Sun Z, Zhang W. Ferromagnetic Co/SiO$_2$ core/shell structured nanoparticles prepared by a novel aqueous solution method. Mater Sci Eng B. 2005;117:147–52.
13. Salgueiriño-Maceira V, Correa-Duarte MA. Cobalt and silica based core-shell structured nanophases. J Mater Chem. 2006;16:3593–7.
14. Salgueiriño-Maceira V, Correa-Duarte MA, Farle M, López-Quintela MA, Sieradzki K, Diaz R. Synthesis and characterization of large colloidal cobalt particles. Langmuir. 2006;22:1455–8.
15. Zhao W, Gu J, Zhang L, Chen H, Shi J. Fabrication of uniform magnetic nanocomposite spheres with a magnetic core/mesoporous silica shell structure. J Am Chem Soc. 2005;127:8916–7.
16. Chen Y, Gao P, Wang X, Zhu C, Wang L, Cao M, et al. Porous Fe$_2$O$_3$/SnO$_2$ core/shell nanorods: synthesis and electromagnetic properties. J Phys Chem C. 2009;113:10061–4.
17. Zhang C, Wängler B, Morgenstern B, Zentgraf H, Eisenhut M, Untenecker H, et al. Silica- and alkoxysilane-coated ultrasmall superparamagnetic iron oxide particles: a promising tool to label cells for magnetic resonance imaging. Langmuir. 2007;23:1427–34.
18. Wang LY, Luo J, Fan Q, Suzuki M, Suzuki IS, Engelhard MH, et al. Monodispersed core-shell Fe$_3$O$_4$@Au nanoparticles. J Phys Chem B. 2005;109:21593–601.

19. Gu HW, Zheng RK, Zhang XX, Xu B. Facile one-pot synthesis of bifunctional heterodimers of nanoparticles: a conjugate of quantum dot and magnetic nanoparticles. J Am Chem Soc. 2004;126:5664–5.

20. Gao JH, Liang GL, Zhang B, Quan Y, Zhang XX, Xu B. FePt@CoS$_2$ yolk-shell nanocrystals as a potent agent to kill HeLa cells. J Am Chem Soc. 2007;129:1428–33.

21. Bao F, Yao JL, Gu RA. Synthesis of magnetic Fe$_3$O$_4$/Au core/shell nanoparticles for bioseparation and immunoassay based on surface-enhanced Raman spectroscopy. Langmuir. 2009;25:10782–7.

22. Burns A, Ow H, Wieszner U. Fluorescent core-shell silica nanoparticles: towards "lab on a particle" architectures for nanobiotechnology. Chem Soc Rev. 2006;35:1028–42.

23. Xu Z, Hou Y, Sun S. Magnetic core/shell Fe$_3$O$_4$/Au and Fe$_3$O$_4$/Au/Ag nanoparticles with tunable plasmonic properties. J Am Chem Soc. 2007;129:8698–9.

24. Lai C, Wang Y, Lai C, Yang M, Chen C, Chou P, et al. Iridium-complex-functionalized Fe$_3$O$_4$/SiO$_2$ core/shell nanoparticles: a facile three-in-one system in magnetic resonance imaging. Luminescence Imaging Photodynamic Ther Small. 2008;4:218–24.

25. Stern EA. Theory of the extended x-ray-absorption fine structure. Phys Rev B. 1974;10:3027–37.

26. Rehr JJ, Albers RC. Theoretical approaches to x-ray absorption fine structure. Rev Mod Phys. 2000;72:621–54.

27. Koningsberger DC, Mojet BL, van Dorssena GE, Ramaker DE. XAFS spectroscopy: fundamental principles and data analysis. Top Catal. 2000;10:143–55.

28. Zhang K, Wang W, Cheng W, Xing X, Mo G, Cai Q, et al. Temperature-induced interfacial change in Au@SiO$_2$ core-shell nanoparticles detected by extended X-ray absorption fine structure. J Phys Chem C. 2010;114:41–9.

29. Wu ZH, Zhang J, Benfield RE, Ding YF, Grandjean D, Zhang Z. Structure and chemical transformation in cerium oxide nanoparticles coated by surfactant cetyltrimethylammonium bromide (CTAB): an X-ray absorption spectroscopic study. J Phys Chem B. 2002;106:4569–77.