A "User-Friendly" Chemical Approach Towards Paramagnetic Cobalt Phosphide Hollow Structures: Preparation, Characterization, and Formation Mechanism of Co_2P Hollow Spheres and Tubes

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User-friendly chemistry principles have been implemented for the synthesis of hollow Co_2P structures. In comparison with the original organometallic approach, the resulting alternative route is safe, simple, and inexpensive. The X-ray diffraction (XRD) pattern, X-ray photoelectron spectra (XPS), field emission scanning electron microscope (FESEM) images, and transmission electronic microscope (TEM) images were used to characterize the products, which exhibit paramagnetic behavior down to 2 K, as determined with a commercial superconducting quantum interference device (SQUID) magnetometer. The experimental investigations suggest that the formation of Co_2P hollow structures, hollow spheres, and tubes can be explained by an aggregation mechanism and a thermodynamically governed regime. Initially formed Co_2P nanoparticles are driven to aggregate into Co_2P hollow spheres by the gas bubbles produced. The formation of Co_2P tubes then occurs from the hollow spheres via hollow vessels in a thermodynamically governed process.

Introduction

Inorganic materials with hollow structures have opened up a new and challenging field in chemistry, biotechnology, and materials science due to their potential applications in controlled-release capsules, medical imaging, artificial cells, chemical sensors, encapsulation of products (cosmetics, inks, and dyes), shape-selective adsorbents, and catalysts.[1–4] Recently, the preparation of magnetic hollow structures has become a promising approach for investigating magnetic properties due to the formation of unusual magnetic domains, the generation of quantum effects, and other phenomena.[5] Besides magnetic functions, they have potential applications in catalysis, coatings, and composite materials, etc., owing to their low density and large surface area.[6] To the best of our knowledge, the studies on hollow structures of transition metal phosphides are much less advanced in comparison to other magnetic materials because of their difficult synthesis.[7–9] All the above factors have driven us to explore the possibility of the preparation of hollow structures of transition metal phosphides under mild conditions.

Up to now, organometallic approaches have been applied to grow transition metal phosphides. Recently, FeP nanorods and nanowires were synthesized in a trioctylphosphane oxide (TOPO)/trioctylphosphane (TOP) solvent system from $Fe(CO)_5$ by a solution-phase injection route.[10] Fe_2P nanorods produced by thermal decomposition of $Fe(CO)_5$ using a syringe pump have also been reported.[11] MnP nanoparticles have been produced by the reaction of $Mn_2(CO)_{10}$ with $P(SiMe_3)_3$ in TOPO/myristic acid.[12] However, the synthetic approach using zero-valent transition metal carbonyl complexes in coordinating solvents possesses several intrinsic disadvantages.[13] For instance, sophisticated equipment such as a glove box or a syringe pump are required, as is an inert gas. Secondly, the reactions are not easy to control. Furthermore, for the tubular structures, controlling this process is difficult and the internal cavity is not always continuous throughout the length.[14] For these fundamental and practical reasons, an alternative route using a "user-friendly" chemical method is much anticipated. This concept, which refers to the synthetic and processing procedures, is different to the traditional "green chemistry".

Among M_2P compounds (M = Mn, Fe, CO, Ni), only Co_2P has a C_{23} orthorhombic structure; the others have a C_{22} hexagonal structure.[15,16] Our previous research on Co_2P nanocrystallites and nanorods gave some interesting results,[17,18] and these attracted us to the unexplored Co_2P nanostructures with special morphologies. Here, for the first time, we report the formation of Co_2P hollow spheres and tubes from metal halides and yellow phosphorus in a mixture of absolute ethanol and water as solvent. We have man-

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aged to eliminate the use of toxic carbonyl complexes, and have developed an easy process for the formation of Co_2P hollow spheres and tubes under solvothermal conditions. On the basis of a series of comparison experiments, a mechanism of formation of Co_2P hollow spheres and tubes was proposed and investigated. We expect that the novel tubular nature of Co_2P together with the tunable interior nanoparticle size of these hollow spheres may make them ideal entities for incorporating other species or surface modification, which might bring novel optical, electronic, and magnetic properties in the near future.

Results and Discussion

The typical XRD patterns of the samples obtained at 220 °C for 30 h and 48 h are shown in Figures 1a and b, respectively. All the diffraction peaks can be indexed to orthorhombic Co_2P [space group *Pnam*(62)] in the JCPDS card no.74-287. Compared with the standard diffraction patterns, no characteristic peaks for impurities such as P or CoP_3, can be detected.

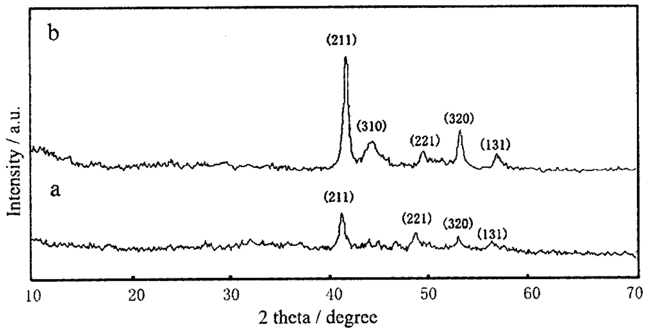


Figure 1. XRD patterns of the as-produced Co_2P hollow spheres (a) and tubes (b).

The purity and elemental composition of the products were determined by X-ray photoelectron spectroscopy (XPS); the XPS spectra of Co_2P are shown in Figures 2a and b. The Co $2p_{3/2}$ binding energy is 778.2 eV, which is in good agreement with the literature,[19] and the P 2p binding energy is 129.8 eV, consistent with our previous results (129.1 eV). From the integral peak areas of Co and P in the XPS spectra, the Co_2P samples obtained at 220 °C for 30 h have a Co/P molar ratio of 1.80:1 – the Co_2P samples obtained at 220 °C for 48 h have a molar ratio of 1.95:1 – both of which are close to the expected stoichiometry of Co_2P. No obvious impurities such as chloride or phosphate could be detected in any of the samples.

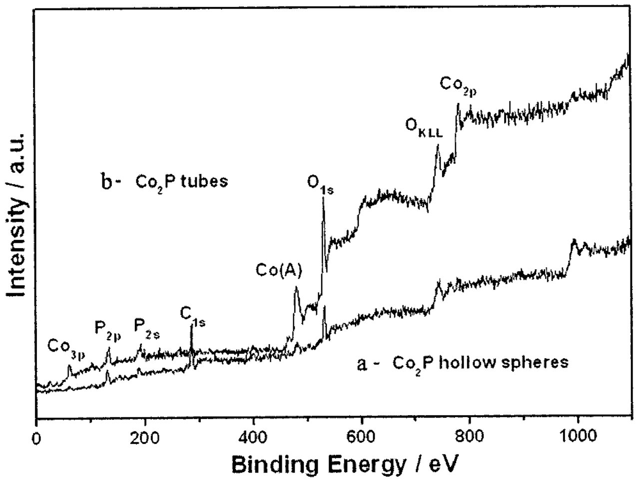


Figure 2. XPS analysis of the as-produced Co_2P hollow spheres (a) and tubes (b).

The morphology of the Co_2P samples obtained at 220 °C for 30 h is shown in Figure 3. The panoramic FESEM images (Figure 3a) show that the sample consists of a large quantity of nearly uniform spheres and clearly indicate that the spheres have diameters of around 1.2 µm; the TEM image (Figure 3b) reveals their partly overlapped hollow nature. The three obvious diffraction rings in the SAED pattern (Figure 3c) recorded from the hollow spheres can be identified as the (211), (310), and (131) planes of orthorhombic Co_2P. The HRTEM image (Figure 3d) clearly shows that the hollow spheres are aggregates of small particles with a size of 3–4 nm.

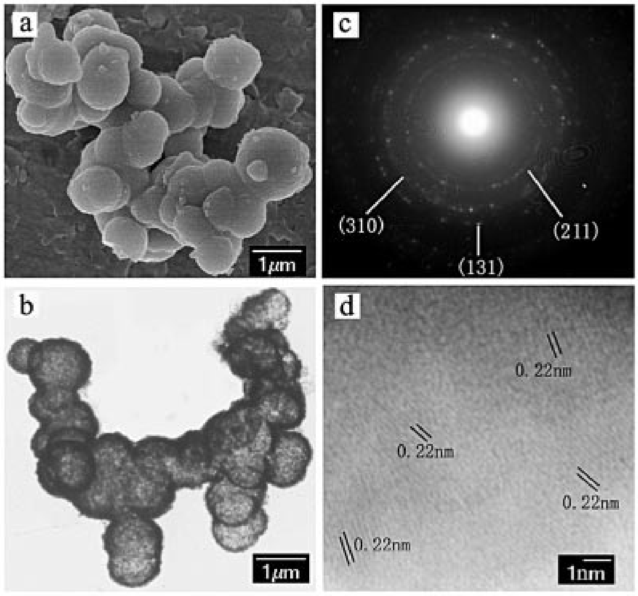


Figure 3. Morphology of the Co_2P hollow spheres formed at 220 °C after 30 h: (a) FESEM image; (b) TEM image; (c) SAED patterns; (c) HRTEM image.

The morphology of the Co_2P samples obtained at 220 °C for 48 h is shown in Figure 4. Both the FESEM and TEM images of the sample (Figure 4a–c) show that Co_2P here is present as tubular structures with a diameter of around 1 µm and length of 3–7 µm. The SAED patterns recorded from the tubes (Figure 4d) clearly show that the tubes are polycrystalline. Six easily observed diffraction rings can be identified as the (211), (310), (221), (131), (232), and (422) diffractions of orthorhombic Co_2P. The direct observation of the structure of the Co_2P tubes was performed by HRTEM, as shown in Figure 4e, which clearly shows that the tubes are aggregates of small particles.

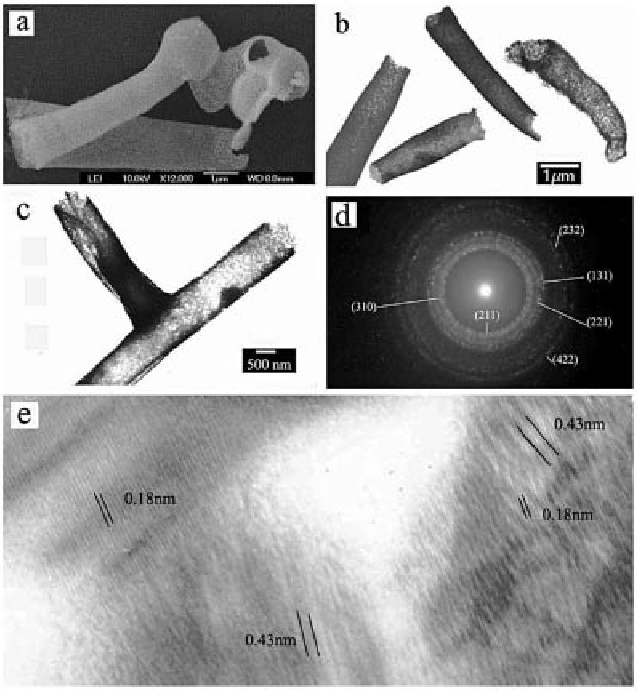


Figure 4. Morphology of the Co_2P tubes formed at 220 °C after 48 h: (a) FESEM image; (b) TEM image; (c) a typical tubular structure; (d) SAED patterns; (e) HRTEM image.

The magnetic properties of the Co_2P hollow spheres and tubes, which have similar properties, were measured with a commercial SQUID magnetometer (Quantum Design, MPMS). The temperature dependence of the magnetization for Co_2P hollow spheres and tubes measured in an applied magnetic field of 500 Oe between 2 K and 300 K is shown in Figure 5a, and the magnetic-field dependence of magnetization (M vs. H) at 2 K for both Co_2P hollow spheres and tubes is shown in Figure 5b. Both reveal that the Co_2P hollow spheres and tubes have no ferromagnetic characteristics and can be expressed as paramagnetic moments.[7–9] The results can be well described by the Curie–Weiss law, and agree well with those obtained from the M vs. H data. The Co_2P hollow spheres and tubes are paramagnetic with no evidence of ferromagnetic ordering, due to their C_{23} orthorhombic structure.[15] This is in agreement with the magnetic properties of Co_2P reported by Fujii, who reported that Co_2P exhibits ferromagnetism only in its hexagonal structure, and that orthorhombic Co_2P is a Pauli paramagnet.[16] The tube structures have stronger paramagnetic properties than the hollow spheres due to their better crystallinity.

The experimental investigations suggest that the formation of Co_2P hollow spheres and tubes can be explained as an aggregation mechanism in a thermodynamically governed process. Initially formed Co_2P nanoparticles are driven to aggregate into Co_2P hollow spheres by the bubbles of PH_3 and C_2H_4 produced. The formation of the Co_2P tubes is suggested to occur from the hollow spheres via hollow vessels in a thermodynamically governed process.

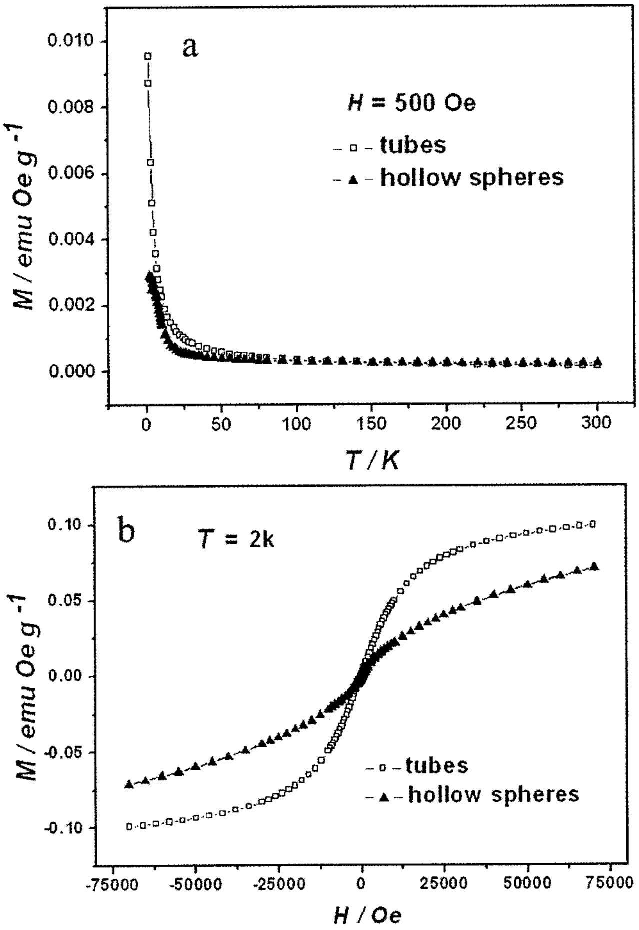


Figure 5. Magnetic properties of the Co_2P hollow spheres and tubes: (a) temperature dependence of magnetization under an applied magnetic field of 500 Oe; (b) magnetic-field dependence of the magnetization at 2 K.

In the present route the synthesis of Co_2P is based on the reaction of Co^{2+} with PH_3, which is produced by the reaction of yellow phosphorus with water and ethanol at 220 °C. Yellow phosphorus (melting point 44.1 °C and boiling point 280 °C) could form droplets dispersed in the aqueous solution to give a heterogeneous liquid–liquid two-phase system at elevated temperature. Obviously, the reactions easily occur at the interfaces of these two phases.

The reaction of phosphorus with water at high temperature and pressures has been studied by several authors who were primarily interested in the overall reaction and its products.[20–22] It is well known that ethanol reacts with yellow phosphorus at high temperatures and pressures.[23] In our approach, the system provides the appropriate conditions to initiate the reactions shown in Equations (1) and (2). Once generated, PH_3 would immediately react with the cobalt ion to form Co_2P, as shown in Equation (3). The by-product, H_3PO_3, undergoes a circular reaction with H_3PO_4, shown in Equations (4) and (5), which increases the amount of PH_3 and accelerates the reaction of PH_3 with the cobalt ion.[24,25] Reaction (3) continues until one of the raw materials runs out. The whole process can be formulated as shown in Scheme 1.

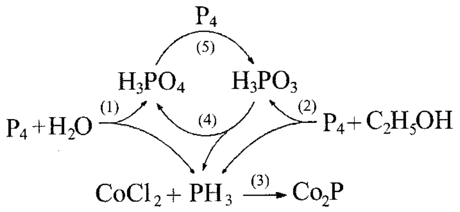
$$2\ P_4 + 12\ H_2O \rightarrow 3\ H_3PO_4 + 5\ PH_3 \tag{1}$$

$$P_4 + 6\ C_2H_5OH \rightarrow 2\ H_3PO_3 + 2\ PH_3 + 6\ C_2H_4 \tag{2}$$

$$12\ CoCl_2 + 7\ PH_3 \rightarrow 6\ Co_2P + PCl_3 + 21\ HCl\ (pH = 2) \tag{3}$$

$$4\ H_3PO_3 \rightarrow PH_3 + 3\ H_3PO_4 \tag{4}$$

$$P_4 + 6\ H_3PO_4 + 6\ H_2O \rightarrow 10\ H_3PO_3 \tag{5}$$



Scheme 1. Schematic growth path of Co_2P. (1)–(5) represent the corresponding reactions in the text.

After the initial nucleation, the newly formed Co_2P nuclei grow into nanoparticles. When the reaction was carried out at 220 °C for between 12 and 24 h, the nanoparticles grew gradually, as shown in Figures 6a and b. When the reaction time was prolonged to 30 h, a large quantity of nearly uniform hollow spheres of Co_2P was formed, as shown by the corresponding TEM images in Figure 6c. When the reaction time was extended further to 36 h, congregated hollow spheres were found in the product, as shown in Figure 6d.

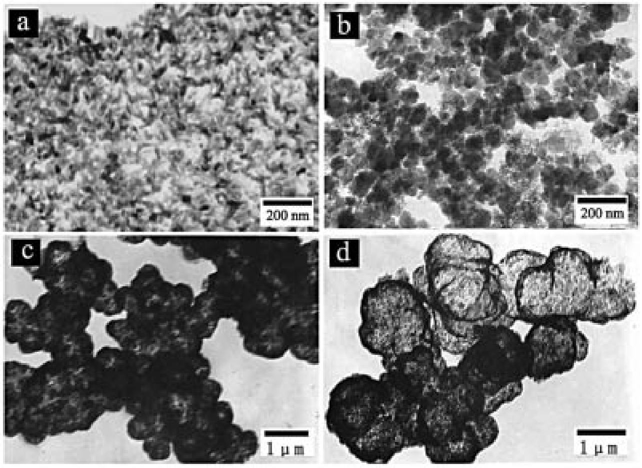
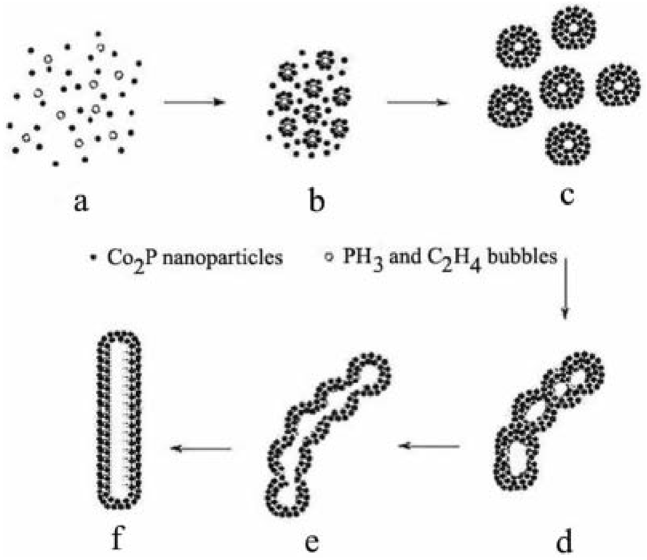


Figure 6. TEM images of the Co_2P structures formed in ethanol at 220 °C at different reaction times: (a) particles after 12 h; (b) particles after 24 h; (c) hollow spheres after 30 h; (d) congregated hollow spheres after 36 h.

Based on these observations and the structure of the hollow spheres we were able to propose an aggregation mechanism, as shown in Scheme 2. The TEM results suggested that these newly formed nanoparticles have a tendency to aggregate at the interface of the gas bubbles and the solution. Similar to the reported case of monodispersed SiO_2 or ZnSe microspheres aggregating under the effects of gas bubbles,[26,27] the gas aggregation centers are the PH_3 and C_2H_4 bubbles in our approach. The mixture of ethanol and water used as solvent could effectively form the bubble templates that are important for the formation of hollow spheres. In comparison with our previous work on Co_2P nanorods,[18] it is easy to show that the gaseous C_2H_4 produced in this approach is the linchpin of the bubble templates as it is not involved in any further reaction and thus can provide the gas aggregation center. Driven by the minimization of interfacial energy, newly formed Co_2P nanoparticles may aggregate around the gas–liquid interface between the gas bubbles and the solution and then form Co_2P hollow spheres.



Scheme 2. Schematic illustration of a proposed mechanism for the formation of hollow Co_2P structures: (a) nanoparticles; (b) aggregated nanoparticles around the gas–liquid interface between PH_3 and C_2H_4 bubbles and the solution; (c) hollow spheres; (d) congregated hollow spheres; (e) connected hollow spheres; (f) tubes.

It was well known that in a thermodynamic process hollow spheres are generally less stable than tubes as they possess a higher internal energy; this favors the transformation of hollow spheres into tubes. When the reaction time was increased from 40 h to 42 h at 220 °C, these hollow spheres became attached end-to-end and a borderline could be detected only dimly (Figure 7a and b). When the reaction time was raised to 46 h, the tubular conductive structure had obviously formed (Figure 7c), as shown by the incurvate walls of the vessels and lack of borderline of the hollow microspheres. Finally, the rough vessels grew into smooth tubular structures (Figure 7d) after 48 h. The whole growth procedure from hollow spheres to Co_2P tubes is illustrated in Scheme 2.

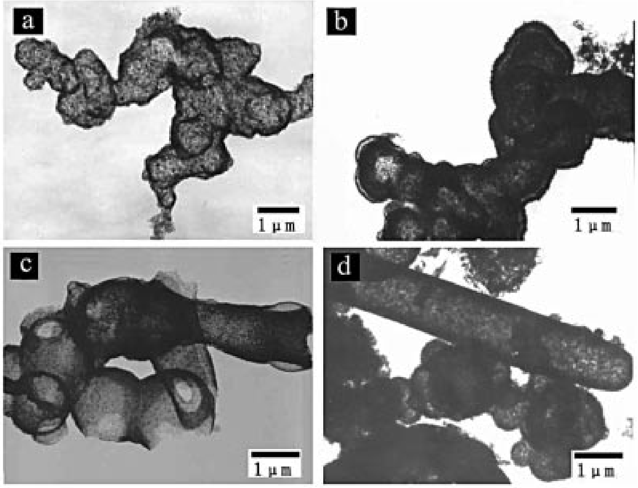


Figure 7. TEM images of the Co_2P structures formed in ethanol at 220 °C at different reaction times: (a) connected hollow spheres after 40 h; (b) connected hollow spheres after 42 h; (c) hollow vessels after 46 h; (d) tubes after 48 h.

Conclusions

In summary, we developed a "user-friendly" one-pot chemical approach to synthesize Co_2P hollow spheres and tubes, which exhibit paramagnetic behavior down to 2 K. In comparison with the original organometallic approach, this route is safe, simple, and inexpensive. The experimental investigations suggest that Co_2P hollow spheres are formed from the initially formed nanoparticles under the effect of PH_3 and C_2H_4 bubbles, and the Co_2P tubes form from the hollow spheres via hollow vessels in a thermodynamically governed process. The use of gas bubbles produced during the reaction to provide aggregation centers is a novel and effective method to fabricate hollow structures. Compared to other templated synthetic methods, this template-free method is very simple and convenient and avoids the introduction of impurities. It is therefore suitable for modern chemical synthesis. This idea might be extended to other solution systems in which easily aggregated monodispersed nanocrystals are produced during the reaction.

Experimental Section

Details of a typical experiment are as follows: $CoCl_2\cdot6H_2O$ (0.475 g, 2 mmol) and yellow phosphorus (1.24 g, 10 mmol) were placed into a 40-mL, Teflon-lined autoclave, which was then filled with absolute ethanol up to 80% of its capacity. To obtain Co_2P hollow spheres, the autoclave was heated to 220 °C for 30 h; To obtain Co_2P tubes, the autoclave was maintained at 220 °C for 48 h. In both cases the autoclave was then allowed to cool to room temperature, and the black precipitate was collected and washed with absolute ethanol and distilled water in sequence to remove any by-products and possible impurities. The final products were dried in vacuo at 60 °C for 3–4 h. The yields of the products synthesized by this method were above 80%.

The phase identification of the samples was performed with a Rigaku D/max-γA X-ray diffractometer equipped with Cu-K_α radiation (λ = 1.54178 Å). The purity and components were determined by X-ray Photoelectron Spectroscopy (XPS) with an ESCALab MKII X-ray photoelectron spectrometer with Mg-K_α radiation as the excitation source. The morphology of the products was determined with a field emission electron microscope (FESEM JEOL JSM-6700F) and transmission electron microscope (TEM Hitachi H-800). Further structural analysis was performed with a high-resolution transmission electron microscope (HRTEM JEOL-2010) and by selected area electron diffraction (SAED). The magnetic properties were measured with a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS).

Acknowledgments

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