Synthesis and characterization of Co–Fe Prussian blue nanoparticles within MCM-41

Vien Vo a,d,*, Nguyen Van Minh b,d, Hyung Ik Lee c, Ji Man Kim c, Youngmee Kim d, Sung Jin Kim d,**

a Department of Chemistry, Quy Nhon University, 170 An Duong Vuong, Quy Nhon city, Viet Nam
b Center of Nano Science and Technology, Hanoi National University of Education, Viet Nam
c Department of Chemistry, BK21 School of Chemical Materials Science and SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, 440-749, Republic of Korea
d Division of Nano Sciences, Department of Chemistry, Ewha Womans University, Seoul 120-750, Republic of Korea

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ABSTRACT
A Prussian blue analogue, K_{0.84}Co_{1.08}[Fe(CN)_6] is prepared by reaction between [Fe(CN)_6]^3– in aqueous solution and ion-exchanged Co^{2+} in the channels of MCM-41. Powder X-ray diffraction, transmission electron microscopy, thermogravimetric analysis, nitrogen adsorption/desorption isotherms, diffuse reflectance UV–vis absorption spectroscopy and magnetic measurements were employed to characterize the product. The results show that the Prussian blue analogue is in nanoparticles within the channels and the hexagonal phase of MCM-41 remains intact during the reactions. A particle size effect on optical and magnetic properties of the nanoparticles was observed.

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1. Introduction

It has been shown that activities in nanomaterials field have grown exponentially in the past couple of decades. The largest activity in this field at this time has been in the synthesis of new nanoparticles of different sizes and new shapes. A noticeable contribution to such synthesis is the use of the well-defined mesoporous materials, such as MCM-41 and SBA-15 as rigid templates. These materials possess a one-dimensional, hexagonally arranged porous system of highly uniform dimensions, as nanoscale reactors for manufacturing and replicating nanomaterials [1]. Therefore, the spontaneous organization of nanoparticles into such one-dimensional arrays is a key of this approach.

In recent years, nano-sized Prussian blue analogues have emerged as a promising subject for applications to the nanomagnetic [2–7], biosensing [8–11], electrochromic [12], and biomedical [13] devices. These nanomaterials often exhibit novel size-dependent properties, which are different from those of their bulk form [3–7,14–18]. So far, there have been several techniques for preparing Prussian blue nanoparticles, in which various agents, such as anionic surfactant sodium bis(2-ethylhexyl)sulfosuccinate [3], polyvinylpyrrolidone [4], sol–gel [5], mesostructured silica [14], sodium hexametaphosphate [15], apoferritin [7], porous alumina [16], stearylamine [17] or nafion [18], were used to stabilize nanoparticles. In this work, we present a new synthesis of Co–Fe Prussian blue nanoparticles using mesoporous material MCM-41 as a rigid template; and their size-dependent optical and magnetic properties are also discussed.

2. Experimental

The as-synthesized mesoporous silica MCM-41 has been prepared according to the literature [19]. The procedure involves mixing cetyltrimethylammonium bromide (CTAB), water, and NaOH. To this solution, tetraethyl orthosilicate (TEOS) was added at room temperature. The molar ratio of TEOS:CTAB:H_2O:NaOH in the resulting mixture is 0.60:0.12:130:0.70. The mixture was then heated at 100 ̊C for 24 h. The solid was isolated by filtration, washed with deionized water, and dried at room temperature. To prepare Co–Fe Prussian blue (Co–Fe PB) nanoparticles inside MCM-41 channels, in a typical synthesis, 0.15 g of the as-synthesized MCM-41 was soaked in 60 ml of 0.2 mM Co(NO_3)_2 methanol (MeOH)–H_2O (5:1, v/v) solution and the suspension was stirred overnight at room temperature. The solid (referred to Co–MCM-41) was filtered off, washed with deionized water, and dried at...
room temperature. 0.15 g of Co–MCM-41 was then slurried in 20 ml of 0.4 mM \( \text{K}_3\text{[Fe(CN)}_6\text{]} \) aqueous solution, and the mixture was stirred for 4 h. The resultant purple solid (denoted Co–Fe/MCM-41) was filtered, rinsed with deionized water, and dried at room temperature. To investigate size-dependent properties, a bulk form of Co–Fe PB, which has the composition similar to that of the Co–Fe PB nanoparticles, was prepared by mixing two aqueous solutions of \( \text{Co(NO}_2\text{)}_2 \) (0.4 mM) and \( \text{K}_3\text{[Fe(CN)}_6\text{]} \) (0.4 mM). The powder X-ray diffraction (PXRD) measurement was carried out on a Rigaku Rint-2000 instrument. The elemental analysis was performed using LEO SUPRA 55 (JEOL) equipped with an EDAX Genesis 2000 X-ray Microanalysis System. Images of transmission electron microscopy (TEM) were achieved with a JEOL JEM-2100F. Nitrogen adsorption/desorption isotherms were obtained on an ASAP 2010 apparatus at 77 K. Optical absorption spectra were measured on a V-570 spectrophotometer (JASCO) in the range from 190 to 800 nm at room temperature. The magnetic measurements were performed using a PPMS 6000 (Quantum Design Inc., USA) instrument. Diamagnetic corrections were estimated from Pascal’s constants.

3. Results and discussion

The PXRD patterns of Co–Fe/MCM-41 and as-synthesized MCM-41 are shown in Fig. 1. An intense peak in the low angle region for Co–Fe/MCM-41 is attributed to the (1 0 0) plane of hexagonal MCM-41, which suggests that the hexagonal phase of MCM-41 remains intact during the reactions. However, compared to the pattern of the as-synthesized form, a significant decrease in intensity of this peak is obtained after the loading. This may result from the filling of the MCM-41 pores during the loading process because the pore filling would reduce the scattering contrast between the pores and the walls of the mesoporous material [20]. The wide angle (2\( \theta \) = 15–40°) pattern of Co–Fe/MCM-41 shows three broad peaks, which can be indexed to reflections of the (2 0 0), (2 2 0) and (4 0 0) lattice planes of the cubic space group \( \text{Fm}3\text{m} \) (JCPDS card no. 73-0687) for Co–Fe Prussian blue. From the width and position of these peaks, the average particle size, calculated using the Scherrer’s equation [21], is about 2 nm, which is concordant with pore size of MCM-41. The results of energy dispersive X-ray analysis (the inset of Fig. 2) show that a general proposed formula for the Co–Fe PB analogue in MCM-41 is \( \text{K}_{0.84}\text{Co}_{1.08}\text{[Fe(CN)}_6\text{]} \). To gain insight into the filling of the pores, the TEM characterization was employed for as-synthesized MCM-41 and Co–Fe/MCM-41 (Fig. 2). It can be seen clearly that the highly ordered pore structure of MCM-41 has been preserved during the formation process of Co–Fe nanoparticles. A comparison between TEM images of as-synthesized MCM-41 and Co–Fe/MCM-41 shows that Co–Fe PB particles appear as dark substances between the walls of MCM-41 (see Fig. 2).

Fig. 3 shows thermogravimetric curves for as-synthesized MCM-41, Co–MCM-41 and Co–Fe/MCM-41. The weight loss of each sample possesses three steps: the first one from room temperature to around 150 °C, the second from 150 to 350 °C and the last from 350 to 700 °C, which may be due to desorption of water, decomposition of the surfactant and dehydration of silanol groups, respectively. In addition, the second step for Co–Fe/MCM-41 may include decomposition of Co–Fe PB nanoparticles [22]. The difference between a and c curves may come from the exchange between the surfactant and \( \text{Co}^{2+} \) cations, and from these curves, amount of the exchanged surfactant was calculated to be about 90% of the total surfactant. In addition, it has been obtained that the molar ratio of the exchanged surfactant CTA to the cobalt cation in Co–MCM-41 is about 2. This suggests that most cobalt cations come from the ion-exchange between them and CTA cations in the channels of MCM-41. The difference between curves
b and c is attributed to the presence of Co–Fe PB nanoparticles in the channels. Loss weight due to the decomposition of the residue surfactant and nanoparticles in Co–Fe/MCM-41 is about 9.9%.

In order to clarify further the ion-exchange between surfactant and Co$^{2+}$ cations, and formation of Co–Fe PB particles in the channels of MCM-41, nitrogen adsorption at 77 K was performed for as-synthesized MCM-41, Co–MCM-41 and Co–Fe/MCM-41. Before the measurement, the solids were completely dehydrated by heating at 95 °C overnight under vacuum. This temperature was applied in order to avoid collapse of the Co–Fe PB framework and removal of the residue surfactant. Fig. 4 shows that as-synthesized MCM-41 possesses no porosity while Co–MCM-41 and Co–Fe/MCM-41 exhibit clearly a Type IV sorption isotherm characteristic of mesoporous materials. The BET surface areas are 438, 260 and 6.7 m$^2$/g for Co–MCM-41, Co–Fe/MCM-41 and as-synthesized MCM-41, respectively. A cation exchange between large CTA$^+$ surfactant and smaller Co$^{2+}$ cations in the channels may lead to the formation of a mesoporous system of Co–MCM-41. The reduction of surface area for Co–Fe/MCM-41 compared to that of Co–MCM-41 probably ensues from the formation of Co–Fe Prussian blue nanoparticles in the channels.

The UV–vis spectra of the Co–Fe/MCM-41 and bulk Co–Fe were shown in Fig. 5. The two spectra are qualitatively similar with a broad intervalence charge-transfer band in the visible region between 450 and 650 nm and a sharp, higher energy peak around 400 nm. However, a remarkable feature in these spectra is that the band around 400 nm of Co–Fe/MCM-41 is blue-shifted by 16 nm from that of the bulk form. In addition, the absorption peaks of nano-sample is sharper than that of the bulk form, which can be understood based on the selection rules [23]. These indicate that the PB particles exhibited size-quantization effects.

The magnetic properties of Co–Fe/MCM-41 and bulk Co–Fe were also characterized (Fig. 6). The magnetization versus temperature plots (Fig. 6A) show a divergence between field cooled (FC) and zero field cooled (ZFC) magnetization curves below 6.3 and 12.3 K for the nanoparticles and bulk form, respectively. The ZFC magnetization curves exhibit maxima at 5.4 and 11.1 K which correspond to the blocking temperatures of Co–Fe/MCM-41 and bulk Co–Fe, respectively. There is a significant difference in the ferromagnetic onset temperature for the two forms with the transition temperature becoming lower for the nanoparticles. The respective Curie temperature ($T_C$) values, estimated from the FC magnetization curves, are 13.2 and 7.2 K for bulk Co–Fe and Co–Fe/MCM-41 (Fig. 6B). The increase in the FC values with decreasing temperatures and the maximum peak in the ZFC magnetization are indications of cluster spin-glass behavior [24]. The expression given by Neel to fit the susceptibility of ferrimagnets in a range of temperature close to the ordering temperature is as follows [25]:

$$kT_C = \frac{z(C_A C_B)^{1/2}}{N A^g \mu_B^2}$$

where $z$ is the number of magnetic neighbors, $J$ is the absolute value of the exchange interaction, $C_A$ and $C_B$ are the Curie constants of $A$ and $B$, $N_A$ is the Avogadro constant, $g$ is a mean $g$ (Lande) factor and $\mu_B$ is the Bohr magneton. As the lattice parameter of the nanocrystals does not change, we suppose that the magnetic interaction constant $J$ of the PB nanoparticles is almost the same as that of the bulk form. Therefore, $T_C$ value should significantly depend on the average number of nearest magnetic interaction neighbors. Apparently, the decrease of $T_C$ for Co–Fe/MCM-41 compared to that of the bulk form can be explained by a great drop of particle size of the PB analogue in MCM-41, which causes a decrease of the average number of the nearest magnetic interaction neighbors.
interaction neighbors. Besides, defects could be present on the surface or internal of the Prussian blue particle, which may affect the $T_C$ value.

4. Conclusion

In conclusion, we have obtained Prussian blue nanoparticles within MCM-41 by reaction between Co$^{2+}$ ion-exchanged MCM-41 and $K_3[Fe(CN)_6]$ in aqueous media. The hexagonal ordered structure of MCM-41 was maintained during the formation process of the nanoparticles inside the pores. The size-dependent properties of the Prussian blue analogue within MCM-41 were evidenced by a blue-shift of the UV–vis peaks and a lower $T_C$ value of the nanoparticles compared to those of the bulk form. This work may be a further example of a simple route to obtain nanoparticles by using channel of mesoporous materials as a nanoscale reactor.

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