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A Facile Route to Prepare Hollow SiO_2 Spheres Decorated with NiO Nanoparticles†

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In this paper, the hollow SiO_2 spheres decorated with NiO nanoparticles (denoted as SiO_2/NiO hollow spheres) are successfully prepared using polystyrene (PS) spheres as hard template. At first, the PS-SiO_2 core-shell structure is prepared by hydrolysis and condensation of tetraethyl orthosilicate (TEOS). Then the Ni source is incorporated by impregnation method. Finally, the SiO_2/NiO hollow spheres are obtained by subsequent annealing process. The morphology of SiO_2/NiO is hollow sphere with diameter of 1.5-2.5 μm by observation of scanning electron microscope and transmission electron microscope. Further investigation indicates that the NiO nanoparticles are dispersed on the shells of hollow spheres with diameter of 3-5 nm. Present work not only provides a facile route for preparation of SiO_2/NiO hollow spheres, but gives an insight on the formation mechanism of hollow composite spheres.

Key Words: SiO_2, Hollow spheres, NiO, Nanoparticles.

INTRODUCTION

Hollow SiO_2 spheres are attracting much attention because of their high surface area, unique morphology and non-toxic properties[1,2]. They may find application in catalyst[3], drug releaser[4] and water retention[2]. The preparation of hollow SiO_2 spheres can be classified into various approaches, such as hard sacrificial cores (or hard template)[5], micelle directed synthesis (or soft template)[6] and layer-by-layer self-assembly techniques, *etc.*[7].

Nickel oxide is an important material that has excellent electronic and magnetic properties which can be used as super-capacitor, catalyst, gas sensors and adsorbent, *etc.*[8]. In general, it can be prepared by thermal treatment of nickel salt or nickel hydroxide and the shape or size could be easily controlled[9].

Based on the above analysis, SiO_2/NiO nanocomposite may integrate the excellent properties of both SiO_2 and NiO. Recently, SiO_2/NiO nanocomposites are reported by several workers[10-12]. They contain various approaches, for example sol-gel[10], electrospin[11] and soakage method[12]. However, there is few literature report preparation of SiO_2 hollow spheres decorated with NiO nanoparticles which may have potential application in catalysis, supercapacity, adsorption and magnetic separation.

Herein, we report a facile route to prepare hollow SiO_2 spheres with NiO nanoparticles dispersed on the shell using polystyrene (PS) spheres as hard template. The nickel source is comprised by impregnation based on the interaction between negative charged silica and positive charged nickel cations. The obtained SiO_2/NiO hollow spheres are about 1.5-2.5 μm in diameter with NiO nanoparticles dispersed SiO_2 as the shell. The formation mechanism is also discussed and verified in the text. Importantly, present work brings forward a facile route and gives insight into understanding the preparation of hollow composite spheres.

EXPERIMENTAL

Aldrich Chemical Co., supplied the following reagents. All the reagents were used without further purification.

Preparation of polystyrene spheres: The polystyrene spheres were prepared following a modified method according to the literature[13]. In a typical synthesis process, 80 g alcohol, 5 g deionized water, 1 g polyvinyl pyrrolidone (PVP) K30 were added in a three-neck flask and formed homogeneous solution under nitrogen atmosphere. Then, 0.1-0.2 g 2,2'-azobisisobutyronitrile (AIBN) was dissolved in 15-20 g styrene to form homogeneous solution. The above two solutions were mixed and reacted at 70 ºC for 24 h under nitrogen atmosphere. The white powders of polystyrene sphere was obtained after centrifugation and washed with alcohol for several times.

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Preparation of PS-SiO_2: The PS-SiO_2 was prepared using a modified stöber method following the literature[14]. 40 g alcohol, 8 g water, 40 mg polystyrene spheres, 500 mg tetraethyl orthosilicate and 1 g 30 % $NH_3 \cdot H_2O$ were mixed together. After stirring for 4 h, the white powders (PS-SiO_2) were collected and washed with alcohol for several times.

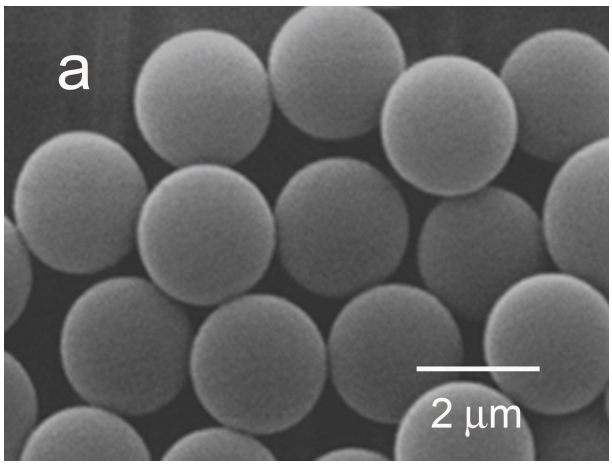
Preparation of PS-SiO_2·Ni: The PS-SiO_2 was dispersed with 3 mL alcohol and then adding 3 mL of $Ni(CH_3COO)_2 \cdot 4H_2O$ saturated alcohol solution, stirred for 0.5 h. The PS-SiO_2·Ni was produced after centrifugation.

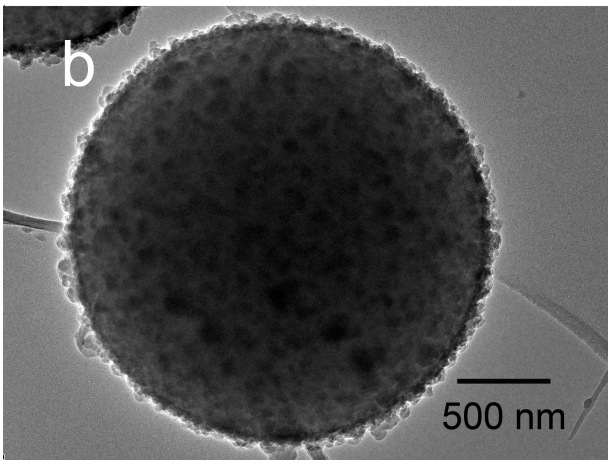
Preparation of SiO_2/NiO hollow spheres: The obtained PS-SiO_2·Ni was subsequently annealed at 550 ºC with a temperature ramp of 1 ºC/min and maintained for 5 h in air. After cooled to room temperature, the final white powders were collected and characterized.

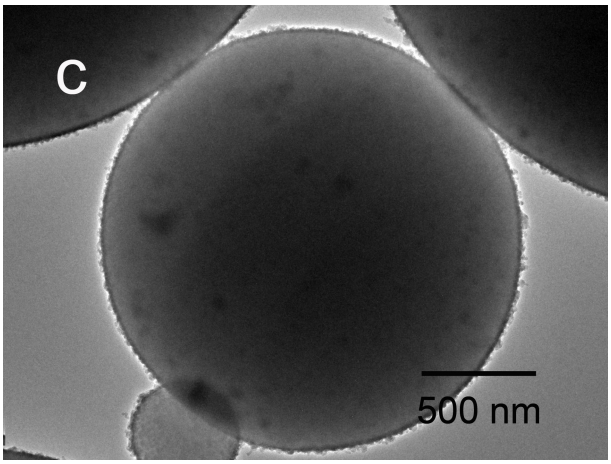
Characterization: X-Ray diffraction (XRD) measurement was performed on a Philips X'pert diffractometer using CuK_α radiation of 0.15419 nm in a 2θ range from 10-70º. SEM analysis was carried on a Sirion 200 FEG field emission scanning electron microscope. The morphology was visualized by TEM examination which carried out on a Jeol-2010 microscope attached with an energy-dispersive x-ray spectrometer (EDS, Oxford, Link ISIS). The thermal gravimetric (TG) measurement was conducted using a thermal instrument (Shimadzu Corp. Japan) with a heating rate of 10 ºC/min under air atmosphere. The fourier transform infrared spectroscopic (FTIR) measurements were obtained on an IR-750 spectrometer.

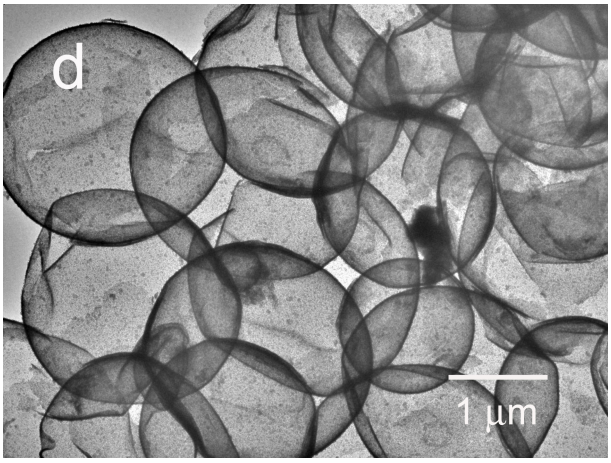
RESULTS AND DISCUSSION

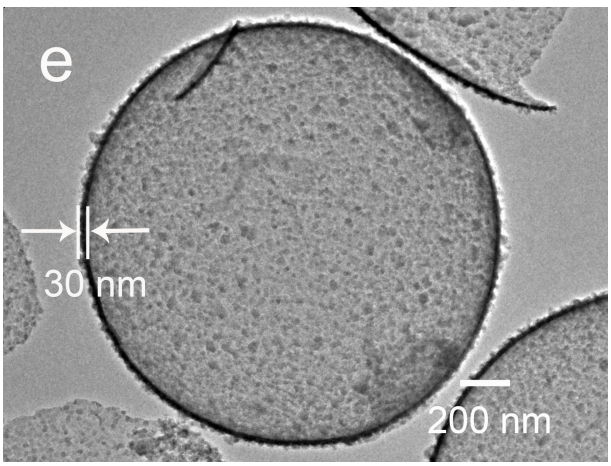
Morphology and structure: The as-synthesized polystyrene spheres are uniform in diameter about 2.2 μm as shown in Fig. 1(a). Further observation from SEM image indicates that the surface of polystyrene sphere is smooth which is a promising hard template for preparation of hollow structures. After encapsulated by silica, PS-SiO_2 structure is obtained, as shown in Fig. 1(b). There are uniform silica nanoparticles adsorbed on the surface of polystyrene spheres due to the hydrolysis and condenzation of tetraethyl orthosilicate at alkaline condition. From observation of Fig. 1(c), the morphology of PS-SiO_2·Ni is similar to that of PS-SiO_2 owing to the adsorbed Ni species are dispersed uniformly on the surface.











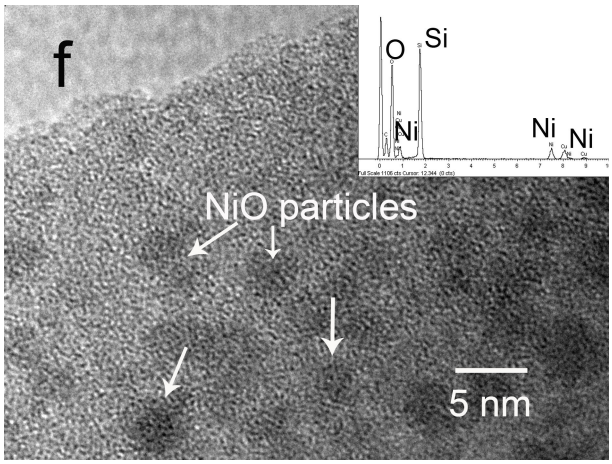


Fig. 1. (a) SEM image of PS spheres and TEM images of (b) PS-SiO_2, (c) PS-SiO_2·Ni and (d,e,f) SiO_2/NiO hollow spheres. [Inset in Fig. 1(f) is EDS image]

The final products SiO_2/NiO hollow spheres can be produced by subsequent annealing process in air as demonstrated by XRD measurement (Fig. 2). The wide peak at 23º corresponds to the signal of amorphous silica. Additionally, the three sharp peaks can be ascribe to the crystalline NiO (111), (200) and (220) planes. The NiO phase can be identified as cubic NiO with face-centered lattice (JCPDS card No. 78-0643, space group $Fm\bar{3}m$) which has lattice parameter of a = 4.176 Å. No other peaks observed in Fig. 2 indicates that the product is SiO_2/NiO composite. After the annealing treatment, the hard template polystyrene spheres are combusted and converted into CO_2 and H_2O and finally disappeared, leading to hollow structures. Fig. 1(d) demonstrates the morphology of SiO_2/NiO hollow spheres. The diameters are within 1.5-2.5 μm which almost the same as that of polystyrene spheres, indicating that the morphology can be well maintained during the annealing treatment. Accordingly, the diameter of the hollow structures could be controlled by the diameter of polystyrene template. Further observation from magnified image [Fig. 1(e)] indicates that the shell is composed of uniform nanoparticles and the thickness of the hollow structure is about 30 nm. More enlarged image of the surface of hollow sphere [Fig. 1(f)] shows that the NiO nanoparticles are dispersed on the silica shell with diameters about 3-5 nm. The EDS measurement shown in Fig. 1(f) clearly demonstrates the existence of NiO and SiO_2. Therefore, the SiO_2/NiO hollow spheres can be successfully prepared using polystyrene spheres as hard template without morphological deformation.

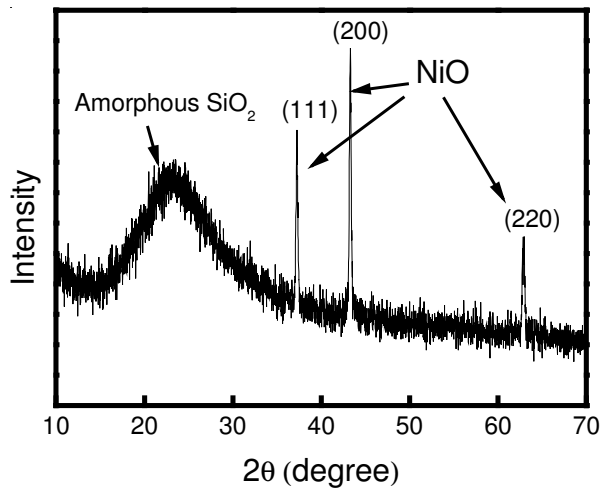
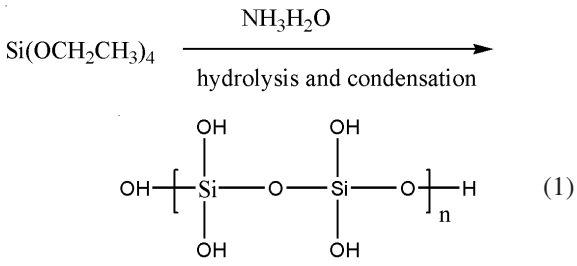


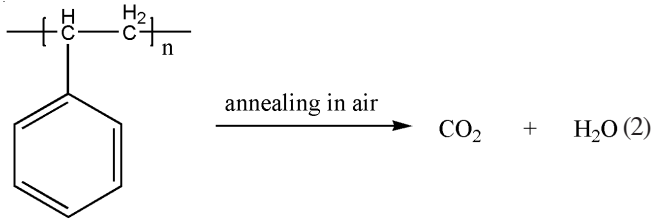
Fig. 2. XRD pattern of as-prepared SiO_2/NiO hollow spheres

Formation procedure of SiO_2/NiO hollow spheres: Template formation of hollow structure is widespread used. The typical strategy contains the formation of core-shell structure and subsequent removal of template by etching or annealing[7]. In present work, the formation mechanism is interesting and may gives an elicitation on the formation of composite hollow structures.

The main chemical reactions in the formation of SiO_2/NiO hollow spheres can be described as following:

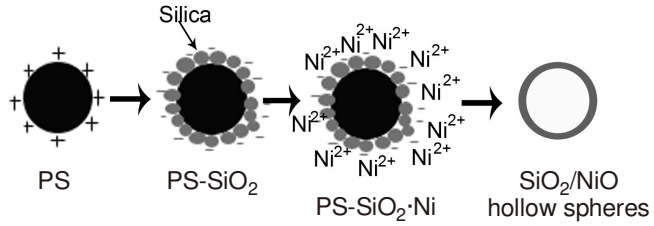


(1)



(2)

The surface of the polystyrene sphere is modified with -NH_2 group when treated with ammonia and hence positively charged[14]. Then, tetraethyl orthosilicate go through hydrolysis and condensation reactions under alkali condition, leading to formation of silica as shown in reaction 1. The negatively charged silica can be adsorbed on the positively charged polystyrene spheres through electrostatic interaction and form PS-SiO_2 core-shell structure as illustrated in **Scheme-I**. Similarly, nickel cations are adsorbed on the surface of PS-SiO_2 by impregnation using nickel acetate solution[9]. In the last annealing step, the polystyrene spheres are combusted and converted into carbon dioxide and water. At the same time, the silica shell go through further condensation reaction and form SiO_2. The adsorbed Ni species are oxidated to NiO nanoparticles during annealing in air. Finally, the SiO_2/NiO hollow spheres are formed with high quality.



Scheme-I: Illustration of formation procedure of SiO_2/NiO hollow spheres

To verify the composition transformation in present experimental process, FTIR measurements are performed and shown in Fig. 3. Curve (a) of Fig. 3 is the spectrum of polystyrene, the main characteristic peaks are indicated. The peaks at 695, 758 and 1027 cm^{-1} correspond to the C-H bending vibrations of benzene ring. The peak at 3022 cm^{-1} is the signal of C-H stretching vibration of benzene. In addition, the existence of benzene ring can also be demonstrated by the peaks at 1490 and 1602 cm^{-1} which correspond to the C=C and C-C stretching vibration of benzene, respectively. The signals at 1450 and 2923 cm^{-1} can be ascribed to the C-H bending and stretching vibrations of -CH_2-, respectively. After encapsulated by silica, the strong peak at 1090 cm^{-1} demonstrates the formation of Si-O-Si groups as shown in spectrum of PS-SiO_2 [Fig. 3(b)]. The peaks of organic groups disappear and the signal at 1090 cm^{-1} become sharper [Fig. 3(c)] due to the combustion of polystyrene spheres and further condensation of silica, leading to formation of SiO_2/NiO hollow spheres.

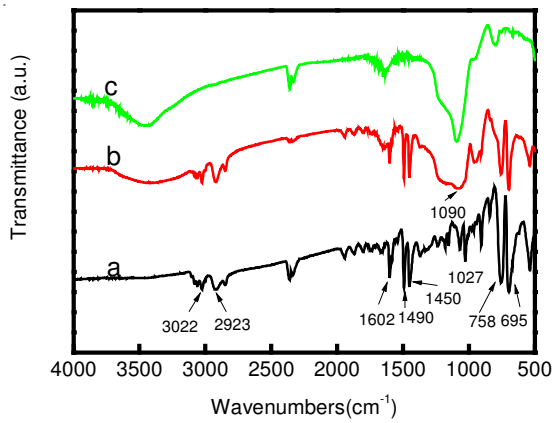


Fig. 3. FTIR spectra of (a) PS spheres, (b) PS-SiO_2 and (c) SiO_2/NiO hollow spheres

The combustion behaviour of PS-SiO_2·Ni is investigated by TG analysis as shown in Fig. 4. A little weight loss from 100-132 ºC owing to the loss of a small amount of water at the surface of PS-SiO_2·Ni sample. Further weight loss from 198-230 ºC corresponds to the volatilization of adsorbed water. Interestingly, the weight of PS-SiO_2·Ni is increasing from 230-368 ºC, because of the oxidation of Ni species in air. The weight loss rate is fast from 368-463 ºC and slow down from 463-550 ºC due to the pyrolysis of polystyrene. From 368-550 ºC, the polystyrene spheres are combusted completely and form hollow structures.

Conclusion

We have developed a facile route to prepare hollow SiO_2 spheres decorated with NiO nanoparticles. The synthetic

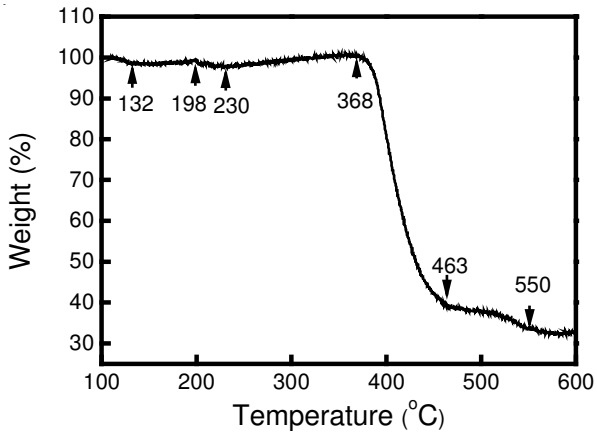


Fig. 4. TG curve of PS-SiO_2·Ni

procedure involves functionalization of polystyrene spheres, sol-gel encapsulation, adsorption of nickel species and annealing treatment. The obtained SiO_2/NiO hollow structures are uniform and well organized. It is important to note that this work also demonstrates the possibility to prepare other hollow composite spheres and supply a general approach.

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