Template-free Approach to Core–Shell-structured Co_3O_4 Microspheres

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Core–shell-structured Co_3O_4 microspheres were fabricated by a solvothermal process combined with subsequent calcination. These Co_3O_4 microspheres were unique as featured by their excellent catalytic activity toward thermal decomposition of ammonium perchlorate.

Recently, inorganic materials with special morphologies have received considerable attention owing to their great application potentials. Among all morphologies ever reported in the literature, inorganic core–shell structure is most attractive since it could show novel chemical and physical properties that are highly needed for many applications.[1] To retain the core–shell structures,[2] many kinds of templates like surfactants or polymers have to be used as additives. However, the addition of templates to the reaction systems may complicate the synthetic procedures and further introduce uncertain impurities that can be harmful to the properties of the final products. As a consequence, it is of great value to develop simple template-free methods to fabricate inorganic core–shell structures.

In this work, core–shell Co_3O_4 is taken as a model target material for study. As an important magnetic p-type semiconductor, spinel oxide Co_3O_4 has great application potentials in heterogeneous catalysts, solid-state sensors, anode materials in lithium ion rechargeable batteries, and magnetic materials.[3] Many routes have been developed to fabricate Co_3O_4 of different morphologies with the aim to acquire special properties. Up to now, Co_3O_4 with different morphologies such as nanocube, nanosheet, hollow microspheres, and mesoporous structures have been successfully achieved.[4] However, there is still no report concerning the fabrication of core–shell-structured Co_3O_4 microspheres by a template-free method. Here, we report on our preliminary results directed toward the facile template-free fabrication of core–shell-structured Co_3O_4 microspheres, which have shown great potential as an additive in promoting the thermal decomposition of ammonium perchlorate (AP).

The synthetic procedure of the samples can be briefly described as follows: Given amounts of $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in ethanol to get a 1 mol/L transparent solution. The resulting red solution was then transferred to a Teflon-lined stainless steel autoclave with a filling degree of 70%, which was allowed to react at 160 °C for 10 h. After cooling to room temperature, the resulting solid products were washed with deionized water several times and dried at 80 °C for 24 h. The solid product was calcined at 400 °C in air for 1 h, and black powders were finally obtained.

Phase compositions of the samples were characterized by powder X-ray diffraction (XRD) on a Rigaku D/MAX25000 diffractometer with a copper target. The morphologies of the samples were investigated by field-emission scanning electron microscopy (SEM) using a JEOL JSM-6700 apparatus. The catalytic activity of core–shell Co_3O_4 microspheres toward the thermal decomposition of AP was studied by a differential scanning calorimeter (DSC) using DTA404PC at a heating rate of $15\,^\circ\mathrm{C/min^{-1}}$ in N_2 atmosphere over a temperature range from 30 to 500 °C. AP and Co_3O_4 microspheres were mixed at a mass ratio of 98:2 to prepare the target samples for thermal decomposition analyses.

The precursor for the core–shell Co_3O_4 was optimized by varying the reaction time at a fixed temperature of 160 °C. At a reaction time of 1 h, the product was a mixture of Co_3O_4 with β-$Co(OH)_2$ and $Co(OH)_{2-x}(NO_3)_x \cdot nH_2O$.[5] With prolonged reaction time, the crystallinity of the Co_3O_4 as featured by diffraction intensity became significantly enhanced (Figure S1[11]), while the morphological transition of the precursor from irregular flowery structure to uniform microspheres was clearly seen (Figure S2). Consequently, the product obtained at a reaction time of 24 h was taken as the optimum precursor for the core–shell Co_3O_4.

Figure 1 shows an XRD pattern and the morphology of the optimized precursor. From Figure 1a, it can be seen that the precursor was composed of Co_3O_4, β-$Co(OH)_2$, and $Co(OH)_{2-x}(NO_3)_x \cdot nH_2O$ phases. Low-magnification SEM observations (Figure 1b) indicate that the precursor was mainly composed of dandelion-like microspheres. The high-magnification SEM image of a single microsphere (Figure 1c) clearly demonstrates a dandelion-like shape. Further high-magnification SEM image for a piece of a single microsphere indicates that the surfaces of the dandelion-like microspheres consisted of nanofibers with widths ranging from 50–100 nm (Figure 1d).

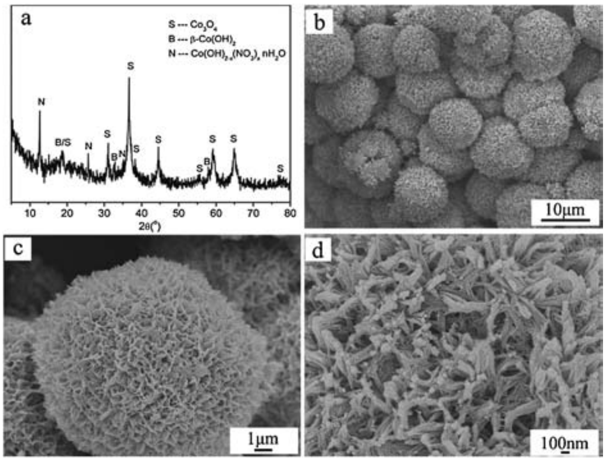

Figure 1. (a) XRD pattern and (b) low-magnification SEM image of the sample directly prepared by solvothermal process, (c) SEM image of a single microsphere, and (d) SEM image of the surface of the microsphere.

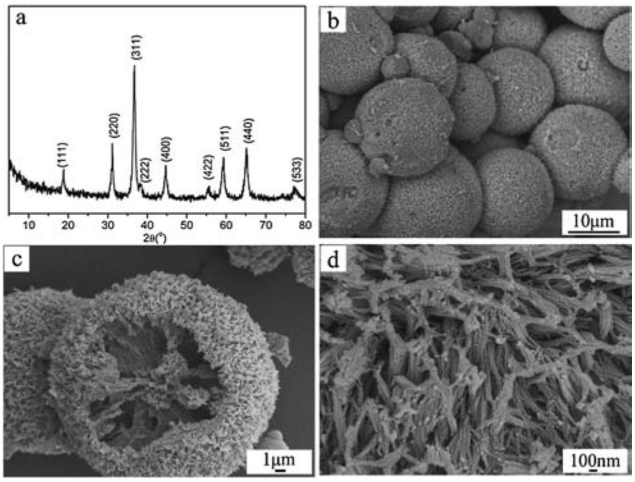

Figure 2. (a) XRD pattern and (b) low-magnification SEM image of as-prepared Co_3O_4, (c) SEM image of a single broken sphere, and (d) SEM image of the surface of Co_3O_4 microsphere.

These dandelion-like microspheres underwent subsequent heat treatment, as indicated by XRD data (Figure 2a), and became a pure phase since the raw XRD data matched well the standard diffraction data for the cubic structure Co_3O_4 (PCPDF-No. 42-1467). The lattice parameter determined by a least-squares method was $a = 0.811$ nm. Using the Scherrer formula for the (311) diffraction peak of Co_3O_4, the mean crystallite size was calculated to be 14.5 nm, which is apparently much smaller than that of 10 micron spheres observed by SEM observation in Figure 2b. It is thus demonstrated that Co_3O_4 spheres are an assembly of tiny nanocrystals. It is interesting to note that Co_3O_4 microspheres basically inherited the size and morphology of the precursor before calcinations. The SEM image of a single broken sphere reveals that the microspheres had a core–shell structure (Figure 2c). The shell consists of nanofibers with widths around 100 nm (Figure 2d), while the core is aggregated by small particles with cracks (Figures 2c and S3).

Core–shell Co_3O_4 microspheres were explored as an additive to the thermal decomposition of AP, the key component of composite solid propellants. Figure 3 shows the DSC curves of pure AP and the mixture of AP with Co_3O_4 microspheres at a 2% mass basis. It is seen that there are three obvious DSC peaks for pure AP. The first endothermic peak appeared at about 245 °C, which is associated with a phase transition of AP from orthorhombic to cubic.[6] The second peak centered at about 338 °C is exothermic, which exactly corresponds to the low-temperature decomposition (LTD). The second endothermic peak centered at about 442 °C is referred to as high-temperature decomposition (HTD).[7] With the addition of Co_3O_4 microspheres, the HTD process disappeared to show a sole exothermic process in a temperature range from 260–380 °C, much lower than that for pure AP, indicating that Co_3O_4 microspheres could accelerate the AP decomposition.

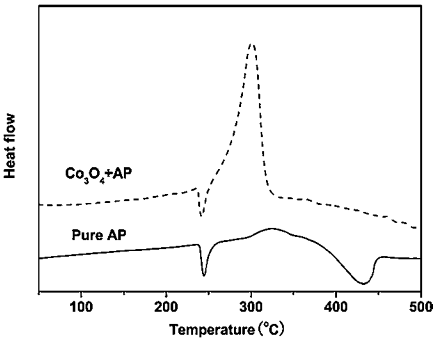

Figure 3. DSC curves of pure AP and the mixture of AP with Co_3O_4 microspheres.

What is the reason for the excellent catalytic role that Co_3O_4 microspheres play in AP decomposition? It is well known that AP decomposition involves two crucial steps: (1) ammonia oxidation and (2) dissociation of ClO_4^- species into ClO_3^- and O_2.[8] In the first step, Co_3O_4 exhibits high and stable catalytic activity and selectivity toward ammonia oxidation, thus promoting AP decomposition. In the second step, Co_3O_4 accepts the electrons donated from ammonia oxidation, which may promote the dissociation of ClO_4^- species into ClO_3^- and O_2.[9] On the basis of these analyses, we propose that the excellent catalytic activity of Co_3O_4 microspheres is probably due to their special core–shell structure assembled from tiny nanocrystals, which provides more active sites to accelerate ammonia oxidation and ClO_4^- species dissociation. Finally, the catalytic activity of core–shell Co_3O_4 microspheres toward thermal decomposition of AP is much better than pure Co_3O_4 nanoparticles reported by Chen et al.,[10] while it is comparable to that of the best catalyst of CoO/Co_3O_4 composite nanostructure ever reported toward AP decomposition.[9]

In short, core–shell-structured Co_3O_4 microspheres were prepared to show noticeable promotion of AP decomposition. The methodology reported here is expected to find broad uses in designing new additives for AP decomposition.

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