Supplementary Information for

Magnesium carbonate recyclable template to synthesize micro hollow structures at large scale

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CAPTIONS:

Experimental Section and characterizations

Fig. S1 EDX patterns of the TiO_2 microtubes show that the samples contain Ti and O.

Fig. S2 XRD patterns of the $MgCO_3 \cdot 3H_2O$ template: (a) the initial template, (b) the tiwce born template; (c) the fifth-born template.

Fig. S3 XRD patterns of the $MgCO_3$ microcubes (a) and TiO_2 microboxes (b).

Fig. S4 SEM image (a) and XRD pattern (c) of the twice-born $MgCO_3$ template; SEM image (b) and XRD pattern (d) of the TiO_2 microboxes prepared by the twice-born $MgCO_3$ template.

Fig. S5 SEM images of the Al_2O_3 microtubes (a) and the SiO_2 microtubes (b) with the insert of TEM images of the samples; EDX patterns of the Al_2O_3 microtubes (c) and SiO_2 microtubes (d); XRD patterns of the Al_2O_3 microtubes (e) and the SiO_2 microtubes (f).

Fig. S6 SEM images of Gd_2O_3 (a) and NiO (b) microtubes; XRD patterns of Gd_2O_3 (c) and NiO (d) microtubes. The inserts in (a) and (b) are the TEM images of the samples with the scale bar of 200 nm.

Fig. S7 (a) SEM image of the SiO_2 microboxes; (b) XRD pattern of the SiO_2 microboxes. The insert of (a) is the TEM image of the sample, and the scale bar is 50 nm.

Table. S1 The analysis of filtrate and starting materials.

Experimental Section

Synthesis of $MgCO_3 \cdot 3H_2O$ template: In a typical synthesis, a $Mg(HCO_3)_2$ glycol-water(v/v = 1:1) solution (0.2 mol/L, 100 mL) was transferred to a 250 mL three-necked flask. The solution was stirred and heated to 45 °C by water bath, then a variable amount of ammonia (2.0 mol/L, 0-10ml) was added into the vigorously stirred (~300 rpm) mixture. After stirring, the mixture was maintained for 15 min. Then a white precipitation was collected, filtered off, and washed with water and ethanol three times. The products were dried in blast drying oven at 55 °C for 4 h.

Synthesis of $MgCO_3 \cdot 3H_2O@TiO_2 \cdot xH_2O$: The as-prepared $MgCO_3 \cdot 3H_2O$ microrods (1.0 g) were dispersed in tetrabutyl titanate-ethanol solution (1.2 mL/75 mL). A 1:5 (v/v) mixture of water and ethanol was added dropwise into the suspension of nesquehonite with vigorous stirring. Thereafter, the suspension was stirred for a further 4 h before centrifugation and washing with ethanol and water.

Synthesis of $MgCO_3 \cdot 3H_2O@SiO_2 \cdot xH_2O$: The as-prepared $MgCO_3 \cdot 3H_2O$ microrods (1.0 g) was redispersed in ethanol-water solution (90 mL/10 mL). The ammonia (1.0 mL, 25 wt%) was then added and the mixture was stirred for 5 min. TEOS was added quickly and the mixture reacted at 25 °C. Thereafter, the suspension was stirred for further 4 h before centrifugation and washing with water and ethanol.

Synthesis of magnesium carbonate@$Al_2O_3 \cdot xH_2O$: The as-prepared $MgCO_3 \cdot 3H_2O$ microrod was dried in blast drying oven at 60 °C for 2 h, then were dispersed in isopropanol. The aluminium isopropoxide-isopropanol solution (25 wt%, 10 mL) were then added into the vigorously stirred mixture by injector, and the mixture was heated from room temperature to 55 °C at the rate of 3 °C/quarter on anhydrous condition. Thereafter, the suspension was stirred for a further 12 h, and then centrifugated and washed with isopropanol and ethanol.

Synthesis of $MgCO_3 \cdot 3H_2O$@gadolinium carbonate: The as-prepared $MgCO_3 \cdot 3H_2O$ microrods (0.6 g, 1.5 mmol) was redispersed in ethanol (50 mL). The $Gd(NO_3)_3$ (5.0 mL, 0.4 mol/L) was then added and the mixture was stirred for a further 1 h at 25 °C, and then centrifugated and washed with water and ethanol.

Synthesis of $MgCO_3 \cdot 3H_2O$@nickel carbonate: The as-prepared $MgCO_3 \cdot 3H_2O$ microrods (0.6 g, 1.5 mmol) was redispersed in ethanol (50 mL). The $Ni(NO_3)_2$ (2.0 mL, 1.0 mol/L) was then added and the mixture was stirred for a further 4 h at 45 °C before centrifugation and washing with water and ethanol.

Synthesis of TiO_2 Al_2O_3, SiO_2 Gd_2O_3 and NiO microcubes: The as-prepared core-shell samples were dispersed in glycol-water solution under stirring for 30 min, while carbon dioxide was flowed into the solution. After three cycles of centrifugation/washing/redispersion with water and ethanol, the samples obtained were dried. Finally the precursors were heated in muffle furnace.

Synthesis of $MgCO_3$ microcubes: In typical procedure, a $Mg(HCO_3)_2$ aqueous solution (0.4 mol/L, 30 mL) containing NH_4Cl was transferred to an autoclave (50 mL capacity) and hydrothermally treated at 160 °C for 24 h. The white product was collected, filtered off, and washed with water and ethanol three times. The products were dried in blast drying oven at 60 °C for 4 h, and $MgCO_3$ microcubes was obtained. To increase etching rate, $MgCO_3$ template need to be heated to 550 °C and maintained for 1h before being used.

Synthesis of TiO_2 microboxes: The as-prepared template (1.2 g) were dispersed in tetrabutyl titanate-ethanol solution (0.6 mL/50 mL). A mixture of water and ethanol (1:5 (v/v)) was added dropwise to the suspension of $MgCO_3 \cdot 3H_2O$ with vigorous stirring. Thereafter, the suspension was stirred for a further 4 h before filtering and washing with water and ethanol. The as-prepared core-shell samples were dispersed in an NH_4Cl aqueous solution under stirring for 30 min, while carbon dioxide was flowed into the water. After three cycles of centrifugation/washing/redispersion with water and ethanol, the samples obtained were dried. Finally the precursors were heated in muffle furnace.

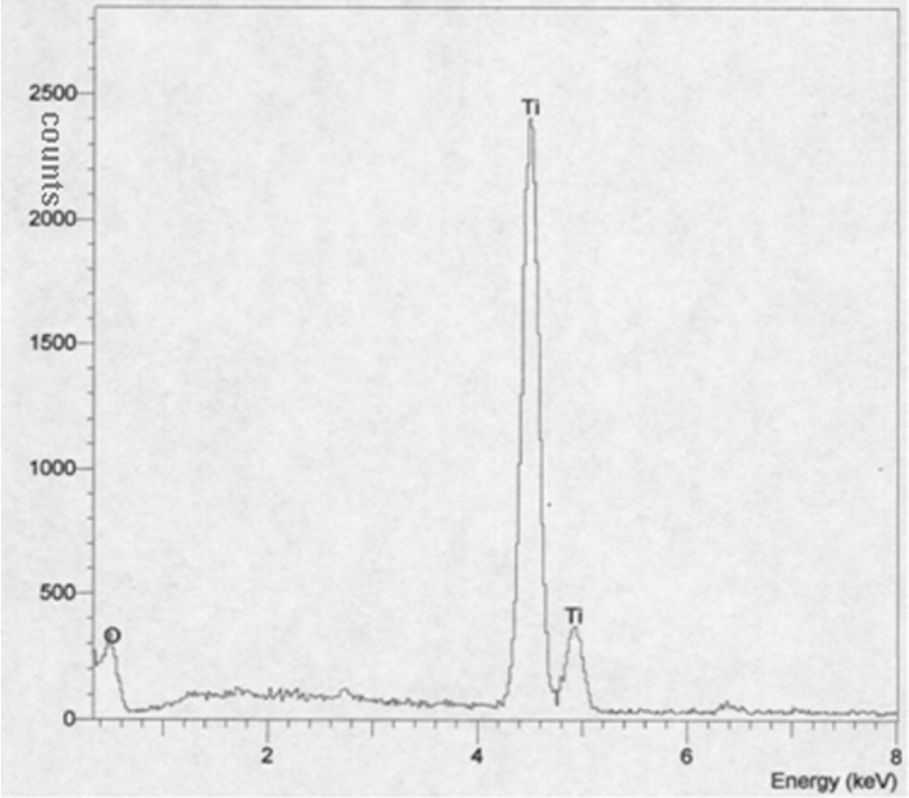
Synthesis of SiO_2 microboxes: The as-prepared template (1.2 g) was redispersed in ethanol-water solution (45 mL/15 mL). The ammonia (1.0 mL, 25 wt%) was then added and the mixture was stirred for 5 min. TEOS (0.5ml) was added quickly and the mixture reacted at 25 °C. Thereafter, the suspension was stirred for a further 4 h, and then filtered and washed with water and ethanol. The as-prepared core-shell samples

were dispersed in NH_4Cl aqueous under stirring for 30 min, while carbon dioxide was flowed into the mixture. After three cycles of centrifugation/washing/redispersion with water and ethanol, the samples obtained were dried. Finally the precursors were heated in muffle furnace.

Synthesis of the twice-born magnesium carbonate template: Magnesium carbonate were recycled by preparation from raw materials of magnesium hydrogen carbonate filtrate as described previously.

Characterizations

The samples were characterized by XRD (Rigaku-DMax 2400) in reflection mode (Cu Kα radiation) at scanning rate of 0.02 S^{-1} in the 2θ from 5 to 80 °. The shape and structure of the products were observed with a scanning electron microscope (JEOL-5600LV, operated at 15 kV; S-4800, operated at 5kV) and a transmission electron microscope (TEM; Philips TecnaiG2 20, operated at 200 kV). EDX was performed during SEM (JEOL-5600LV). The Mg^{2+} concentration of filtrate was measured by EDTA titration method, and the pH was measured by pH-meter (SHANGHAILEICI, PHS-3C).



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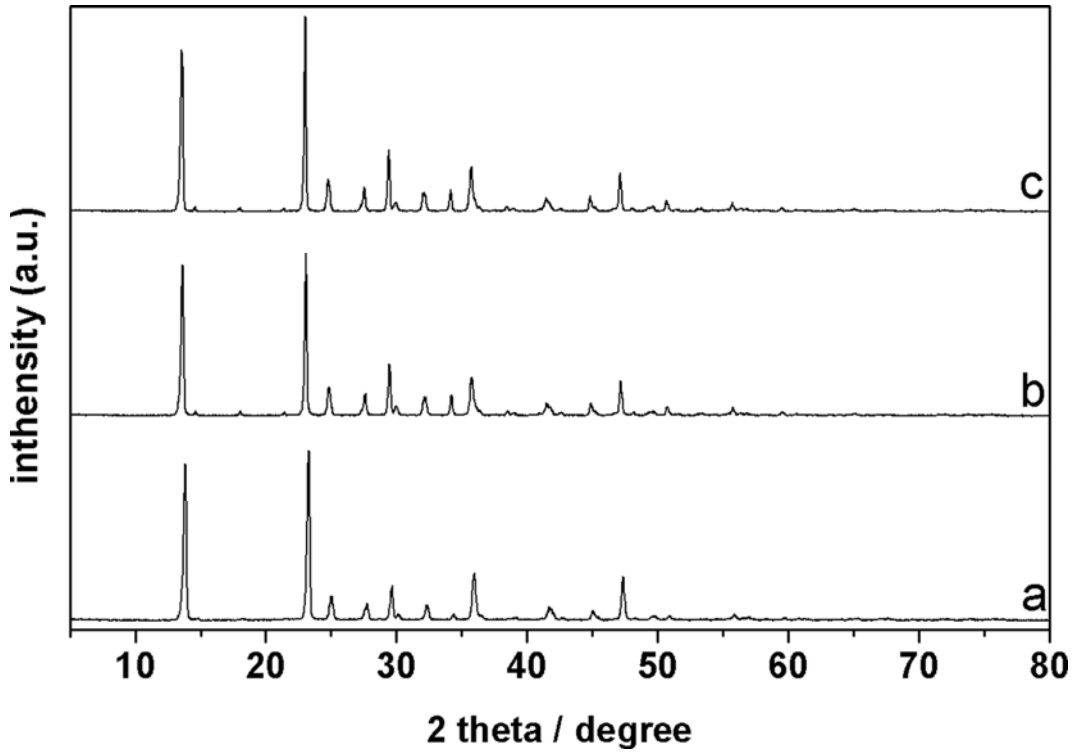

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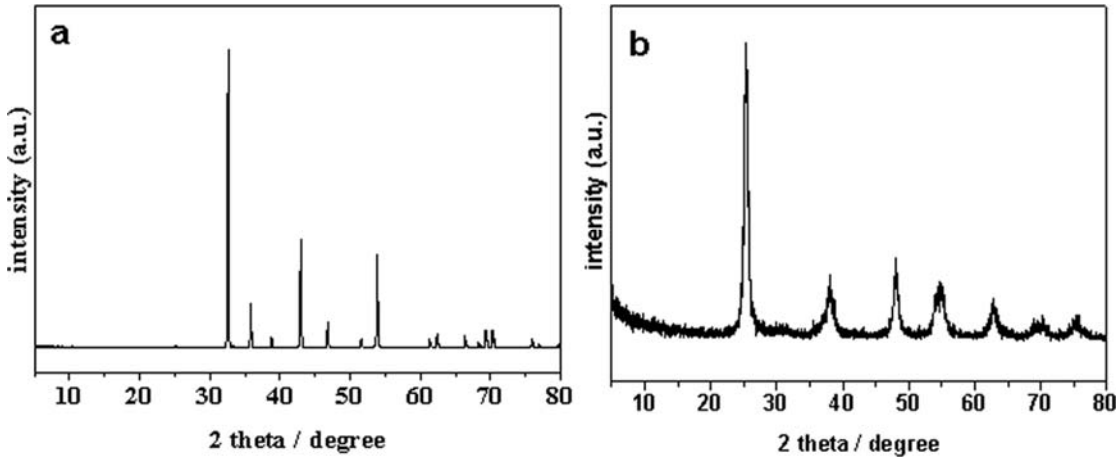

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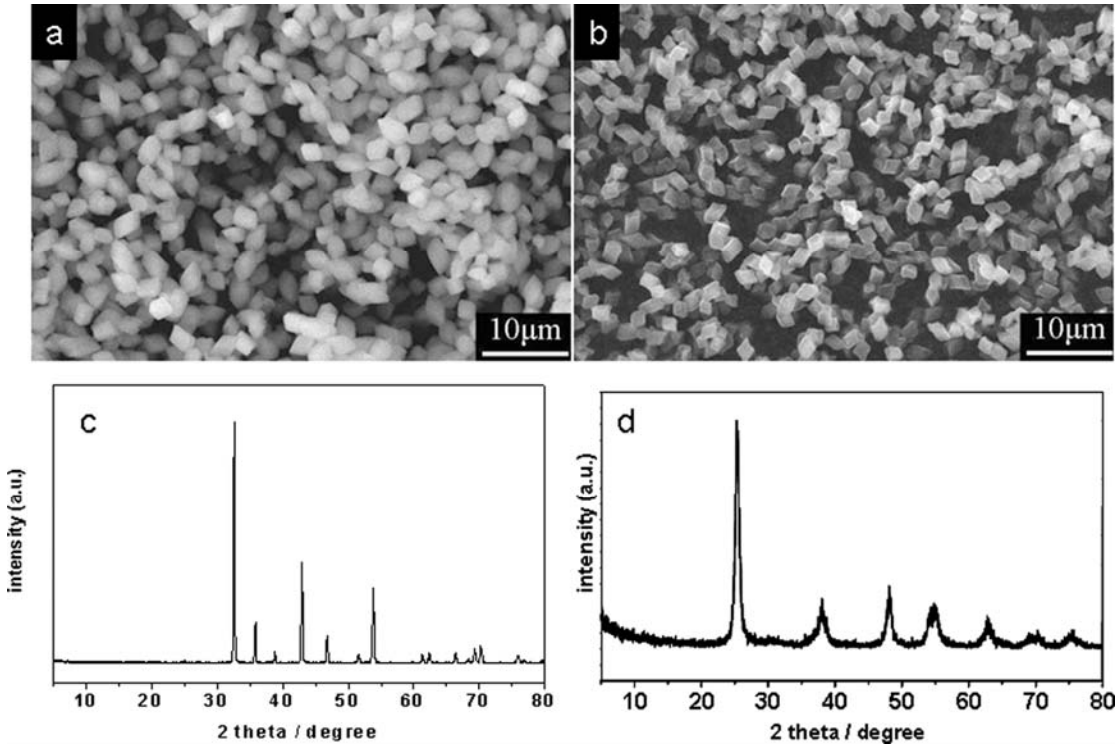

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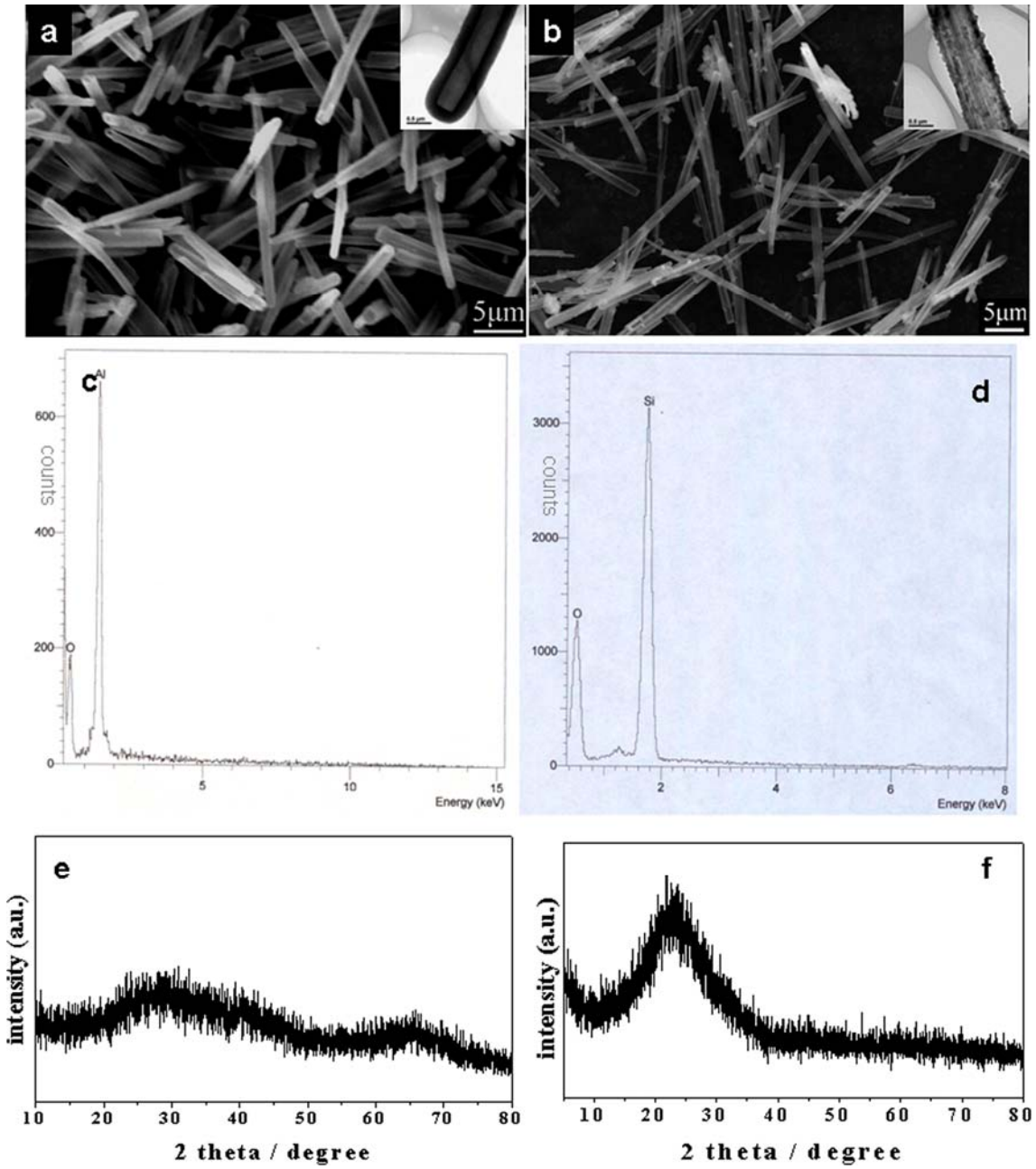

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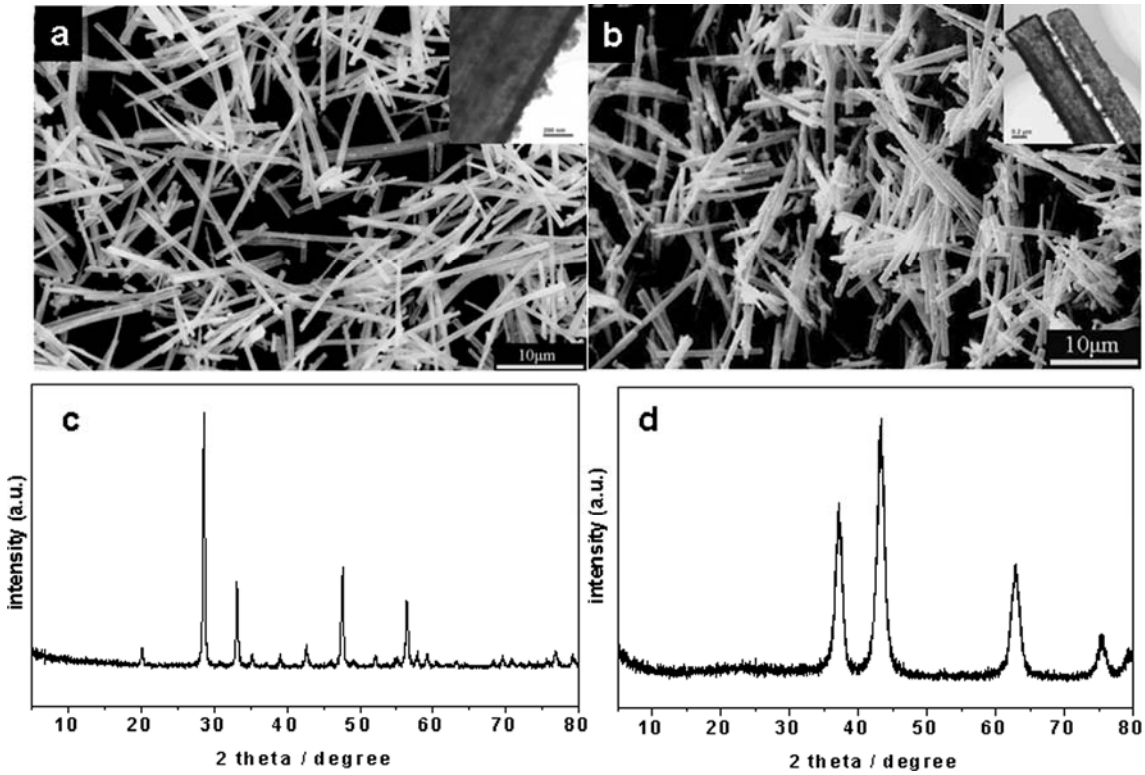

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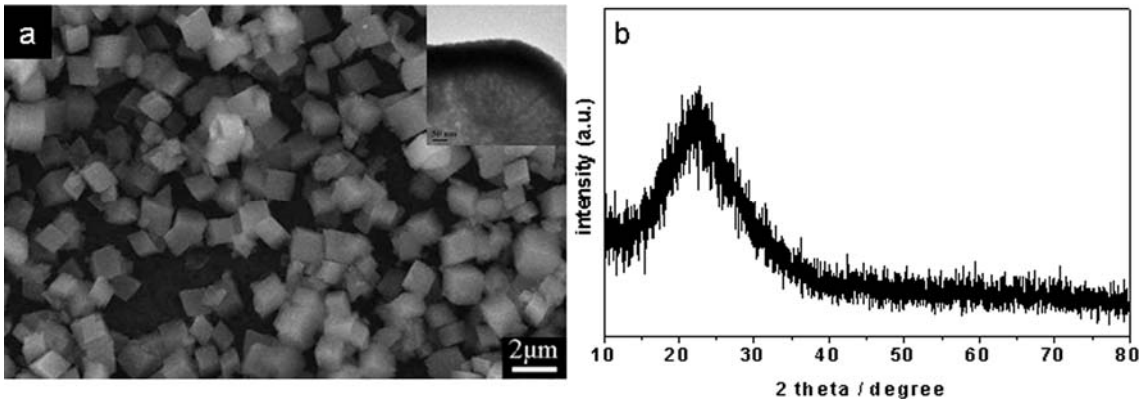

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Sample	$C(Mg^{2+})$	pH
Starting materials Sample	0.203M	7.15
Once-filtrate Sample	0.205M	7.20
Fourth-filtrate Sample	0.198M	7.13