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ARTICLE TYPE

Supporting Information

Controlled synthesis of Co_3O_4 single-crystalline nanofilm enclosed by (111) facets and exceptional activity in the catalytic of ammonium perchlorate

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10 1 Experimental:

All the reagents were of analytical grade and used without further purification. In a typical process, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9% purity) and NaOH (99.9% purity) were dissolved in 20 mL distilled water, respectively. Then, CoNO_3 and above-mentioned solution were mixed slowly and reacted in a micro-wave oven for five minutes for producing blue precursor precipitation. Subsequently, the blue precipitation was frozen quickly by liquid nitrogen and then dialyzed in ice water for 6 15 h to purify the product. Finally, the samples were dried by freeze-drying and annealed in a muffle furnace at 320-420 °C for 2-4 h in air, and then cooled down to room temperature naturally.

2 Results:

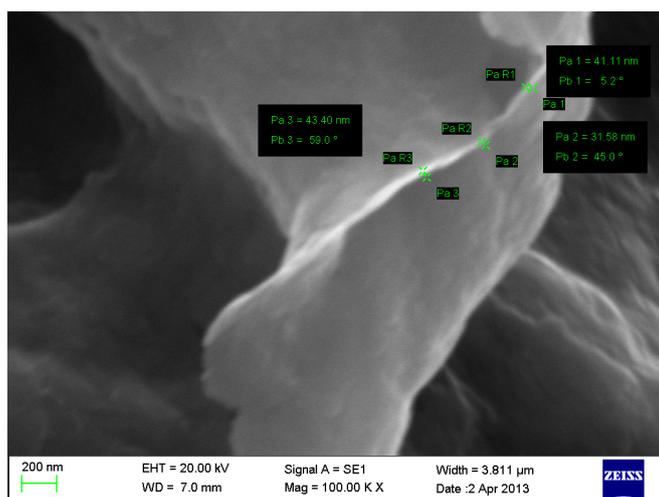


Figure1S. FESEM image of Co_3O_4 nanofilm. The image show the thickness of film is about 30-40 nm.

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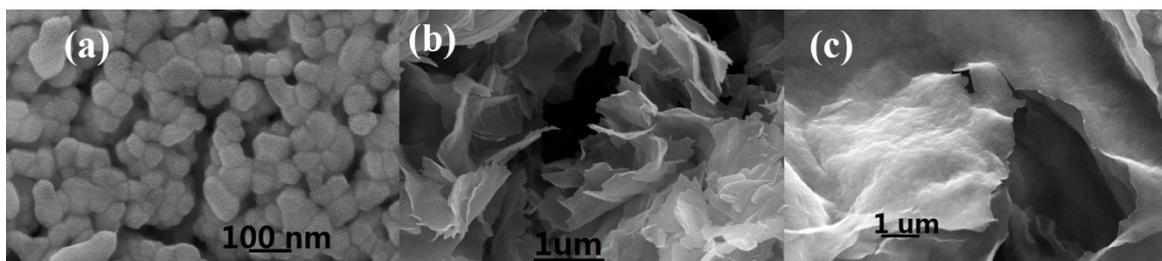


Figure 2S the FESEM images of precursor with different synthesis conditions: (a) without liquid nitrogen cooling, (b) liquid nitrogen cooling 0.5 min and (c) liquid nitrogen cooling 2 min.

The precursor show nano-particles without liquid nitrogen cooling (Figure 2S(a)). A large number of nuclei undergo a self-assembly process and arrange into oriented nanosheets. The nanosheets further aggregate to form nanofilm with high surface area under liquid nitrogen cooling.

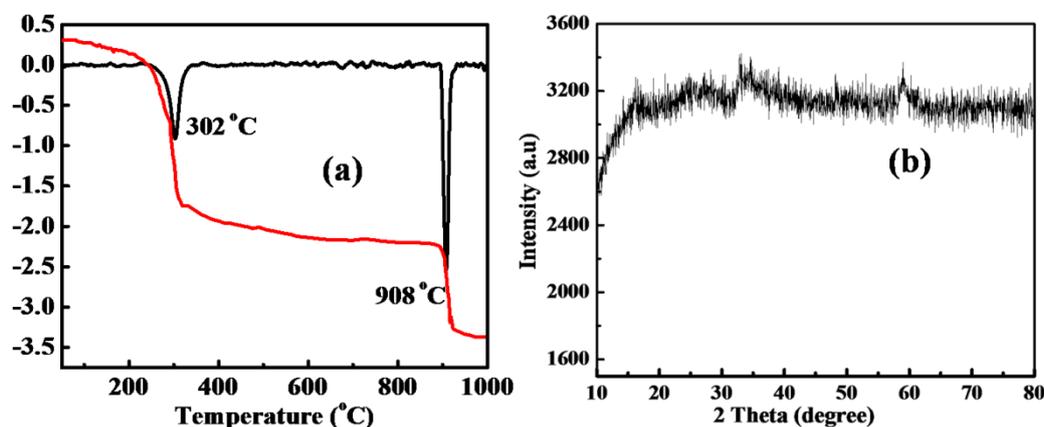


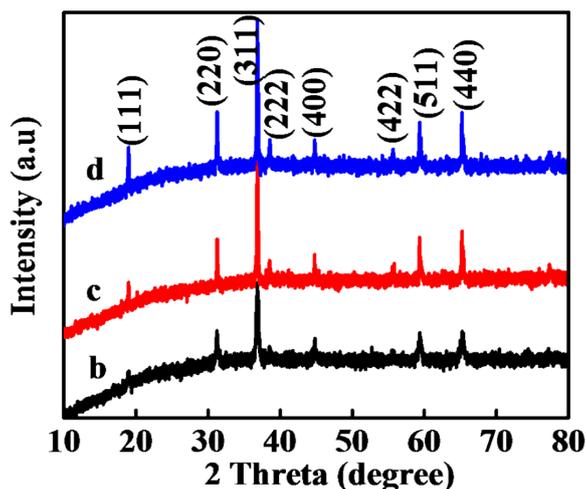
Figure 3S (a) TG-DSC curves and (b) XRD pattern of the precursor

There are some weak diffraction peaks from the precursor shown in Figure 3S(a). The diffraction peaks can be indexed to cobalt hydroxide ($\text{Co}(\text{OH})_2$), which is consistent with the value in the standard card (JCPDS Card No.51-1731). We further investigated the precursor by the thermogravimetric analysis (DSC/TGA) shown in Figure 3S(a). The DSC analysis shows that a major thermal event took place at 302 °C during the heating process in air. Above 302°C, the total weight loss of the sample is about 22.7%, originating from the decomposition of this precursor into Co_3O_4 and H_2O in the presence of oxygen in the air stream used in the DSC measurement. This value is slightly smaller than the theoretical value (25.63%) for this thermal decomposition, maybe due to partial loss of H_2O in the crystal structure in the process. For instance, if the dehydrated precursor is considered as being $\text{Co}(\text{OH})_2$, the related theoretical weight loss would then be 23.2%, which is close to the experimental value of 22.7%. Another thermal event took place at 908 °C, which is the Co_3O_4 further decomposed to CoO . The reactions involved in this process are expressed as follows:



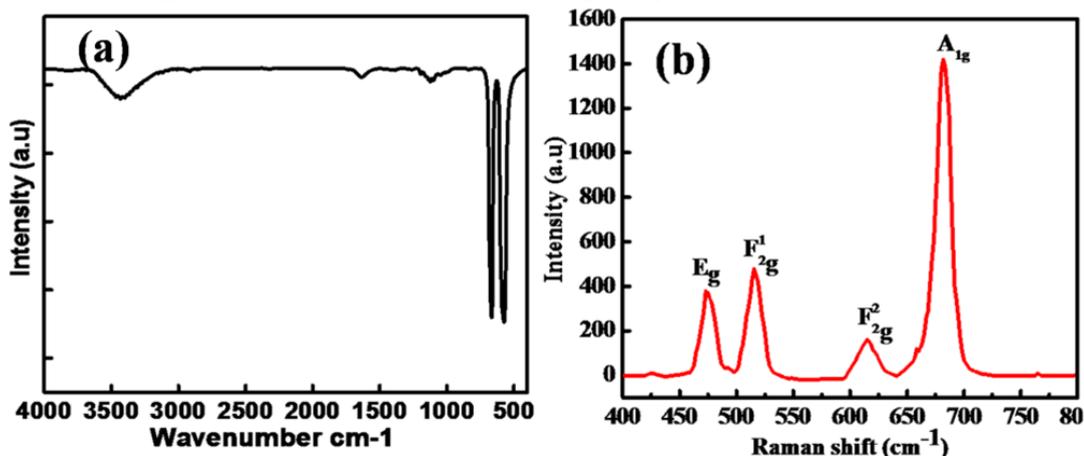
Based on above results, synthesized sample (before annealed) should be cobalt hydroxide $\text{Co}(\text{OH})_2$. We also tried to

confirm this by using XRD characterization. However, as shown in figure 3s (b), the XRD pattern of the synthesized sample (before annealed) exhibited no obvious peaks, which may be because the crystallization of the as prepared sample is not good.



5 Figure. 4S XRD of Co_3O_4 samples; (b) 320 °C, (c) 370°C, (d) 420°C.

From Figure. 4S, the intensity of the diffraction peaks increase along with annealing temperature increased. The sample annealing at high temperature (420 °C) exhibits diffraction peaks higher than those of the other two samples annealing at low temperature, indicating its better crystalline features under high temperature.



10 Figure.5S (a) FTIR spectrum of Co_3O_4 , (b) The Raman spectrum of Co_3O_4

Figure.5S(a) show two very strong peaks centered at 576 cm^{-1} and 672 cm^{-1} characteristic of spinel Co_3O_4 . The Raman spectrum of the product measured at room temperature (Figure.5S (b)) displays four bands located at 475, 526, 621, and 693 cm^{-1} , corresponding to the E_g , F_{2g} , F_{2g} , and A_{1g} modes of the spinel Co_3O_4 phase, respectively. This result is consistent with the XRD data clearly.

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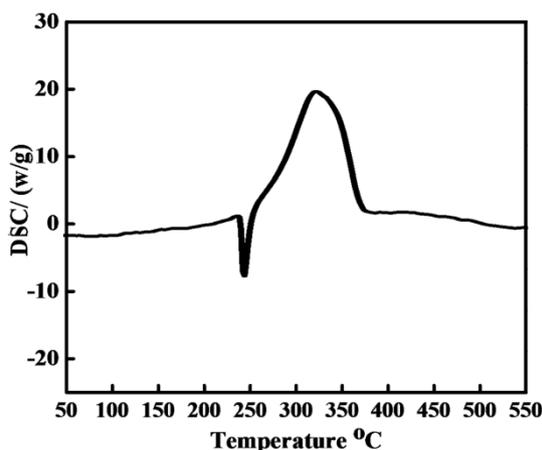


Figure 6S DSC of AP+3% w/w Co₃O₄ nanosheet

In order to illustrate the catalytic activity of (111) plane, we also prepared Co₃O₄ particles (according to RSC advances, DOI: 10.1039/c4ra04352a) and researched effect on the temperature of AP. The BET surface area of the particles is 28.93 m²g⁻¹, which is close to nanofilm (22.69 m²·g⁻¹) in this work. The DSC curve is shown in Figure 6S. A exothermic peak 5 appeared at 316°C is corresponding to the decomposition of AP. As can be seen that the addition of catalysts (Co₃O₄ particles, 3%) has decreased the temperature of the decomposition from 457 to 316 °C. However, Compared with AP+3% w/w Co₃O₄ (111) nanofilm, the temperature of the decomposition of AP is not significant low. Thus, the results show that Co₃O₄ nanofilm with (111) plane have more catalytic activity compared to particles with similar surface area.

10 To determine the thermal decomposition kinetic parameters of the AP and AP in the presence of the prepared Co₃O₄ nanofilm catalysts, AP and AP/Co₃O₄ nanofilm at different heating rate were tested. The Kissinger method was used, and the calculated equation was as follows:

$$\ln\left(\frac{T_p^2}{\phi}\right) = \frac{E_a}{RT_p} - \ln\frac{RA}{E_a}$$

where T_p was the temperature of exothermic peak in DSC curve, K; ϕ was the heating rate, K · min⁻¹; E_a was the activation energy, J · mol⁻¹; A was the pre-exponential factor; R was the gas constant, 8.314 J · mol⁻¹ · K⁻¹.

Table 1s kinetics data for the thermal decomposition of pure AP and AP + 3w/w % Co₃O₄ nanofilm catalysts

Sample	the activation energy/kJ mol ⁻¹	The pre-exponential factor/ s ⁻¹	Rateof reaction/s ⁻¹
AP	214.78	3.27 × 10 ¹¹	3.59 × 10 ⁻³
AP+3% w/w Co ₃ O ₄	153.62	1.96 × 10 ¹³	5.64 × 10 ⁻³