Supporting Information

Controlled Synthesis of Co_3O_4 Nanopolyhedrons and Nanosheets at Low Temperature

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1. Experimental Section

Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), hexamethylenetetramine ($C_6H_{12}N_4$, HMT), hydrogen peroxide (H_2O_2) were purchased from Alfa Aesar and used without further purification. Solutions of cobalt nitrate and HMT were prepared in the desired concentrations and stirred separately for 30 minutes at room temperature. The two solutions were subsequently mixed together for 30 minutes, and then the appropriate amount of H_2O_2 was added drop by drop for 30 minutes. The solution color changed from pink to light brown or dark brown depending on the molar ratio of HMT and cobalt nitrate. After that, the mixture was transferred to an 80^{o}C water bath reactor. After 3 hours reaction at 80^{o}C, the black precipitate was collected by high-speed centrifugation and washed with de-ionized water. The obtained powders were dried at 50°C in air before characterization.

The X-ray diffraction (XRD) measurements were recorded on a Philips X-Pert diffractometer employing Cu-Ka radiation. Size and shape of nanoparticles were examined with transmission electron microscopy (TEM, JEOL JEM-100 CX). The particle size was determined by measuring the diameters of more than 50 particles for each sample from the TEM images. The high-resolution transmission electron microscopy (HRTEM) images were taken at Center for Functional Nanomaterials (CFN) at BNL using a JEOL JEM2100F operating at 200 kV. Fast Fourier transform was performed on lattice images with ImageJ [1] software to obtain diffraction patterns.

(1) M. D. Abramoff, P. J. Magelhaes and S. J. Ram, "Image Processing with ImageJ" *Biophotonics International*, **2004**, 11(7), 36-42.

2. Figures

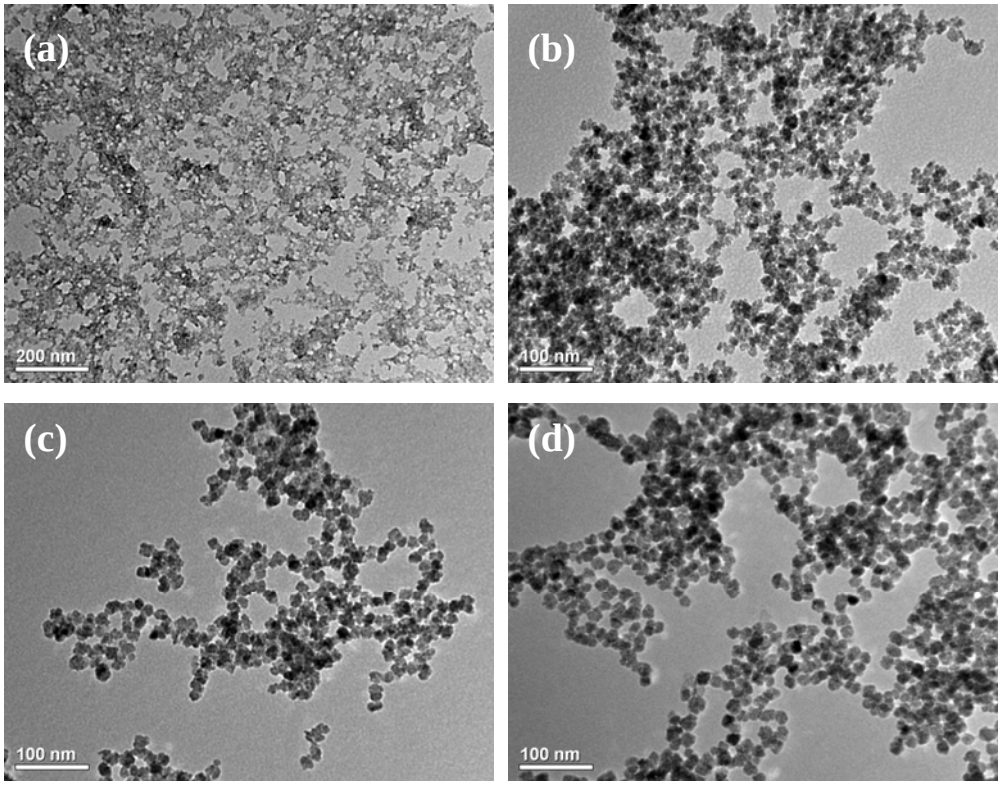

Fig. S1 TEM images of samples prepared with 0.5M HMT and 0.02M $Co(NO_3)_2 \cdot 6H_2O$ at 80 ^oC with different reaction time (a) 0 h (b) 1 h (c) 2hrs (d) 3hrs.

Fig. S1 shows the TEM images of the samples at different reaction times. The particle size increased very fast in the first 1 hour. After that, the particle size increased very slowly. The particle size of the samples allowed to react for 2 hours and 3 hours are almost same. Although these TEM grids were prepared at various stages in the reaction, all the samples were collected by centrifugation after 3 hrs at 80^oC, and the supernatants were clear and colorless.

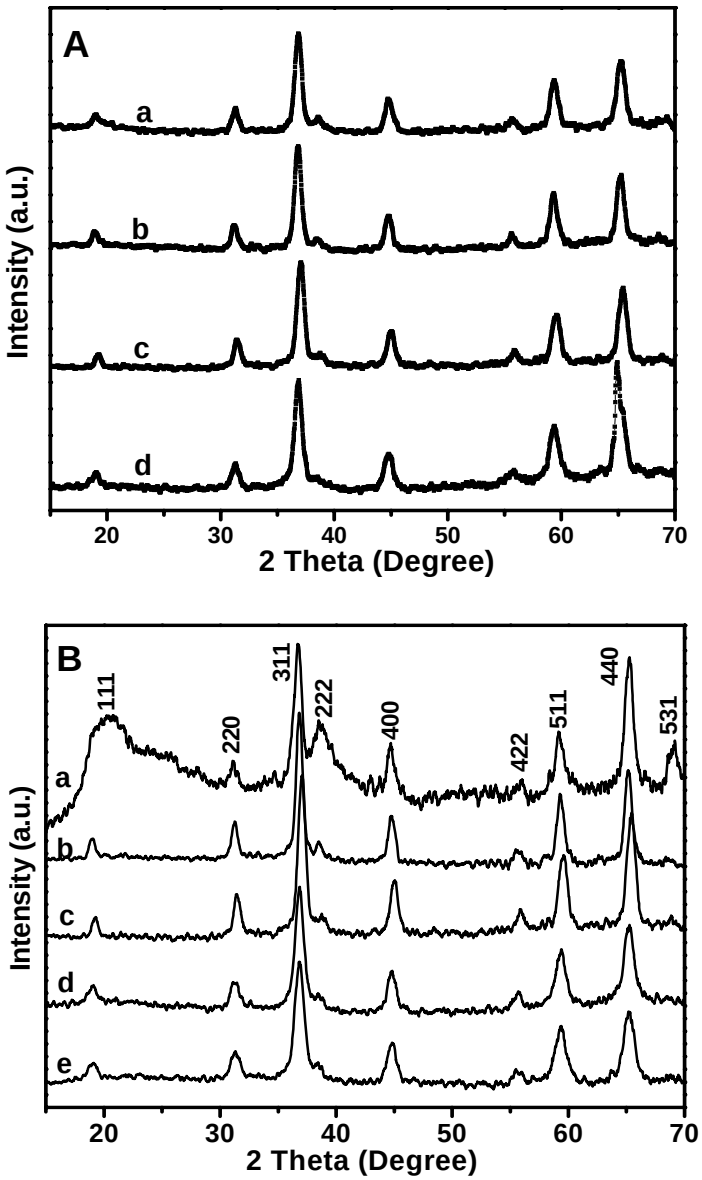

Fig. S2 XRD patterns of Co_3O_4 obtained with (A) 0.5 M HMT and varied $Co(NO_3)_2{\cdot}6H_2O$ concentrations: (a) 0. 1 M, (b) 0.04M, (c) 0.02 M, (d) 0.01M and (B) 0.02M $Co(NO_3)_2{\cdot}6H_2O$ and varied HMT concentrations: (a) 0.1M, (b) 0.25M, (c) 0.5M, (d) 1M, (e)1.5M.

Fig. S2 shows the XRD patterns of the samples prepared with different $Co(NO_3)_2{\cdot}6H_2O$ and HMT concentrations. All the diffraction peaks can be indexed according to the JCPDS card (No. 00-042-1467)[2] for Co_3O_4 having a cubic spinel structure. No peaks from other phases are observed. The broadening of the diffraction peaks demonstrates the nanocrystalline character of the Co_3O_4 powders. All the XRD data were analyzed with XFit[3] software to get the full width at half maximum (FWHM) of the XRD

peaks and accordingly estimate the particle size. In Fig. S2A, the particle sizes are almost the same at the same HMT concentration according to TEM results, but the FWHM of (111) XRD peak of the sample prepared with 0.5M HMT and 0.1 M $Co(NO_3)_2 \cdot 6H_2O$ is bigger than the others because the crystallite platelets are very thin. These nanosheets are only about 3 nm thick in the <111> direction as determined by HRTEM. In Fig. S2B, the particle size decreased with the increased HMT concentration according to TEM results, but the sample prepared with lowest HMT concentration shows the broadest (111) and (222) peaks as seen in Fig. S2B(a). The reason for this broadness is that this sample is only about 2-3 nm thick in the <111> or <222> direction as shown in Fig. 3d and Fig.S3.

(2) K. Martin and G. McCarthy, North Dakota University, Fargo, North Dakota, USA. ICDD Grant-in-Aid (1990)

(3) A software for XRD analysis downloaded from www.ccp14.ac.uk.

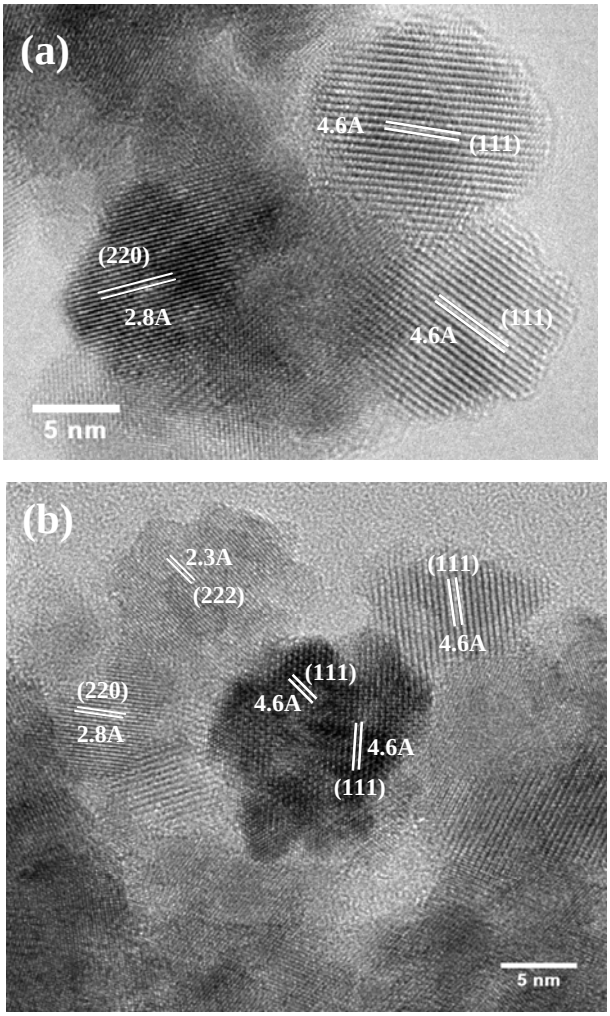

Fig. S3 HRTEM images of a sample prepared with 0.5M HMT and 0.02 M $Co(NO_3)_2 \cdot 6H_2O$

Fig. S3 shows the HRTEM images of Co_3O_4 prepared with 0.5M HMT and 0.02 M $Co(NO_3)_2 \cdot 6H_2O$. The interlayer spacing is about 0.46, 0.28 and 0.23 nm, respectively, which corresponds to the interlayer distance of the {111}, {220}, and {222} crystal plane of cubic Co_3O_4, revealing that the Co_3O_4 nanopolyhedra are dominated by the {111} and {110} facets.

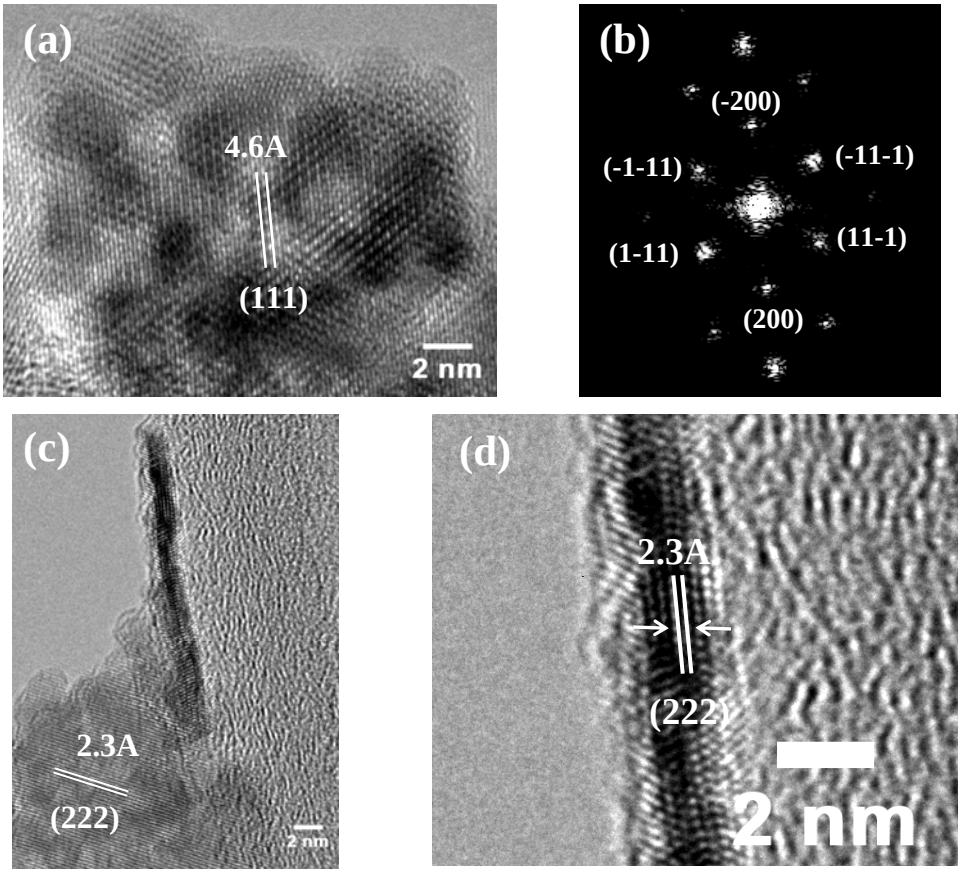

Fig. S4 HRTEM images of a sample prepared with 0.1M HMT and 0.02 M $Co(NO_3)_2 \cdot 6H_2O$

Fig. S4a shows a typical image of a individual particle prepared at 0.1M HMT and 0.02M $Co(NO_3)_2 \cdot 6H_2O$, the interlayer spacing is about 0.46 nm, which corresponds to the interlayer distance of the (111) crystal plane of cubic Co_3O_4. Fig. S4b shows a fast FFT of Fig. S4a and the diffraction points can be indexed to {111} and {200} planes. Fig. S4c shows a side-view of an individual nanosheet and a perpendicular view of another nanosheet. The particles are bigger at lower concentrations of the reactants, but the same ratio of HMT to $Co(NO_3)_2 \cdot 6H_2O$. The interlayer spacing of the perpendicular view particle is about 0.23 nm (Fig. S4c), which corresponds to the interlayer distance of the (222) crystal plane of cubic Co_3O_4. The interlayer spacing of the side-view particle is also about 0.23 nm (Fig. S4d), which is similar with the perpendicular view particle, corresponds to the interlayer distanceof the (222) crystal plane of cubic Co_3O_4. The nanosheets of this sample are about 2-3 nm thick in the<111> or <222> direction (see Fig.3b, 3d and Fig. S4d). Therefore, there is a large broadening of diffraction peaks (111) and (222) in Fig S2a.

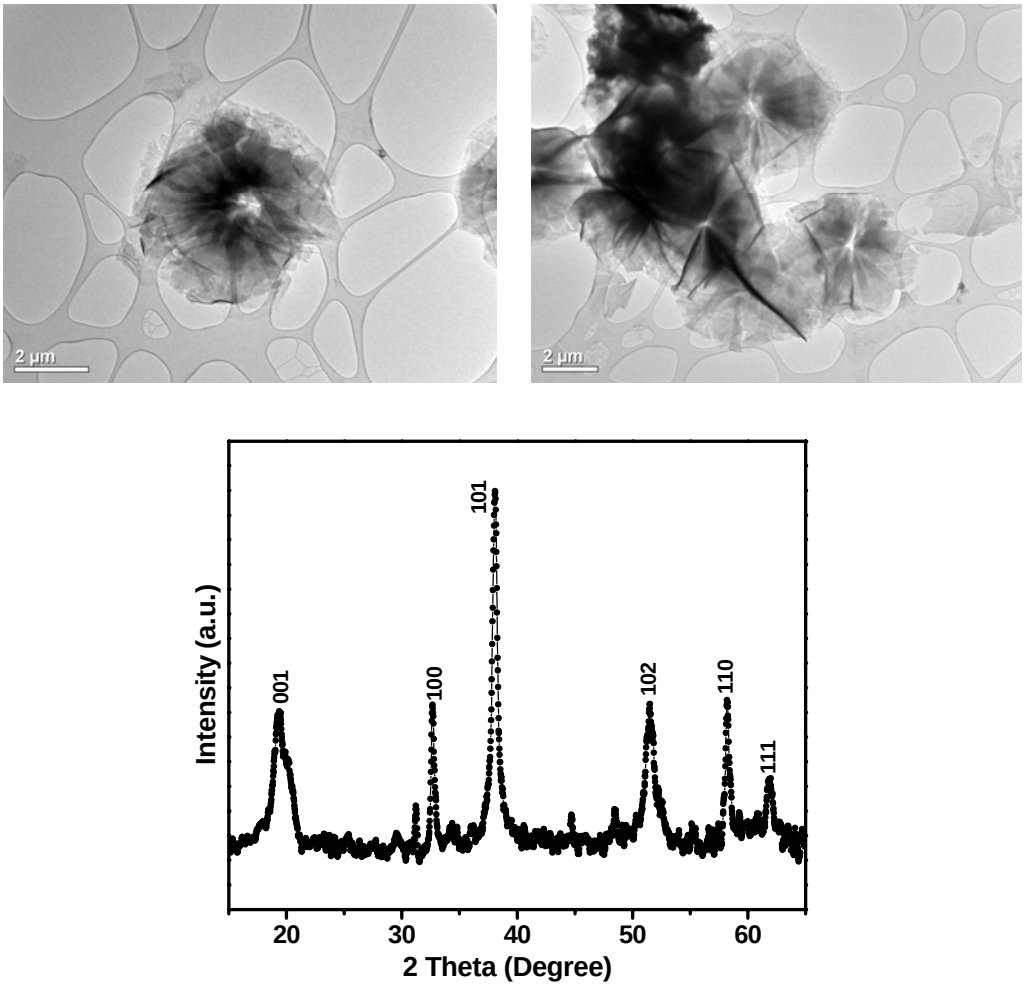

Fig. S5 TEM images and XRD pattern of $Co(OH)_2$ prepared with 0.5M HMT and 0.02M $Co(NO_3)_2 \cdot 6H_2O$ at 80 ^oC for 3 hours.

Fig. S5 shows the TEM images of $Co(OH)_2$ prepared with 0.5M HMT and 0.02M $Co(NO_3)_2 \cdot 6H_2O$ at 80^oC for 3 hours. The precipitate was composed of mainly pink particles mixed with a little amount of green particles. The particles are about 4-6 μm in size. XRD indicates the product were mostly composed of β-$Co(OH)_2$ (JCPDS card, No. 00-030-0443) with some impurities.