## Supplementary information for

## Systematic shape evolution of $Co_3O_4$ nanocrystals from octahedron to sphere under the influence of $C_2O_4^{2-}$ and PVP

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The hydrothermal treatment was also performed using 0.3 mmol of  $Na_2C_2O_4$  and 1.7 mmol of  $Co(NO_3)_2 \cdot 6H_2O$  at 220 °C without the addition of PVP. Fig. S1 shows the SEM images of the samples obtained at the reaction time of 1 h, 2 h, 4 h, 8 h, 16 h, 20 h and 24 h. Apparently, rod-like samples with larger size are obtained when the reaction time is lower than 4 h. With the increase of reaction time, the particle size decrease greatly and more octahedra can be obtained. And a large number of homogeneous and well-shaped octahedra can be obtained with the further prolongation of reaction time to 24 h.



**Fig. S1** SEM images of samples obtained at reaction time of (a) 1 h, (b) 2 h, (c) 4 h, (d) 8 h, (e) 16 h, (f) 20 h, (g) and (h) 24 h.



Fig. S2 XRD pattern of samples obtained at different reaction time without the addition of PVP.

Fig. S2 shows the XRD patterns of samples obtained at different reaction time without the addition of PVP. It can be seen that  $CoC_2O_4 \cdot 2H_2O$  is the sole composition of the sample obtained at the reaction of 1 h. And  $Co_3O_4$  appear after 2 h hydrothermal reaction. Moreover,  $CoC_2O_4 \cdot 2H_2O$  even disappear and only  $Co_3O_4$  is prepared with the reaction time longer than 4 h. This indicates that the transformation of  $CoC_2O_4 \cdot 2H_2O$  to  $Co_3O_4$  occur under the present hydrothermal conditions.



Fig. S3 The relationship between corner-truncated cube and globate polyhedron.

After careful examine the shape of corner-truncated cube and globate polyhedron, we found that the remaining edges of corner-truncated cube transform into small rectangle (as shown by the red circle), leading to the formation of "over-truncated cube" (Fig. S3d). As a result, more facets are exposed under the influence of PVP. Surprisingly, "over-truncated cube" could exhibit the shape of globate polyhedron via 3D rotation. Based on the above analysis, the formation of globate polyhedra and micro-spheres  $Co_3O_4$  particles exposing more facets might due to the further evolution of corner-truncated cube under high PVP concentration.