## **Electronic Supplementary Information**

## pH-controlled assembly of three-dimensional tungsten oxide hierarchical

## nanostructures for catalytic oxidation of cyclohexene to adipic acid

Lei Wang<sup>a,b</sup>, Mengqiu Huang<sup>a,b</sup>, Zhangxian Chen<sup>a,b,\*</sup>, Zeheng Yang<sup>a,b,\*</sup>, Maoqin Qiu<sup>a,b</sup>, Kai Wang<sup>a,b</sup>, Weixin Zhang<sup>a,b,\*</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei, China 230009. E-mail: wxzhang@hfut.edu.cn (W.X. Zhang)

<sup>b</sup> Anhui Key Laboratory of Controllable Chemical Reaction & Material Chemical Engineering, Hefei, China 230009



Fig. S1 FTIR spectra of the as-prepared (a) o-WO<sub>3</sub>·0.33H<sub>2</sub>O and (b) h-WO<sub>3</sub>.



Fig. S2 FESEM images of the synthesized WO<sub>3</sub>-2.0.



Fig. S3 FESEM images of the as-prepared WO<sub>3</sub>-2.5.



Fig. S4 (a, b) FESEM images and (c) TEM image of the as-prepared  $WO_3$ -1.0.



Fig. S5 Reaction scheme for the condensation of tungstate ions in aqueous solutions.



Fig. S6 As-synthesized products prepared at 30 min with the final pH of the mixed solution is 1.0.





Fig. S7 The SEM images and XRD pattern of the commercial WO<sub>3</sub>.



**Fig. S8** (a) FTIR, (b) <sup>1</sup>H NMR and (c) <sup>13</sup>C NMR spectra of the synthesized adipic acid. 1695 cm<sup>-1</sup>~v(C=O); 2500–3300 cm<sup>-1</sup>~overlap of v(CH<sub>2</sub>) and v(O-H); 1426 cm<sup>-1</sup>, 1411 cm<sup>-1</sup>, 1281 cm<sup>-1</sup>, 1197 cm<sup>-1</sup>~overlap of v(C-O), δ(O-H) and δ(CH<sub>2</sub>). **a** (12.02 ppm, –COOH); **b** (2.20 ppm, –CH<sub>2</sub>–COOH); **c** (1.49 ppm, –CH<sub>2</sub>–COOH). **d** (174.41 ppm, –COOH); **e** (33.52 ppm, –CH<sub>2</sub>–COOH); **f** (24.18 ppm, –CH<sub>2</sub>–COOH).



Fig. S9 Plausible pathway for the catalytic oxidation of cyclohexene to adipic acid.