Supporting Information

Synthesis of Hierarchical Rippled Bi_2O_3 Nanobelts for Supercapacitor Applications

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Experimental section

Synthesis: All chemical reagents were analar (AR) grade. The hierarchical rippled Bi_2O_3 nanobelts were electrodeposited in solution of 0.005 M $Bi(NO_3)_3$+0.05 M Na_2EDTA+0.1 M sucrose with current density of 4.0 mA/cm^2 for 60 min. The Ti plates (99.99%, 1.5 cm^2) were used as the substrate for electrodeposition, and they are prepared complying the following steps before each experiment: firstly polished by SiC abrasive paper from 300 to 800 grits, then dipped in HCl solution (5%) for 5 min and rinsed with acetone in ultrasonic bath for 5 min, and finally washed by distilled water. A simple three-electrode cell was used in our experiments. The graphite electrode was used as a counter electrode (spectral grade, 1.8 cm^2). The saturated calomel electrode (SCE)

was used as the reference electrode that was connected to the cell with a double salt bridge system. All potential values determined in this study were the values vs SCE. The electrodeposition experiments were carried out at room temperature by galvanostatic electrolysis.

Characterizations: The deposits were analyzed by X-ray diffraction (XRD, PIGAKU, D/MAX 2200 VPC) to determine the film structures. The surface morphologies of the deposited products were observed by thermal field emission environment scanning electron microscope (TFE-SEM, FEI, Quanta 400), transmission electron microscope (TEM, JEM- 2010HR), and high-resolution TEM (200 kV). The surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. Poresize distributions were calculated by the Barrett-Joyner-Halenda (BJH) method.

Electrochemical measurements: All electrochemical measurements were carried out in a three-electrode experimental setup. The obtained Bi_2O_3 thin films with thickness of about 0.356 μm on Ti substrate was used as the working electrode. Platinum foil with the same area as the working electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All the electrochemical measurements were carried out in 1.0 M Na_2SO_4 aqueous electrolyte by using a CHI 750A electrochemical workstation (CHI Instruments).

XRD pattern

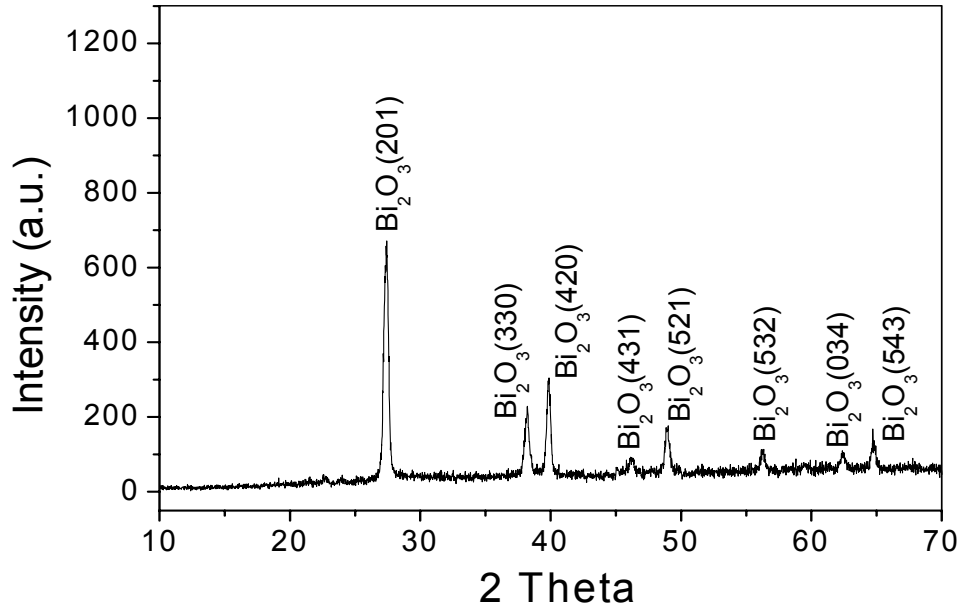


Figure S1. XRD pattern of hierarchical rippled Bi_2O_3 nanobelts.

EDS pattern

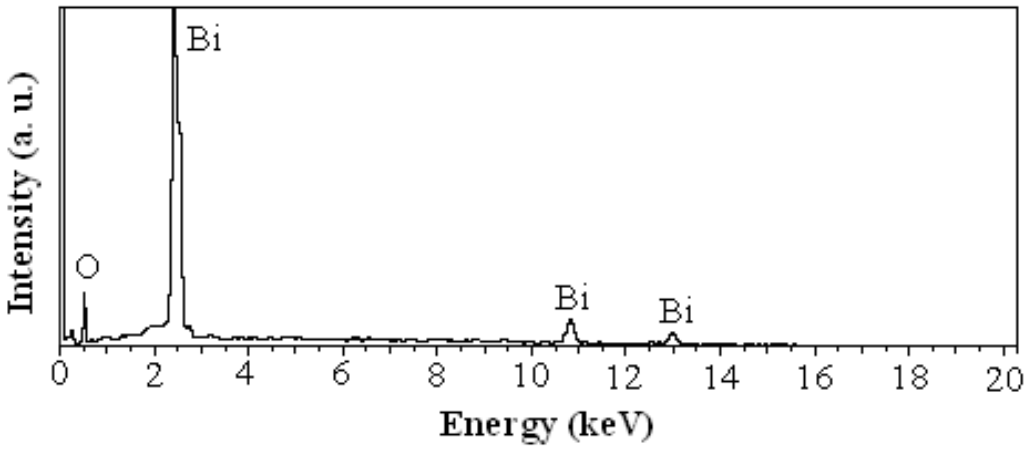


Figure S2. EDS pattern of with hierarchical rippled Bi_2O_3 nanobelts prepared in solution of 0.1 M sucrose+0.005 M $Bi(NO_3)_3$+0.05 M Na_2EDTA with current density of 4.0 mA/cm^2.

A typical EDS spectrum was shown in Figure S2, and the compositional analysis shows the stoichiometry Bi/O in the deposits is about 2/3, which proves that the nanobelt consists of pure Bi_2O_3.

SEM images of various Bi_2O_3 nanobelts electrodeposited with different current densities

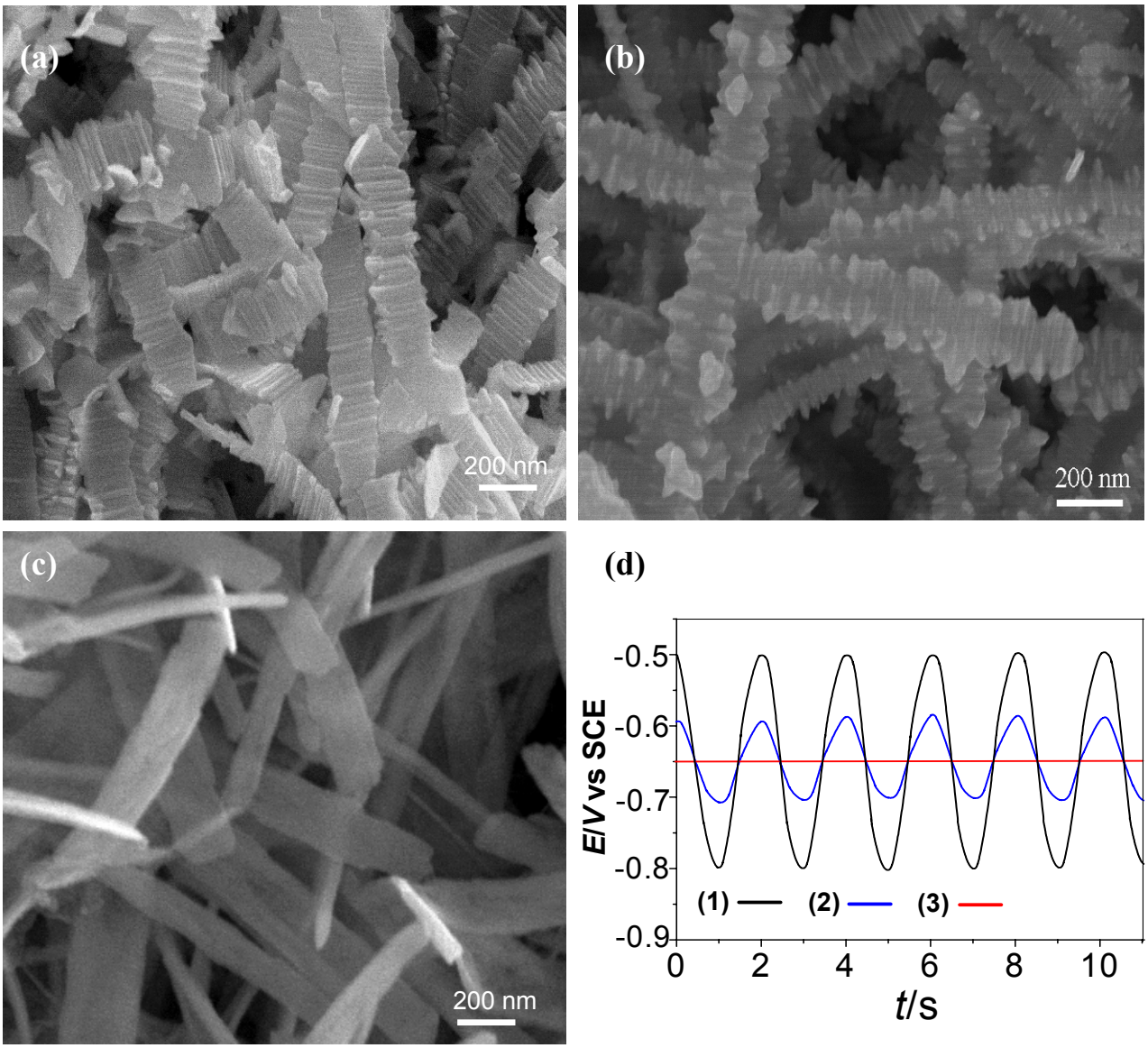


Figure S3. SEM images of various Bi_2O_3 nanobelts prepared in solution of 0.1 M sucrose+ 0.005 M $Bi(NO_3)_3$ +0.05 M Na_2EDTA with current density of (a) 4.0 mA/cm^2; (b) 2.0 mA/cm^2; and (c) 1.0 mA/cm^2. (d) The electrode potential oscillations at current density of (1) 4.0 mA/cm^2 (strong); (2) 2.0 mA/cm^2 (weak); and (3) 1.0 mA/cm^2 (no oscillation).

XPS spectra

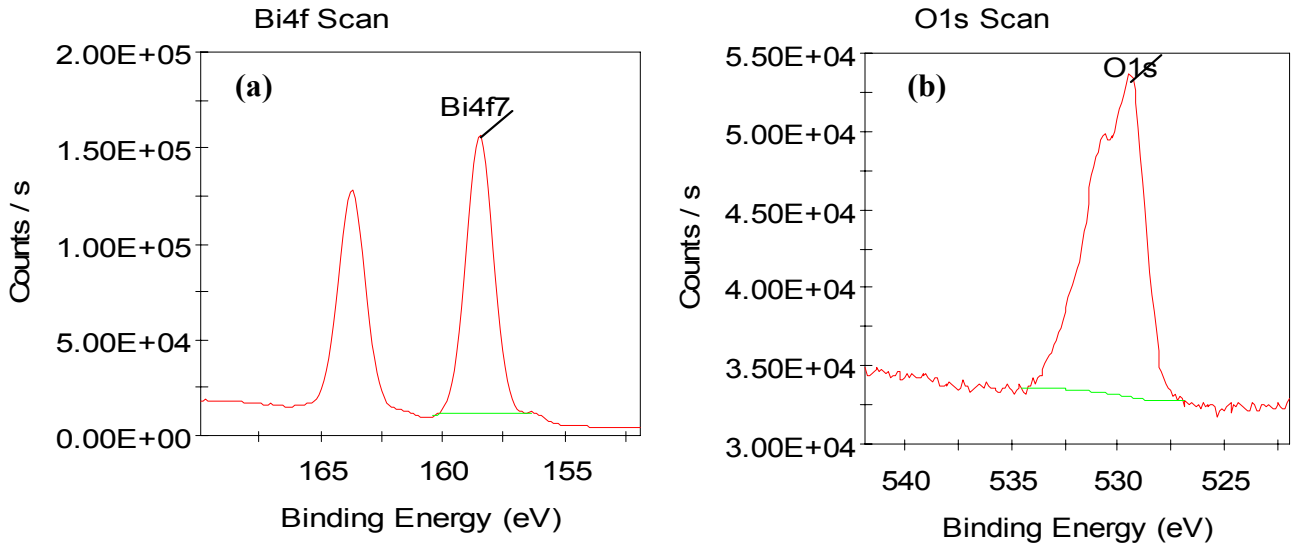


Figure S4. XPS spectra of (a) Overall , (b) Bi4f , and (c) O1s of the hierarchical rippled Bi_2O_3 nanobelts.

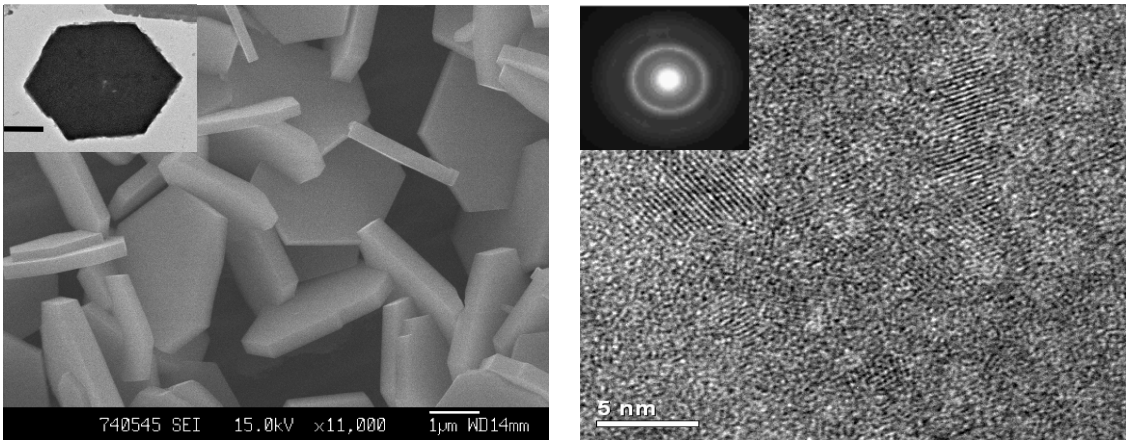
The illustration of the roles of Na_2EDTA and sucrose in the formation of Bi_2O_3 nanobelts with hierarchical rippled structures

In our experiment, when only Na_2EDTA was added into deposition solution, the prepared Bi_2O_3 products were consisted of hexagonal plates. Figure S5(a) shows the SEM and TEM images of Bi_2O_3 deposits prepared in solution of 0.005 M $Bi(NO_3)_3$+0.05 M Na_2EDTA with current density of 4.0 mA/cm^2, and it can be clearly observed Bi_2O_3 hexagons were prepared. The edges of the Bi_2O_3 hexagons are about 1.0 μm and thicknesses are approximately 200 nm. The HRTEM image shown in Figure S5(b) and the SAED pattern in the inset both showed that the deposited Bi_2O_3 hexagons were polycrystalline. However, the Bi_2O_3 nanobelts with hierarchical rippled surfaces can be successfully prepared when the sucrose was also added into deposition solution as shown in Figure S3(a) and (b). Therefore, it is reasonable to indicate that the growth of Bi_2O_3 nanobelts can be attributed to specific interactions between Bi_2O_3 nuclei and the sucrose. In the synthesis of nanomaterials, it is well known that some capping molecules can block the crystal growth of certain directions and enhance the crystal growth of other directions.[1-2] Herein, we believe that the capping effect of the sucrose plays a key role for the growth of Bi_2O_3 nanobelts with hierarchical rippled surfaces.

References

(1) Epifani, M.; Arbiol, J.; Diaz, R.; Peralvarez, M. J.; Siciliano, P.; Morante, J. R. *Chem. Mater.* **2005**, *17*, 6468-6472.

(2) Shevchenko, E. V.; Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *J. Am. Chem. Soc.* **2002**, *124*, 11480-11485.



(a) **(b)**

Figure S5. (a) SEM image and TEM (inset) of Bi_2O_3 hexagons prepared in solution of 0.005 M $Bi(NO_3)_3$+0.05 M Na_2EDTA with current density of 4.0 mA/cm^2 with different magnifications; (b) HRTEM image and SAED (inset). (The scan bar in TEM is 500 nm)

The charge/discharge curves of the rippled Bi_2O_3 nanobelts electrode with different current densities

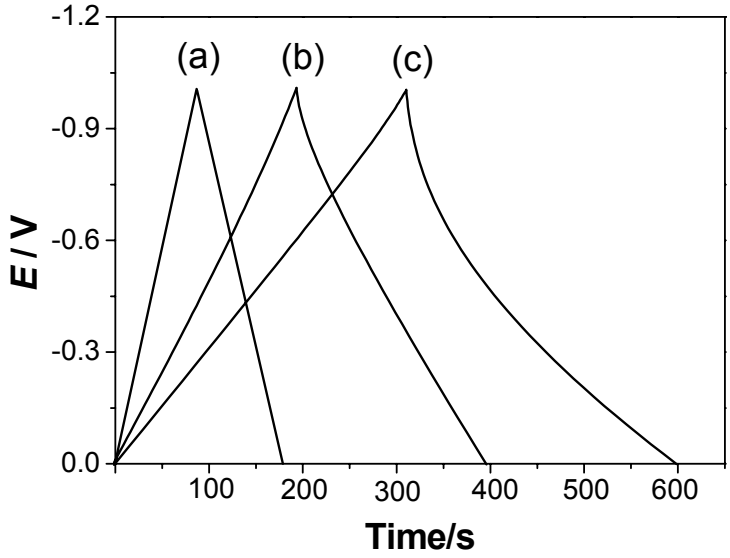


Figure S6. The charge/discharge curves of the rippled Bi_2O_3 nanobelt electrode in 1.0 M Na_2SO_4: (a) 2.0 mA/cm^2; (b) 1.5 mA/cm^2; (c) 1.0 mA/cm^2.

Calculation method for the specific capacitance (C_{sp}):

The specific capacitance (C_{sp}) is calculated by dividing the capacitance by the weight of Bi_2O_3 nanobelt electrode, namely:

$$C_{sp} = i/\upsilon w \qquad (1)$$

Where i, υ, and w are the average current (mA), the scan rate (mV/s), and the weight (g) of deposited Bi_2O_3, respectively.