

Supporting Information

Synthesis of mesoporous Co^{2+} doped TiO_2 nanodisks derived from metal organic frameworks with improved sodium storage performance

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EXPERIMENTAL SECTION

1. Materials synthesis

MIL-125(Ti)-Co was fabricated by a modified method for the synthesis of MIL-125(Ti) reported in previous literature.²⁸ Terephthalic acid (H_2BDC) (3 g) was dissolved into a solution containing dimethylformamide (DMF) (54 ml) and MeOH (6 ml) solution through stirring for 10 min. Tetra-n-butyl titanate $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (1.5 ml) was added into the above solution and was stirred for 15 min. Then, a certain amount of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (16 or 32 mg) was added and keep stirring for 10 min. The above solution was transferred to a 100 ml Teflon liner and heated at 150°C for 48 hours.

After reaction, the resultant suspension was filtered, washed with DMF and methanol. The resulting precipitate was collected by centrifugation, washed thoroughly with distilled water and ethanol, dried at 60 °C overnight. The samples were denoted as MIL-125(Ti)-16Co and MIL-125(Ti)-32Co, respectively. The as-prepared MIL-125(Ti) was synthesized through the same procedure without the addition of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Finally, TiO_2 and Co^{2+} doped TiO_2 with mesoporous structure were harvested by calcining of MIL-125(Ti) and MIL-125(Ti)-Co at 400 °C for 5 h under air condition, respectively. The corresponding samples were denoted as TiO_2 , TiO_2 -16Co and TiO_2 -32Co.

2.Characterizations of the samples

X-ray diffraction (XRD) patterns were obtained from the measurement on a Rigaku Ultima IV diffractometer, using Ni filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM, S8010 instrument) and transmission electron microscopy (TEM, FEI F20 S-TWIN instrument) were used for the characterization of morphology and structure of the samples. N_2 adsorption-desorption analysis was measured on a Micro-meritics TriStar II 3020 instrument (USA). Pore size distribution plots were obtained by the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum2000 XPS system with a monochromatic Al K α source and a charge neutralizer. The surface potential measurements were conducted by Kelvin probe atomic force microscopy (KPAFM) (Bruker Dimension Icon, Germany)

3. Electrochemical measurements

For the electrochemical measurement of Na-ion storage, the active material was admixed with super-P and polyvinylidene fluoride (PVDF) binder additive in a weight ratio of 70:15:15. The

mixture was pressed on copper foil circular flakes as working electrodes (WE), and dried at 120 °C in vacuum for 12 h. Na-ion cells were assembled in coin-type cells (CR 2025) with a Na metal foil as the negative electrode, glass fiber separator (Whatman GF/F), and 1 M NaClO₄ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1/1 in volume) as the electrolyte. The cells were fabricated in a glove box filled with highly pure argon gas (O₂ and H₂O levels < 1 ppm), and charge/discharge profiles were tested on a Land automatic batteries tester (Land CT 2001A, Wuhan, China). Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy (EIS) were performed on Zennium (Zahner).

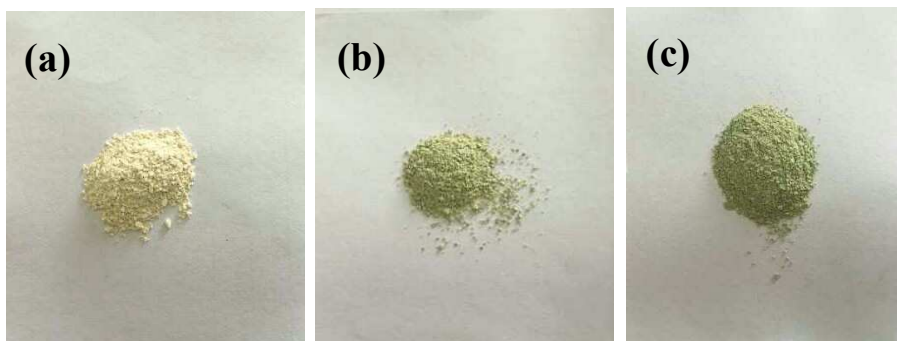


Figure S1. Photographs of (a) TiO₂, (b) TiO₂-16Co and (c) TiO₂-32Co.

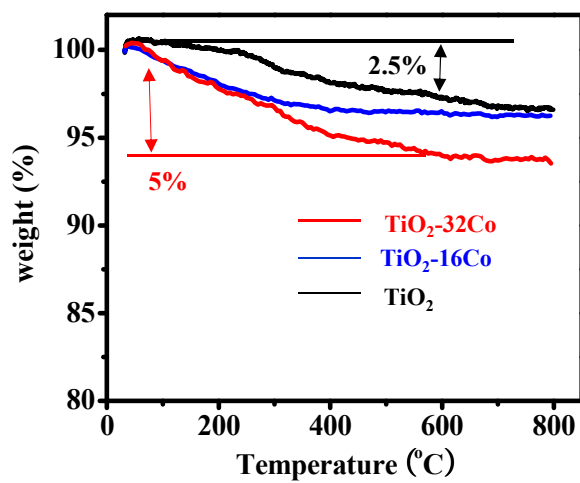


Figure S2. TG curves of TiO_2 , $\text{TiO}_2\text{-16Co}$ and (c) $\text{TiO}_2\text{-32Co}$.

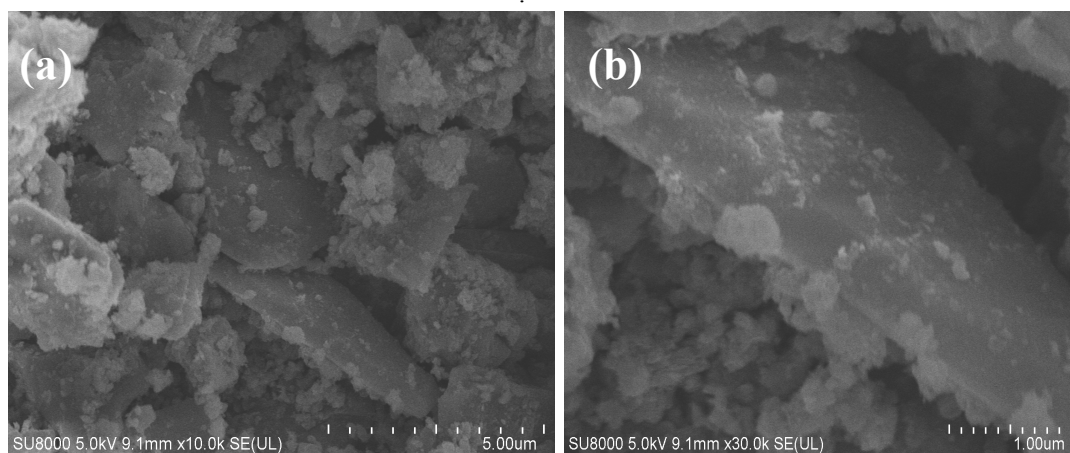


Figure S3. SEM (a, b) images of MIL-125(Ti)-64Co.

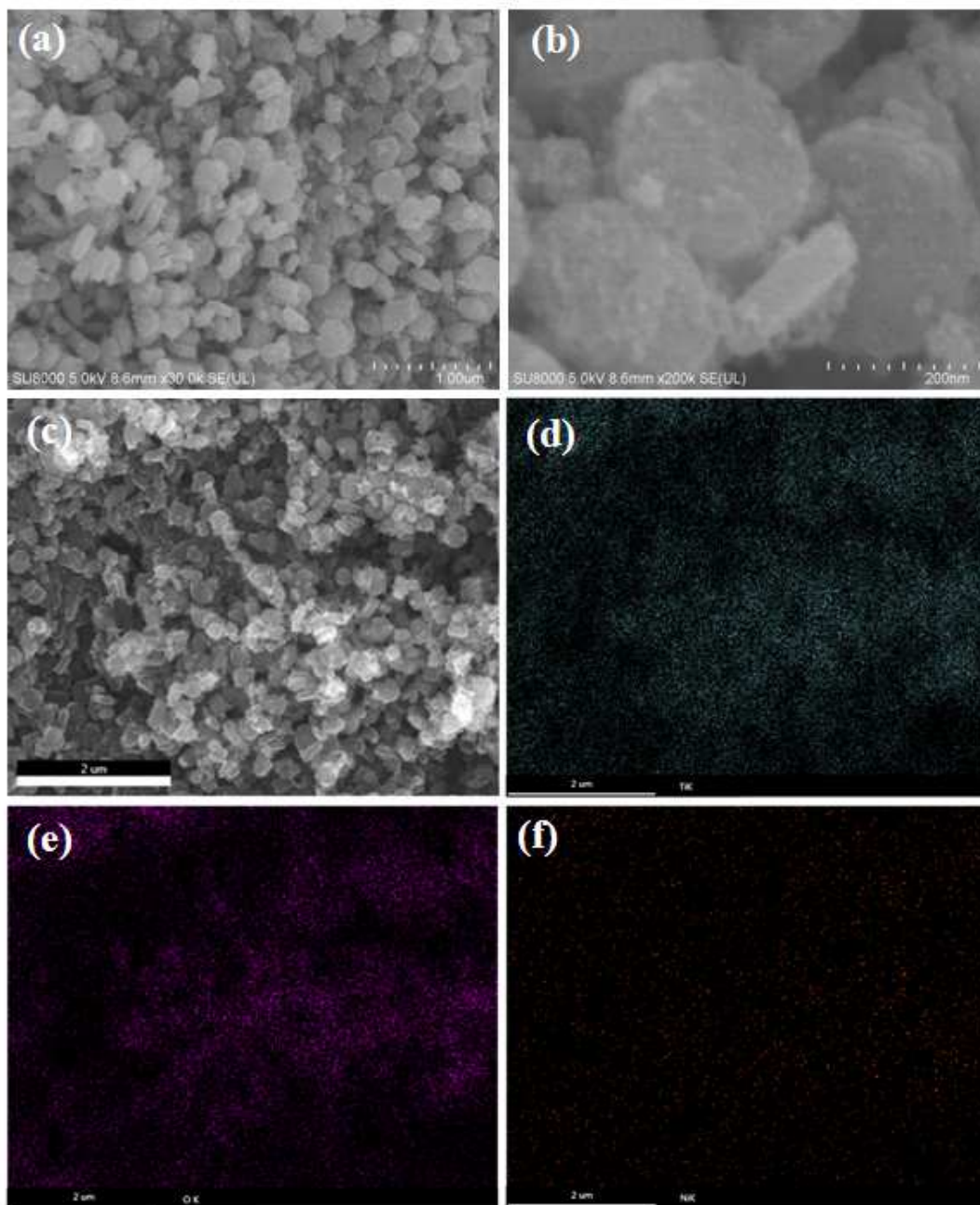


Figure S4. (a) and (b) SEM images of Ni^{2+} doping TiO_2 nanodisks, (c-f) corresponding EDX elemental mapping Ti, O and Ni.

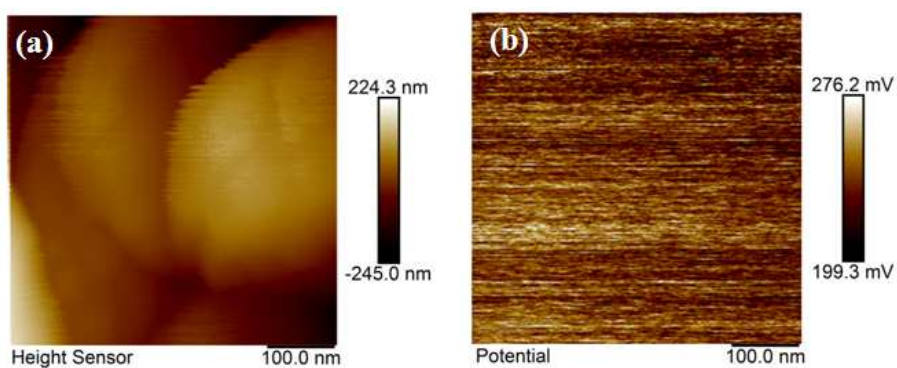


Figure S5. Topography (a) and (b) surface potential maps of $\text{TiO}_2\text{-16Co}$.

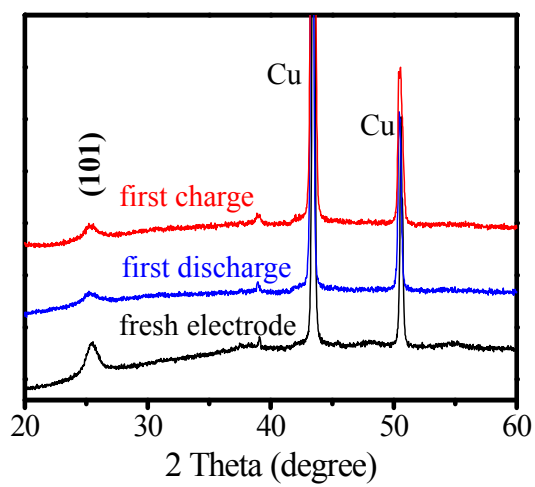


Figure S6. XRD patterns $\text{TiO}_2\text{-32Co}$ electrode at various states.