

## Electronic Supplementary Information

### Experimental section

#### Synthesis of Ni-btc MOFs

All chemicals were of analytical grade and used without further purification. In a typical procedure, 1.274 g nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), sucrose (1.2 g) and 0.512 g benzene-1,3,5-tricarboxylic acid ( $\text{C}_6\text{H}_3(\text{COOH})_3$ ) were dissolved in a 70 mL absolute methanol under stirring together for 1 h. And then the nickel nitrate alcohol solution was transferred into 100 mL Teflon cup. The autoclave was heated to 150 °C for needed time. The resulting green product was harvested by several rinse-precipitation cycles with methanol. Finally, the green powder of Ni-btc MOFs was dried in vacuum at room temperature at 60 °C for further characterization.

#### Synthesis of hierarchical yolk-shell NiO@C products

Certain amount of Ni-btc MOFs precursors were successively annealed in Air flowing at 450 °C for 2 h with a slow ramp rate of 1 °C  $\text{min}^{-1}$  to make yolk-shell NiO@C microspheres.

#### Characterization

X-ray diffraction (XRD) was carried out to identify the phase composition of synthesized samples over the  $2\theta$  range from 20° to 90° using a Rigaku D/max-A diffractometer with Co  $K\alpha$  radiation. A Fourier transform infrared spectroscope (FTIR, Thermo Nicolet 670FT-IR) was used for recording the FTIR spectra of the sample ranging from 400 to 4000  $\text{cm}^{-1}$ . Morphologies of the synthesized samples were observed with a AMRAY 1000B scanning electron microscope (SEM), and the microstructural characteristics of samples were observed by high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2010) working at 200 kV accelerating voltage and the lattice structure was identified by selected area electron diffraction (SAED) technique. Nitrogen adsorption-desorption measurements were conducted at 77 K on a Micromeritics Tristar apparatus. Specific surface areas were determined following the Brunauer-Emmet-Teller analysis.

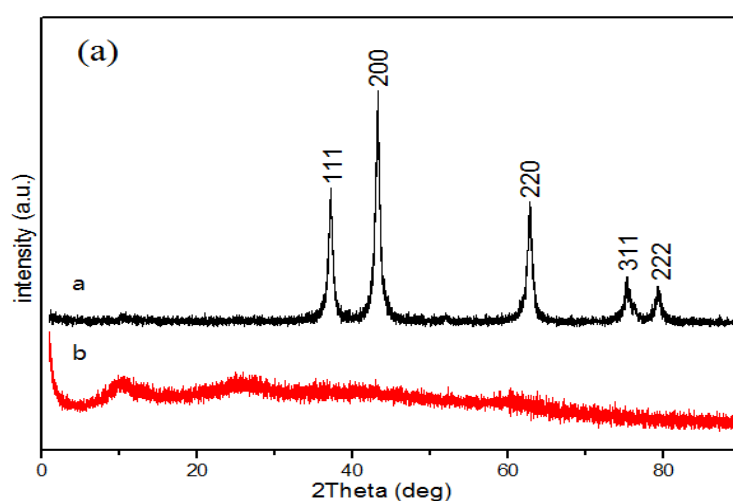
#### Electrochemical Measurements

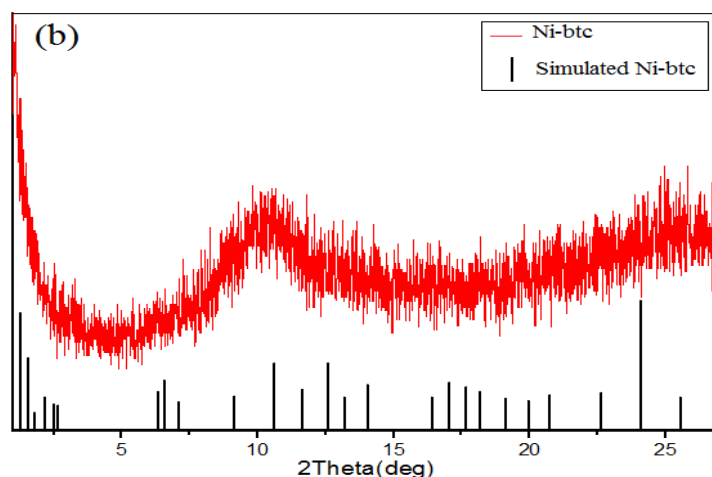
For electrochemical performance evaluation, half-cell studies were performed. In the experimental electrode, acetylene black powder and polyvinylidene fluoride (PVDF) were used as conductive additive and binder. The synthesized active materials were mixed with acetylene black and PVDF dissolved in N-methyl-pyrrolidinone in the weight ratio of 80:10:10 to form slurry, which was painted on a copper foil used as current collector.

After solvent evaporation, the electrode was pressed and dried at 120°C under vacuum for 48 h. The cells were assembled in argon filled glove-box. Metallic lithium foil was used as counter electrode. The electrolyte was 1M LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in vol. ratio). Cycling tests were carried out at the charge and discharge density of 1 C, 5 C, 10 C and 20 C, in the voltage range of 0.01-3.0 V versus Li/Li<sup>+</sup> by Land 2100A tester. Cyclic voltammetry was performed between 0.01 and 3.0 V with scan rate of 0.01 mVs<sup>-1</sup>.

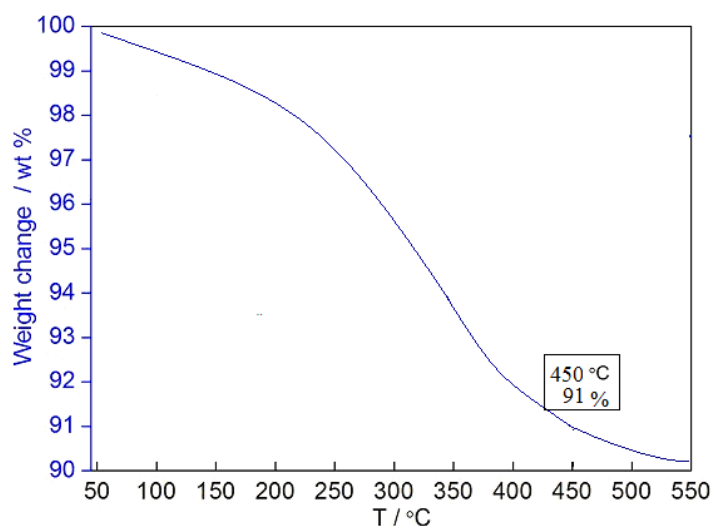
### The XRD, FTIR spectrum and TG analysis of the hierarchical yolk-shell structured NiO@C sample.

The crystallographic structure and phase purity of yolk-shell structured NiO@C sample and the NiO-C@MOF precursor were analyzed by XRD, as shown in Fig. S1a. All the diffraction peaks can be indexed to the monoclinic phase of copper oxide (JCPDS card no. 47-1049). No other impurity peaks are observed, indicating a complete thermal conversion of the MOF precursors into NiO nanostructures. Detailed analysis of the peak broadening of the (2 0 0) reflection of NiO using the Scherrer equation indicates an average crystallite size ca. 4 nm, suggesting that these particles are composed of nanocrystal subunits. Fig. s1b presents X-ray diffraction (XRD) patterns of the Ni–btc MOFs and their simulated results which reveal that the composition of the Ni-MOF precursors is Ni-btc (btc=benzene-1,3,5-tricarboxylate). All the diffraction peaks of the formed Ni–btc MOFs in the 2θ range of 1–27° are in agreement with the results. The relatively high background implies the co-existence of amorphous components 9% (wt.%) carbon is remained in the composite according to TG analysis, seeing supporting information (Fig. S2).





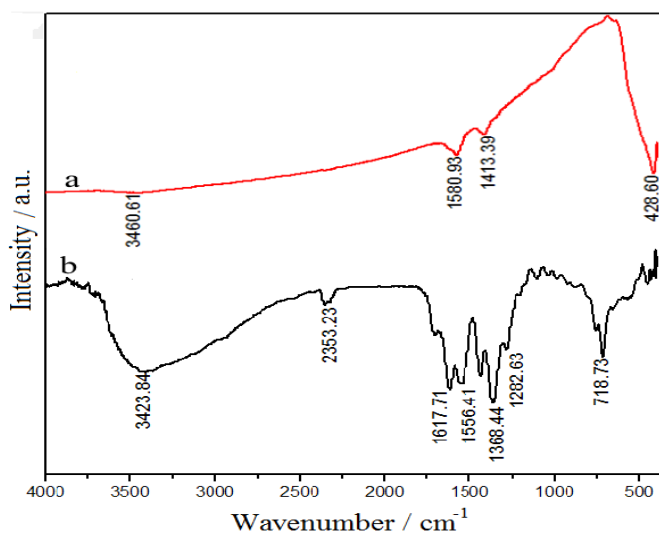
**Fig. S1** (a) XRD patterns of yolk-shell structured NiO@C sample and the NiO-C@MOF precursor corresponding to curve a and b, respectively. (b) XRD patterns of Ni-MOF in the 2 $\theta$  range of 1-27 $^{\circ}$ .



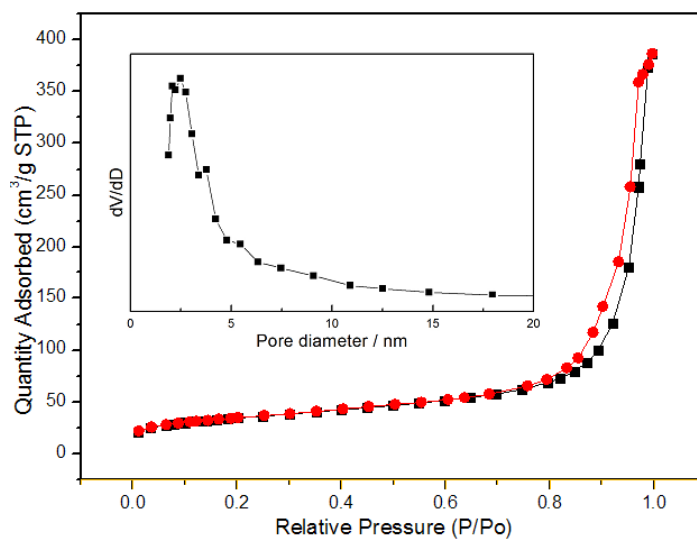
**Fig. S2** TG analysis of the carbon content of the prepared NiO@C sample after calcinations.

The FTIR spectrum analysis of the prepared yolk-shell structured NiO@C sample and its Ni-MOF precursor are listed in Fig. S3. The broad absorption peaks centered at ca. 3423 and 2350  $\text{cm}^{-1}$  are associated with the stretching vibrations of the -OH group of absorbed water molecules and absorption of  $\text{CO}_2$  in the air, and those peaks from 1617 to 1556  $\text{cm}^{-1}$  are assigned to the bending vibrations of the water molecules. For the precursor, the spikes from 1617 to 1282  $\text{cm}^{-1}$  are assigned to the asymmetric and symmetric stretching vibrations of the carbonyl group of btc. These peaks disappeared in the spectrum of synthesized NiO@C samples, indicating these groups have decomposed after calcinations. The strongest broad peaks in the range of 400-1000  $\text{cm}^{-1}$  are contribution from the face-centered cubic phase Ni-O. The peak intensity of Ni-O bond for NiO@C

products is different from that of precursor, implying the structure of prepared sample has some discrepancy with its precursor.



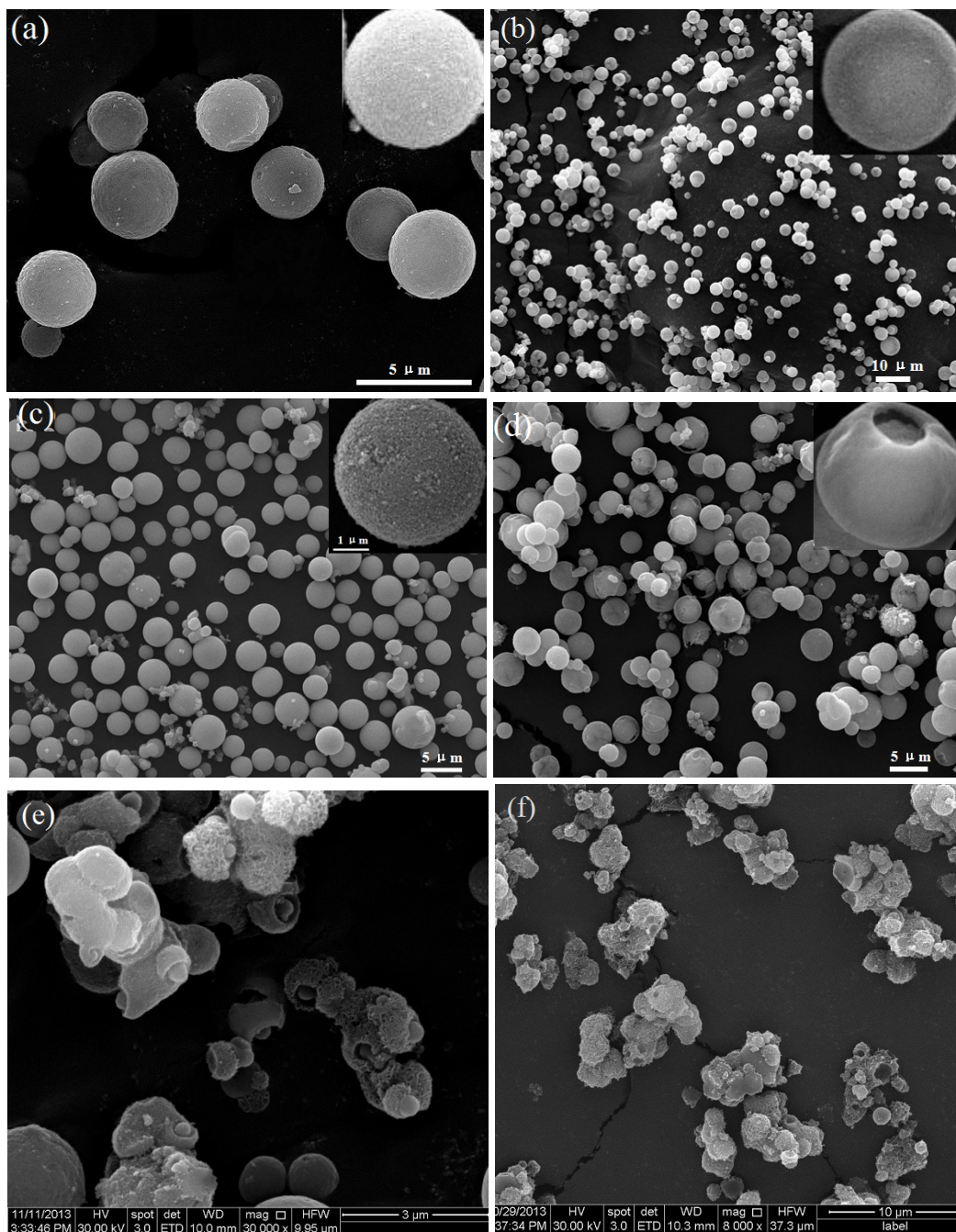
**Fig. S3** FTIR spectra of yolk-shell structured NiO@C sample and the NiO-C@MOF precursor corresponding to curve a and b, respectively.



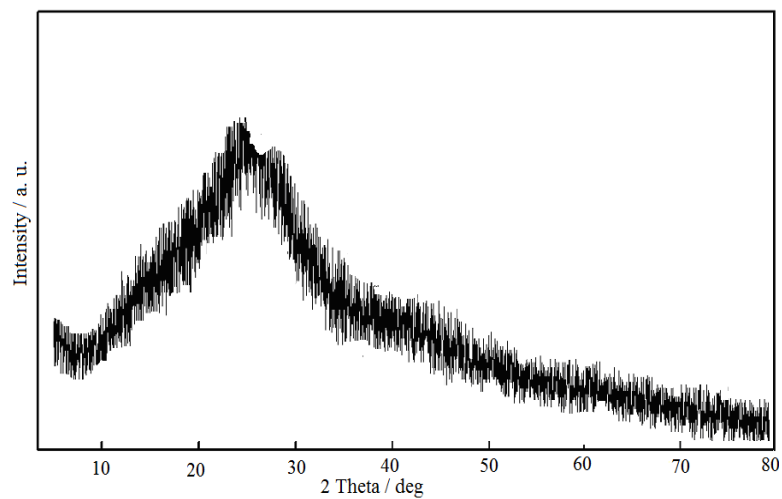
**Fig. S4** Nitrogen adsorption/desorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution plot (inset) of the prepared yolk-shell structured NiO@C products.

### **Synthesis of hierarchical yolk-shell NiO@C with controlled morphologies.**

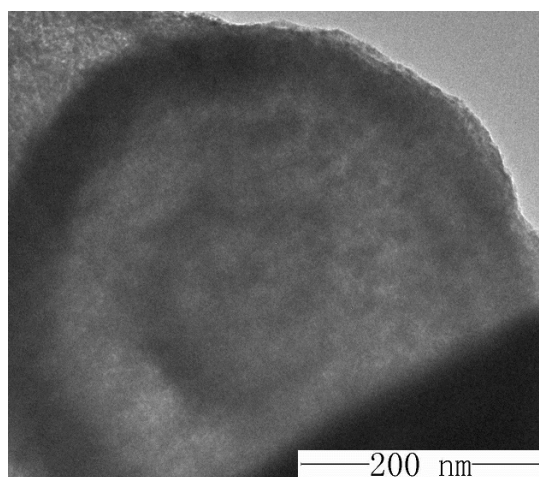
The formation mechanism is tracked to investigate according to Fig. S5, which is SEM images of solvothermal reaction at 150 °C for 2 h, 6 h, 12 h, 18 h, 30 h and 48 h and after calcination at 450 °C for 2 h. It is found that only solid NiO aggregates with a smooth surface exist in solution (Fig. S5a) after the solvothermal was conducted for 2h. When the reaction is conducted for 6 h, the surface of sample becomes a little coarse (Fig. S5b). Then its surface becomes more coarse with the increase of reaction time (Fig. S5c, 12 h). It is significant noticed that the coarse solid spheres transformed into hollow core-shell ones while the time arrived at 18 h (Fig. S5d). Further prolonging the reaction time, the interior of the sphere changed empty gradually (Fig. S5e, 30 h). Finally, the hollow core-shell structure are broken wholly (Fig. S5f, 48 h). According to above experiments, it can be speculated that the formation of the unique yolk-shell NiO@C hybrid nanoparticle aggregates go through the formation of solid core and the transformation of the solid spheres to hollow ones is based on the Ostwald ripening process, and which process was promoted by the water during the solvothermal process. To confirm the component of the resulting samples, HCl was used to remove the NiO at 70 °C and gave rise to carbon according XRD (Fig. S6) and TEM (Fig. S7), which confirms the amorphous carbon is well-proportioned loaded with NiO nanoparticles. So the hollow structure nanoparticle forms uniformly. The formation mechanism of hollow NiO@C composite can be revealed as Scheme 1. The water promoted the hydrolysis of Ni<sup>2+</sup> to form NiO, which are loaded the amorphous carbon resulted from carbonization of organics uniformly and formed NiO@C hybrid nanoparticles. These particles quickly aggregated to form solid spheres because of the high surface energy under solothermal conditions at 150 °C. Because a certain amount of water existed in the system, the surface nanoparticles exhibited relative higher crystallinity, which was at the shell of the spheres. Then, with the increase of water, the dissolution of the less crystallized inner particles and the recrystallization on the spheres' shell were carried out. And thus yolk-shell NiO@C-MOFs was formed. This process is in good agreement with our previous report. After calcinations in air flowing at 450 °C for 2 h, the organics of Ni-btc MOFs is removed and thus forms net frame hierarchical structure in the surface of the core-shell structure.



**Fig. S5** SEM images of yolk-shell structured NiO@C samples after solvothermal alcoholysis at 150 °C for 2 h (a), 6 h (b), 12 h (c), 18 h (d), 30 h (e) and 48 h (f) and after calcination at 450 °C for 2h.



**Fig. S6** XRD of the resulting graphitized carbon after HCl is used to remove the NiO.



**Fig. S7** TEM image of the resulting graphitized carbon after HCl is used to remove the NiO.