Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Flexible all solid state supercapacitor with high energy density employing black titania nanoparticles as conducive agent

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Preparation of 3D graphene. Ni foams were used to catalyze the graphene growth. Firstly, Ni foams were immersed in a dilute solution of acetic acid for 30 min to remove the oxide layer on their surface, then washed in isopropanol and acetone for 10 min, respectively, and finally rinsed with deionized water and dried for use. Secondly, the Ni foams were heated to 1000 °C in 40 min under H_2 (200 sccm), then a gas mixture flow of CH_4, H_2 and Ar was introduced to initiate graphene growth for 10–30 min. After growth, the samples were rapidly cooled to 500 °C at a rate of 200 °C min^{-1} under Ar and H_2. The Ni foams covered with graphene were drop-coated with a poly(methyl methacrylate) (PMMA) solution (4% in anisole), and then baked at 100 °C for 2 h. The PMMA/graphene/Ni foam structure was obtained after solidification. Then the samples were put into a 5 M HCl solution for 5 h to completely dissolve the Ni foams to obtain the PMMA/graphene. Finally three dimensional graphene networks were obtained after removing PMMA in acetone.

Preparation of mesoporous graphene. 0.61 g of phenol was melted at 40-42 °C in a flask and mixed with 0.13 g of 20 wt% sodium hydroxide (NaOH) aqueous solution under stirring. After 10 min, 1.05 g of formalin (37 wt% formaldehyde) was added dropwise below 50 °C. Upon further stirring for 1 h at 70-75 °C, the mixture was cooled to room temperature. The pH was adjusted with 0.6 M HCl solution until it reached a value of 7.0, and water was removed by vacuum evaporation below 50 °C. The final product was dissolved in ethanol. In a typical preparation of the sol of mesoporous carbon precursor, 1.0 g of F127 was dissolved in 20.0 g of ethanol. Then 5.0 g of resol precursors in ethanol solution containing 0.61 g of phenol and 0.39 g of formaldehyde was added. After stirring for 10 min, a homogeneous solution was obtained. The previous fabricated 3D-graphene (1 cm × 1 cm) was then dipped into the sol, and removed immediately. the product was transferred into dishes to evaporate ethanol at room temperature for 5-8 h, followed by heating in an oven at 100 °C for 24 h. Calcination was carried out in a tubular furnace under an Ar atmosphere at 350 °C for 3 h, and the heating rate was 1 °C min^{-1} .

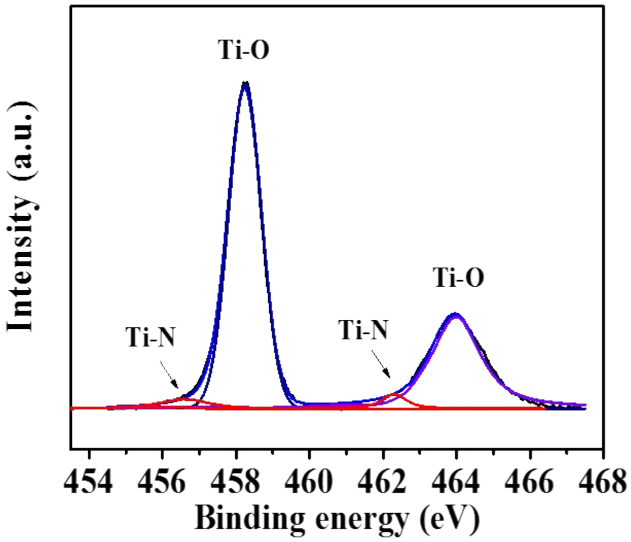

Figure S1: Ti 2P XPS spectra of TiO_{2-x}:N.

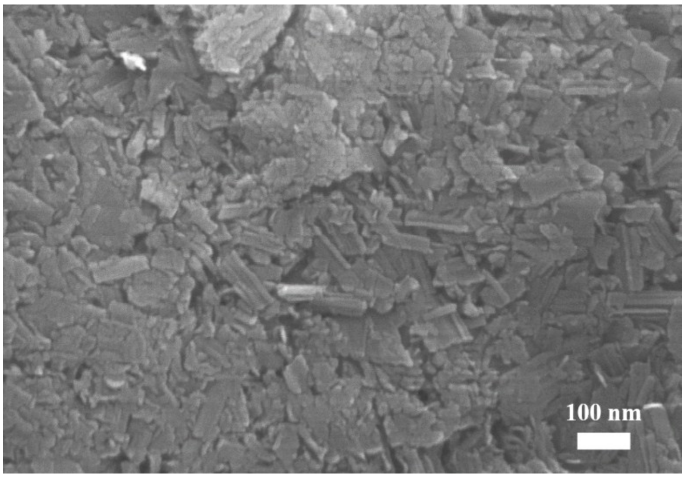

Figure S2: SEM image of NiO calcined at 450°C.

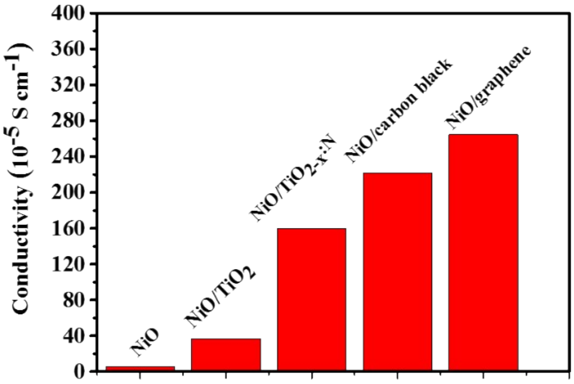

Figure S3: Comparison of the electrical conductivities of NiO, NiO/TiO$_2$, NiO/TiO$_{2-x}$:N NiO/carbon black and NiO/graphene samples.

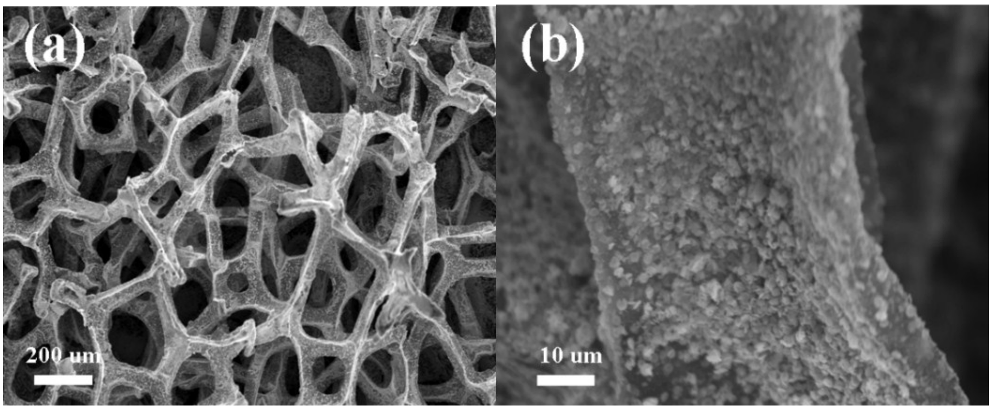

Figure S4. SEM (a) and high resolution SEM (b) of NiO/TiO$_{2-x}$:N coated on 3D graphene foam

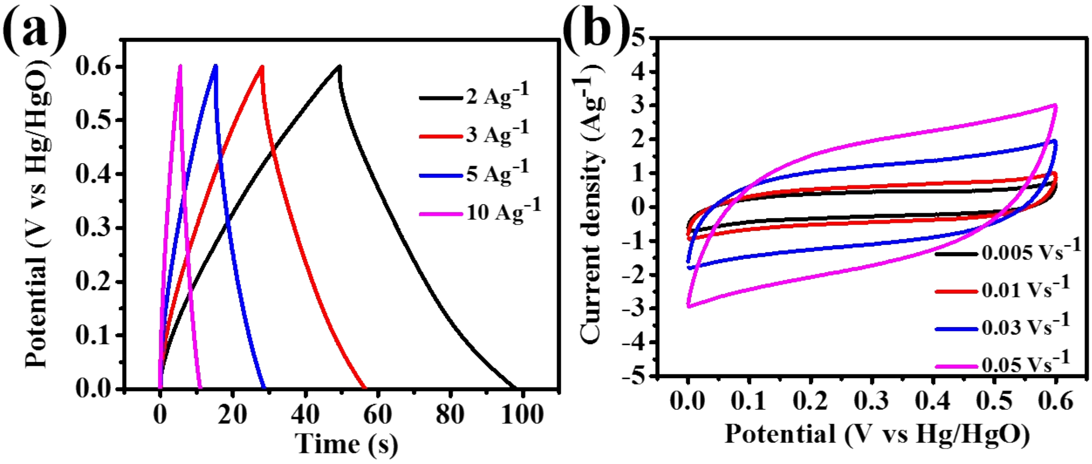

Figure S5. (a) charge-discharge curves of TiO$_{2-x}$:N at different current densities. (b) CV curves of TiO$_{2-x}$:N at different scan rates.

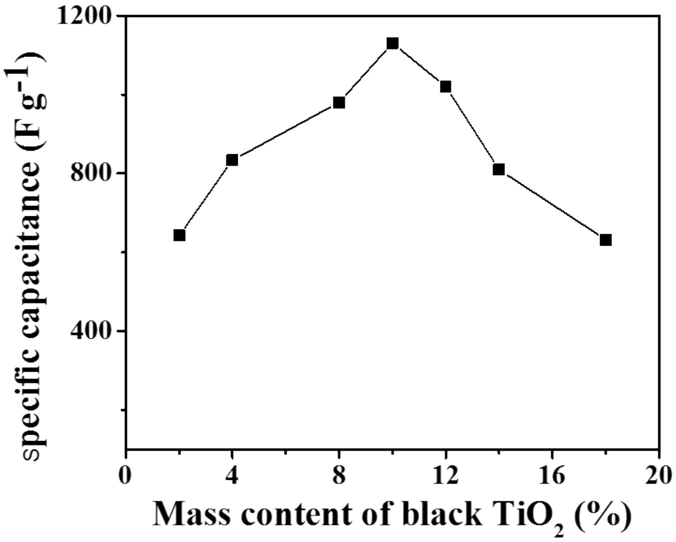

Figure S6. Specific capacitance of NiO/TiO_{2-x}:N originated from the CV curves of 0.05 V s^{-1} as a function of mass content of TiO_{2-x}:N.

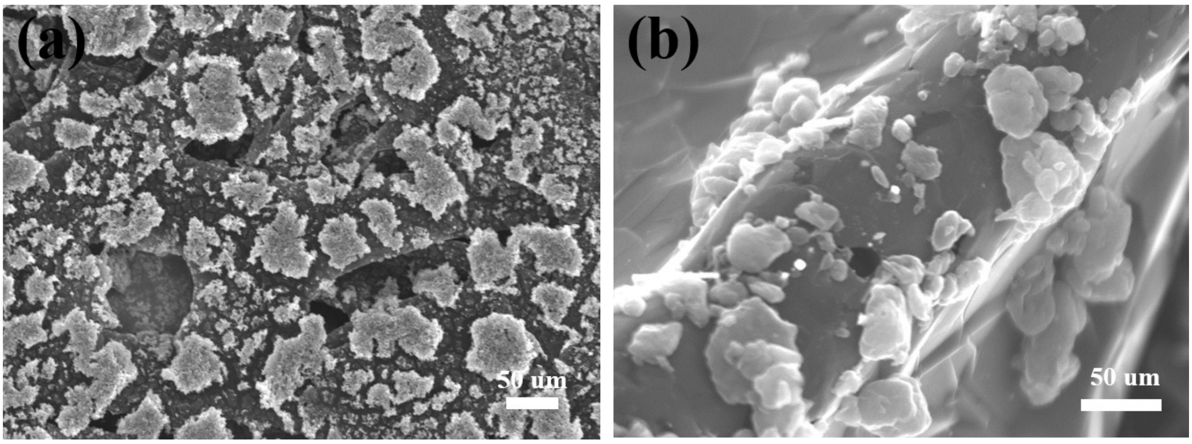

Figure S7. SEM image of NiO/carbon black (a) and NiO/graphene composites (b) supported on 3D graphene.

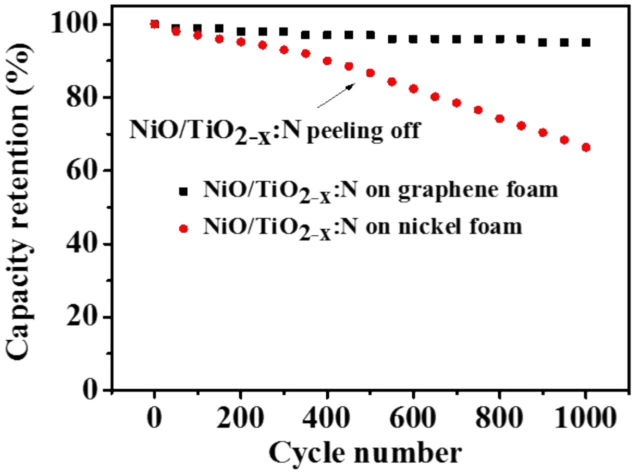

Figure S8. Cycle performance of NiO/TiO$_{2-x}$:N on different current collectors at a scan rate of 0.2V s^{-1}.

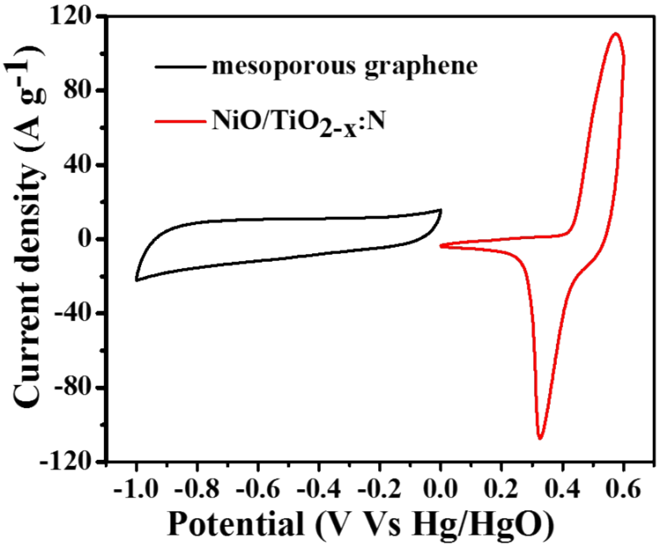

Figure S9: CV curves of NiO/TiO$_{2-x}$:N and TiO$_{2-x}$:N electrodes performed in a three-electrode cell in a 6 M KOH solution with a Hg/HgO reference electrode at a scan rate of 0.05V s^{-1}

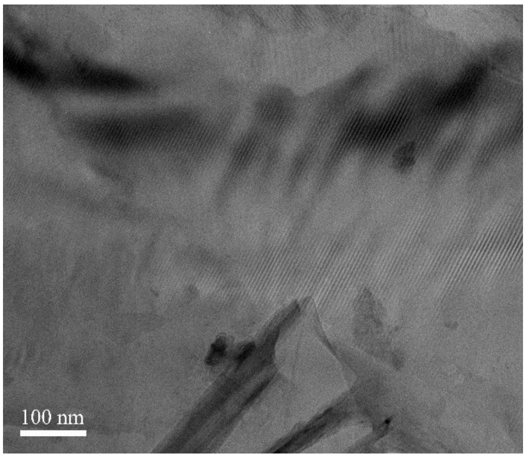

Figure S10: TEM image of mesoporous graphene

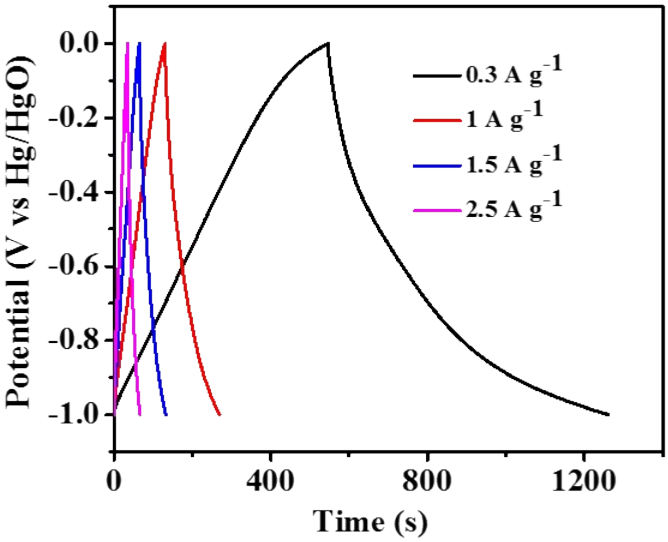

Figure S11: galvanostatic charge-discharge measurements of mesoporous graphene at various charge-discharge current densities.

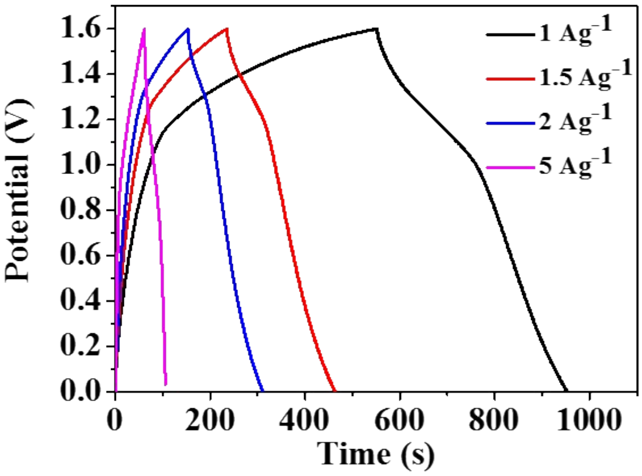

Figure S12: galvanostatic charge-discharge measurements of NiO/TiO_{2-x}:N//mesoporous graphene at various charge-discharge current densities.

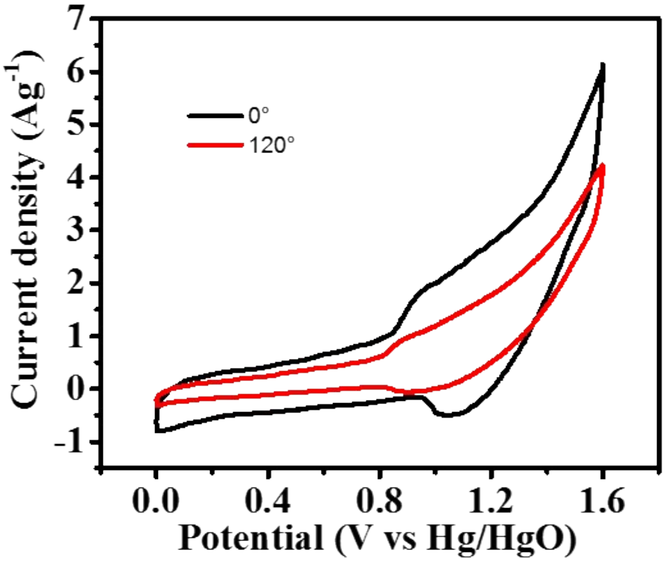

Figure S13: CV curves of NiO/carbon black//mesoporous graphene at different bending angles at the scan rate of 0.2 Vs^{-1}.