Electronic Supplementary Material (ESI) for ChemComm.

# Support information

## Experimental section

Synthesis of G@$TiO_2$ composites: 0.97 g nanosized $TiO_2$ was mixed with 0.03 g graphene and then the mixture was subjected to milling for 30 min to obtain G@$TiO_2$ composites.

Synthesis of NC@$TiO_2$ composites: Firstly, 1.08 g 2-amino benzene dicarboxylic acid and 0.52 ml tetrabutyl titanate were placed in a polytetrafluoroethylene container, and 18 ml N,N-dimethylformamide (DMF) was added, followed by 2 ml methanol. After continuous magnetic stirring for 30 min, the resulting mixture was sealed in 100 ml stainless steel autoclave and annealed at 150 $^oC$ for 72 h in a convection oven. Then the obtained products were separated via centrifugation and rinsed with DMF and methanol thoroughly, and dried in an oven at 100 $^oC$. Finally, the synthesized powders was placed in the center of a quartz tube and heated under argon atmosphere for 4 h at 600 $^oC$ to obtain NC@$TiO_2$ composites.

Synthesis of G-NC@$TiO_2$ composites: First, 1 g graphene-oxide was dissolved in a 20 ml mixture of DMF/methanol (9:1, v/v) and sonicated for 1 h. Second, 1.08 g 2-amino benzene dicarboxylic acid and 0.52 ml tetrabutyl titanate were added into the resulting mixed solution followed by magnetic stirring for 30 min. Third, the above-obtained mixture was transferred to a 100 mL Teflon-lined autoclave and annealed in an oven at 150 $^oC$ for 72 h. After cooling to room temperature, a brown powder product was recovered by filtration and washed with DMF/methanol, then dried at 100 $^oC$ for 12 h. Subsequently, the as-prepared products were annealed at 600 $^oC$ for 4 h under argon protection to obtain G-NC@$TiO_2$ composites.

Material characterizations: the crystallographic phases of the as-synthesised products was studied by X-ray diffraction (XRD using a Rigaku Dmaxrc diffractometer ). A JEOL JEM-2100 TEM was used to further investigate the microstructure of the obtained composites. The morphology of samples was characterized using a scanning electron microscope (SEM, Zeiss SUPRA 55). Thermogravimetric analysis (TGA) was conducted by a Mettler-Toledo TGA/SDTA851e Thermo Analyzer from room temperature to 800 $^oC$ in air. Micromeritics Automatic Surface Area Analyzer Gemini was employed to determine the BET surface areas of the products. Pore size distribution plot was calculated using Barrett-Joyner-Halenda (t-plot) method. X-ray photoelectron spectroscopy (XPS) was performed by ESCALAB 250Xi using a monochromatic Al K$\alpha$ radiation. Raman spectra were tested by a Horiba Jobin-YVON co-focal laser Raman system using He-Ne 632 nm laser as the excitation source.

Electrochemical characterization: In order to investigate the electrochemical performance of G-NC@$TiO_2$ composite, 2016-coin type cells were assembled in an Ar-filled glove box with a water and oxygen content below 0.1 ppm. The active material G-NC@$TiO_2$, carbon black and polyvinylidene fluoride were mixed with a weight ratio of 8:1:1. Then the obtained mixture was dissolved into 2 ml N-methyl-2-pyrrolidone (NMP), followed by stirred for 8h. Finally, the slurry was coated on the Cu-foil current collector and dried in a vacuum oven. The

NC@$TiO_2$ and G@$TiO_2$ electrode were also prepared using the same method. 1 M $NaClO_4$ dissolved in ethylene carbonate and dimethyl carbonate (1:1 by volume) were used as electrolyte. The galvanostatic charge/discharge tests were conducted under various rates within the voltage range of 0.05-2.5 V (vs Na/$Na^+$). The specific capacity was calculated based on the weight of titanium dioxide. The electrochemical impedance spectroscopy (EIS) measurement was performed on an electrochemical workstation (CHI 660E, Shanghai China) at a frequency range of 0.01 Hz-1M Hz.

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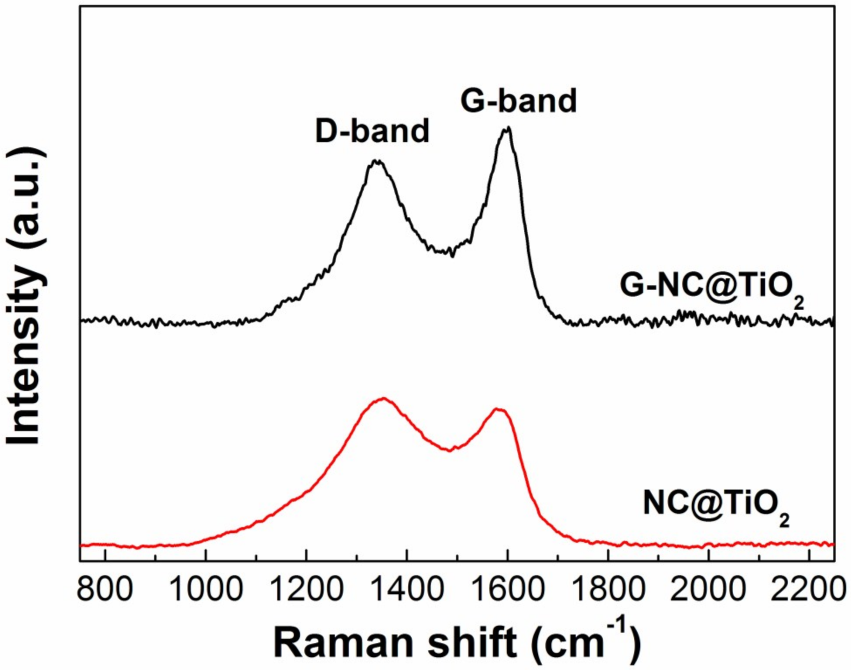

Fig. S1 Raman spectra of G-NC@$TiO_2$ composite and NC@$TiO_2$ composite

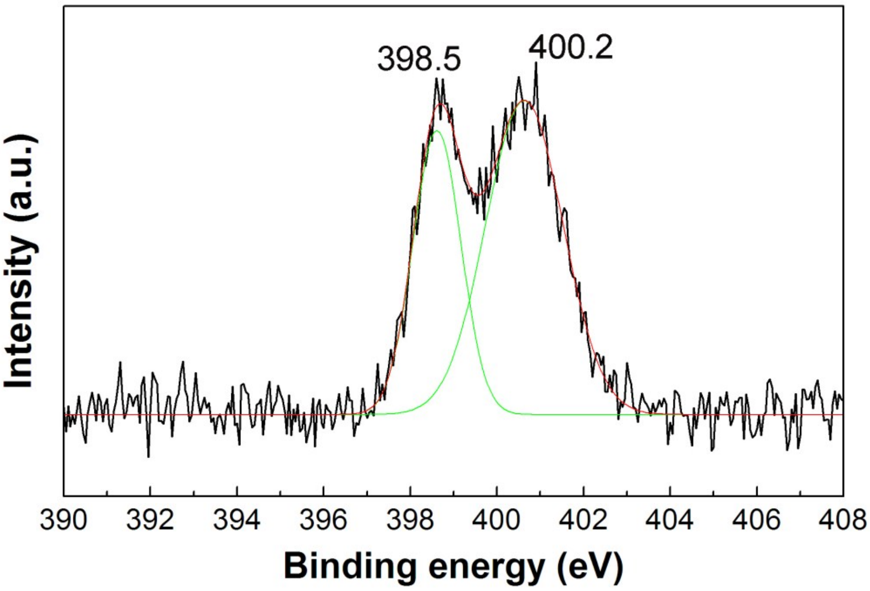

Fig. S2 N 1s core level XPS spectra of G-NC@$TiO_2$ composite

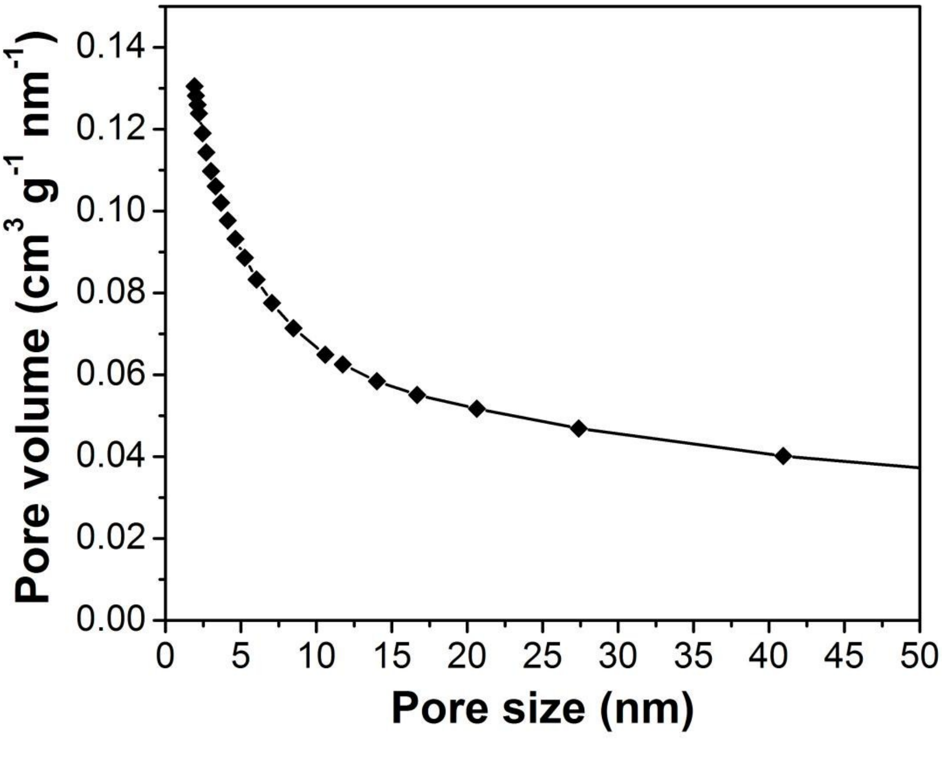

Fig. S3 the pore size distribution of G-NC@$TiO_2$ composite

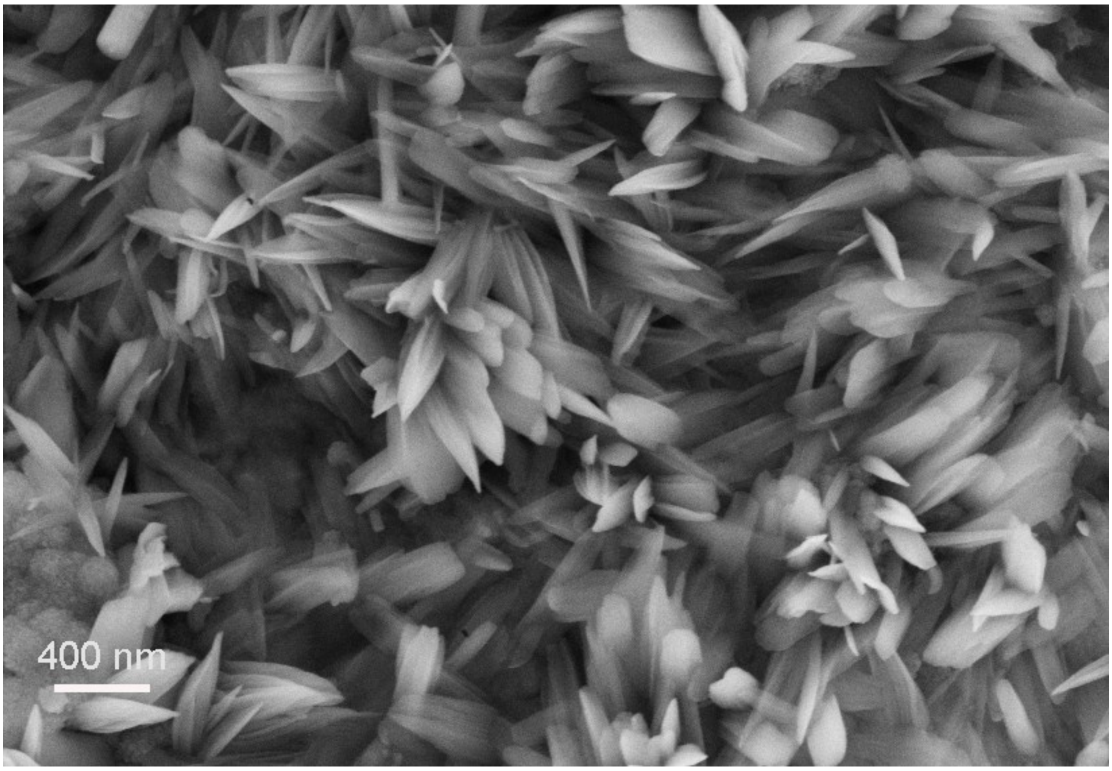

Fig. S4 SEM image of G-NC@$TiO_2$ composite

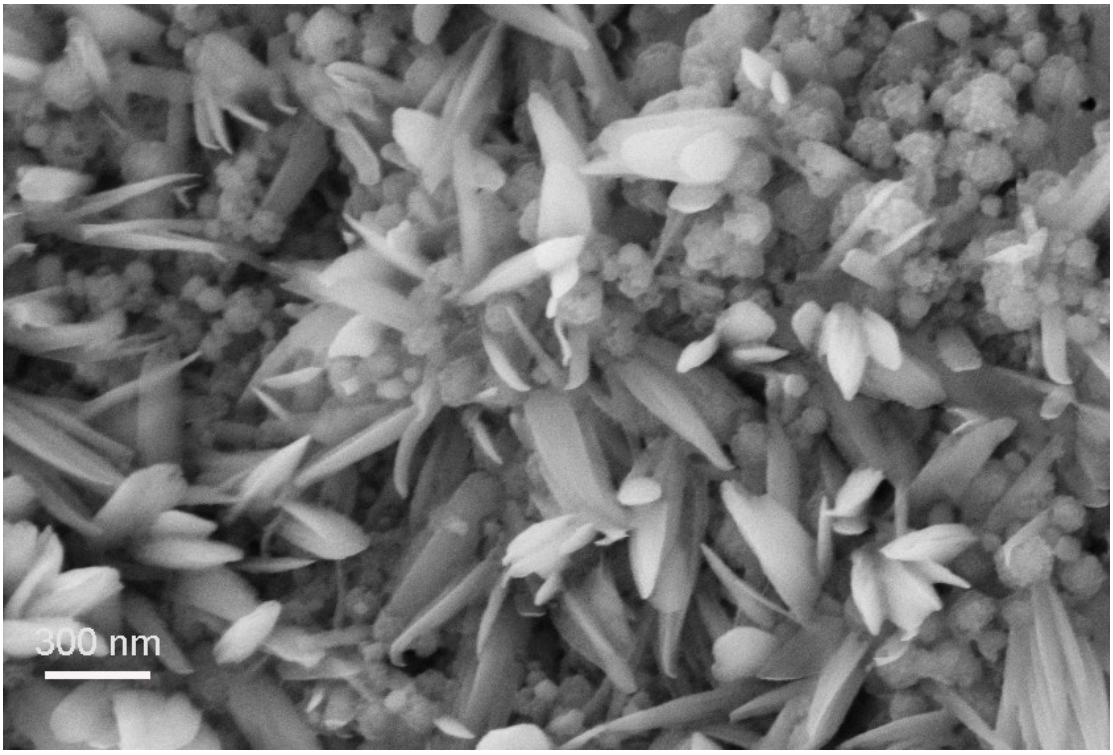

Fig. S5 SEM image of G-NC@$TiO_2$ electrode after 5000 cycles

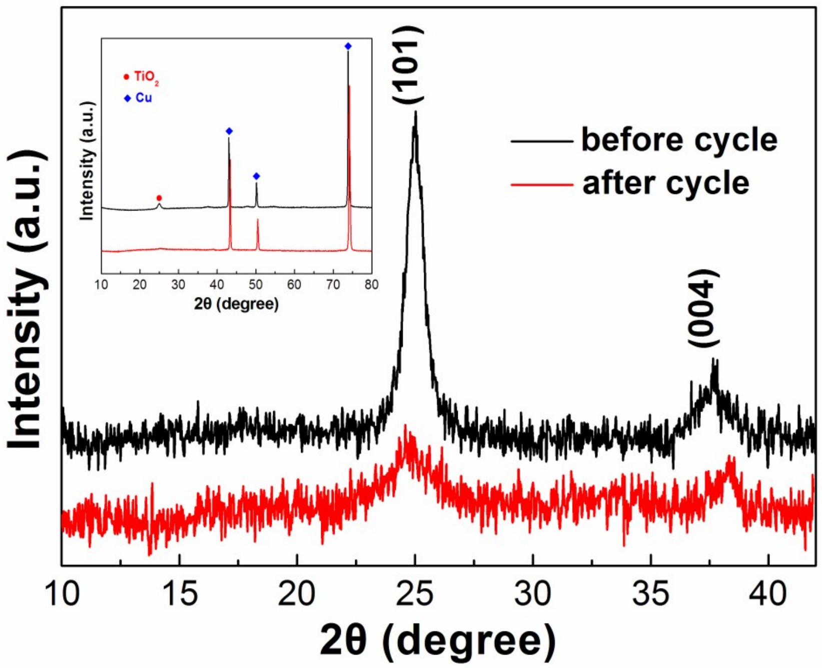

Fig. S6 XRD patterns of G-NC@$TiO_2$ electrode before and after 5000 cycles