

Novel Composites of Graphitic C₃N₄ and NiO Nanosheet Arrays as an Effective Photocathode with Enhanced Photocurrent Performances

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1. Experimental Section:

Preparation of NiO/GCNS

All reagents were analytical grade and used without further purification.

Synthesis of NiO electrode: The Ni-based nanosheets precursor was prepared using a modified method which was reported by previous literature.¹ In a typical run, 4 mmol nickel acetate and 8 mmol hexamethylenetetramine (HMT) were dissolved in 35 mL of distilled water under vigorous stirring for 30 min to form a transparent solution. In the meantime, a piece of FTO glass (1 cm × 4 cm) was cleaned ultrasonically with acetone, ethanol and distilled water. Then the cleaned FTO glass was put into a Teflon-lined autoclave with its conductive side facing the wall of the Teflon. The mixture was transferred into the autoclave, sealed and heated at 120 °C for 12 h. Next, the autoclave was allowed to cool down to room temperature, and the film coated FTO glass was then taken out of the autoclave, washed with distilled water and then air dried. The glass was heated to 500 °C with a rate of 10 °C/min in air and maintained for 3 h.

Synthesis of g-C₃N₄ nanosheets: Bulk g-C₃N₄ was synthesized by heating dicyandiamide in a muffle roaster at 600 °C and holding the sample at the same temperature for another 4 h in air. GCNS were prepared according to a previously reported method:² the as-prepared GCN (4 g) was mixed with 52 g of H₂SO₄ (98 wt.%) and 20 g of oleum (with free SO₃ 20 wt.% ~ 25 wt.%) in a 100 mL of flask and stirred at 140 °C for 3 h. Then the mixture was then heated up to 170 °C and held at that temperature for another 3 h before being cooled down to ambient temperature. After that, the mixture was injected into 800 mL of deionized water at 70 °C under vigorous stirring, and a suspension was formed. 85.58 g NH₄Cl (1.60 mol) was added into the solution afterward, and the solution was maintained stirring at 70 °C for 2 h, allowed to stand for 1h, and then hot filtered to remove residues. The obtained clear and colorless filtrate which was maintained at 70 °C was quickly placed in an ice bath and stirred for 1.5 h. Pure white precipitation generated and was collected by filter, washed with deionized water and ethanol, and finally dried at 60 °C in vacuo. The obtained pure white fine powder was GCNS. The detailed physical characterization of GCNS was reported elsewhere.²

Synthesis of NiO/GCNS: 0.5 mg of as-prepared GCNS was dispersed in 0.5 mL distilled water to form suspension, which was then dip-coated on the NiO electrode and air dried. The NiO/GCNS

film was heated at 350 °C for 2 h under Ar flow.

Characterization of samples

Field emission scanning electron microscope (SEM) was performed using JEOL-JSM6701F (Japan) at an accelerating voltage of 5 kV. Scanning transmission electron microscopy (STEM) measurements were performed using a TECNAI G² F20 field emission transmission electron microscope operated at acceleration voltage of 200 kV. All samples were ultrasonically dispersed in ethanol and drop-cast onto micro-grid supported by copper mesh before being transferred into the TEM chamber. Powder X-ray diffraction (XRD) patterns were recorded with a Shimadzu XD-3D X-ray diffractometer with monochromatized Cu K α radiation. Fourier transform infrared (FT-IR) spectra were collected on a Nexus 870 spectrophotometer in KBr pellets. X-ray photoelectron spectroscopy (XPS) were collected on a photoelectron spectrometer (VG ESCALAB 210) with a monochromatic X-ray source of Mg K α ($h\nu = 1253.6$ eV), calibrated internally by carbon deposit C (1s) binding energy (BE) at 284.8 eV. UV-visible diffuse reflectance spectra were taken on a UV-2550 (Shimadzu) spectrometer.

Photoelectrochemical Characterization

All photoelectronchemical properties of the samples were performed in a 3-electrode system with a piece of Pt foil (3×2 cm) as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode, and the as-prepared NiO/GCNS electrode was employed to be the working electrodes, respectively. 0.2 M Na₂SO₄ aqueous solution (pH = ~6.5) worked as electrolyte. The electrochemical measurements were tested on an electrochemical workstation (CHI660D). All photoelectrodes were illuminated from the front side by a 300 W Xe lamp (HSX-F/UV 300) equipped with a visible light cutoff filter (HSX-F 300, Beijing NBeT Technology Co., Ltd) calibrated to 100 mW/cm².

Linear sweep voltammograms were measured under a bias voltage between -0.375 V to 0.624 V (*vs.* RHE) with a scan rate of 0.05 V/s. Amperometric I-t curves were tested at a bias voltage of 0.42 V (*vs.* RHE). The electronic impedance spectroscopy (EIS) measurements were performed via the CHI660D workstation in a three-electrode cell by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01Hz to 100 kHz under open circuit potential conditions.

2. Supporting information for SEM.

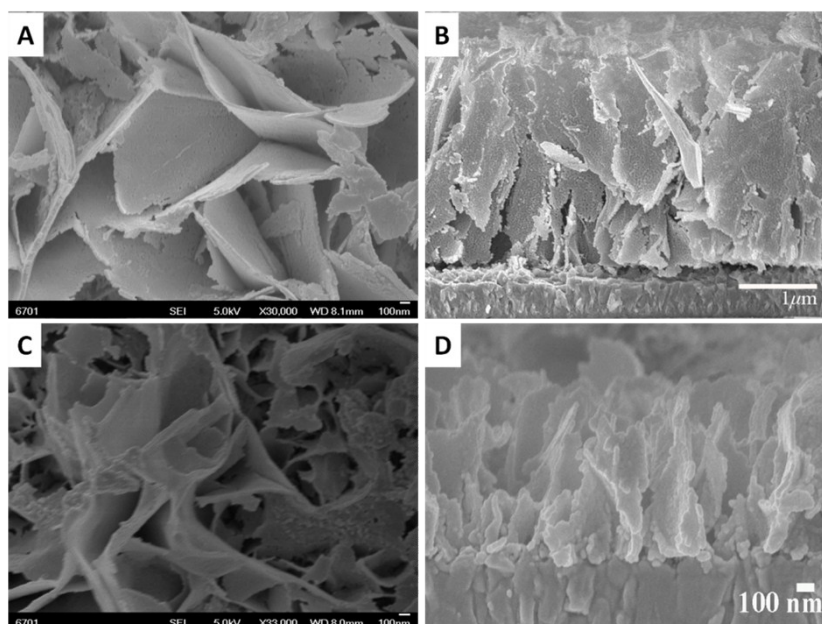


Figure S1. SEM images of (A) NiO and (C) NiO/GCNS, and the corresponding cross-sectional images (B) and (D).

3. Supporting information for TEM.

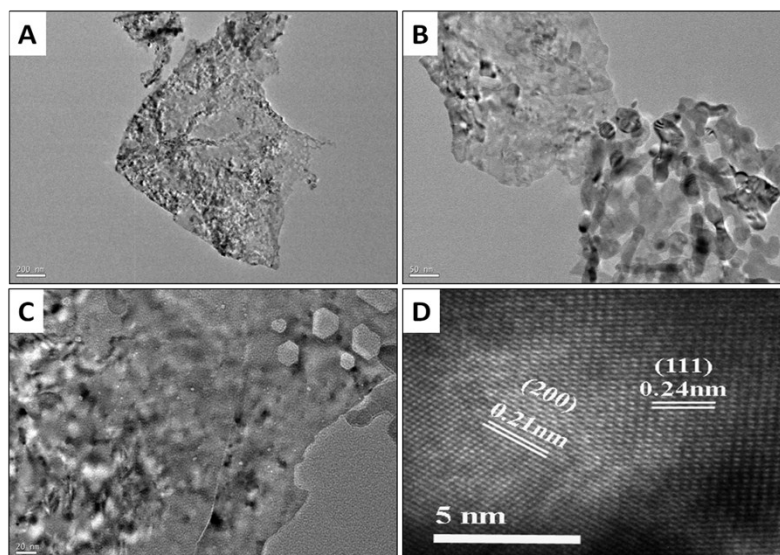


Figure S2. TEM images of NiO/GCNS.

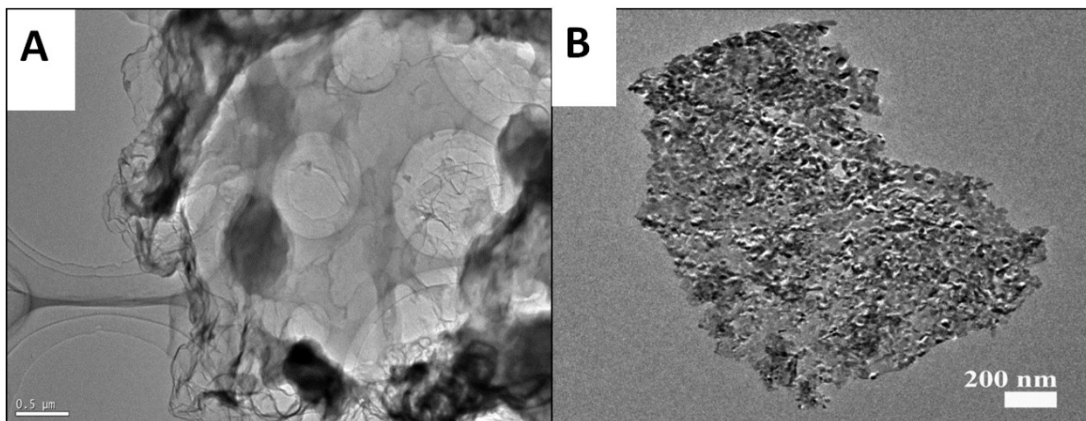


Figure S3. TEM images of pure GCNS and NiO.

4. Supporting information for XRD.

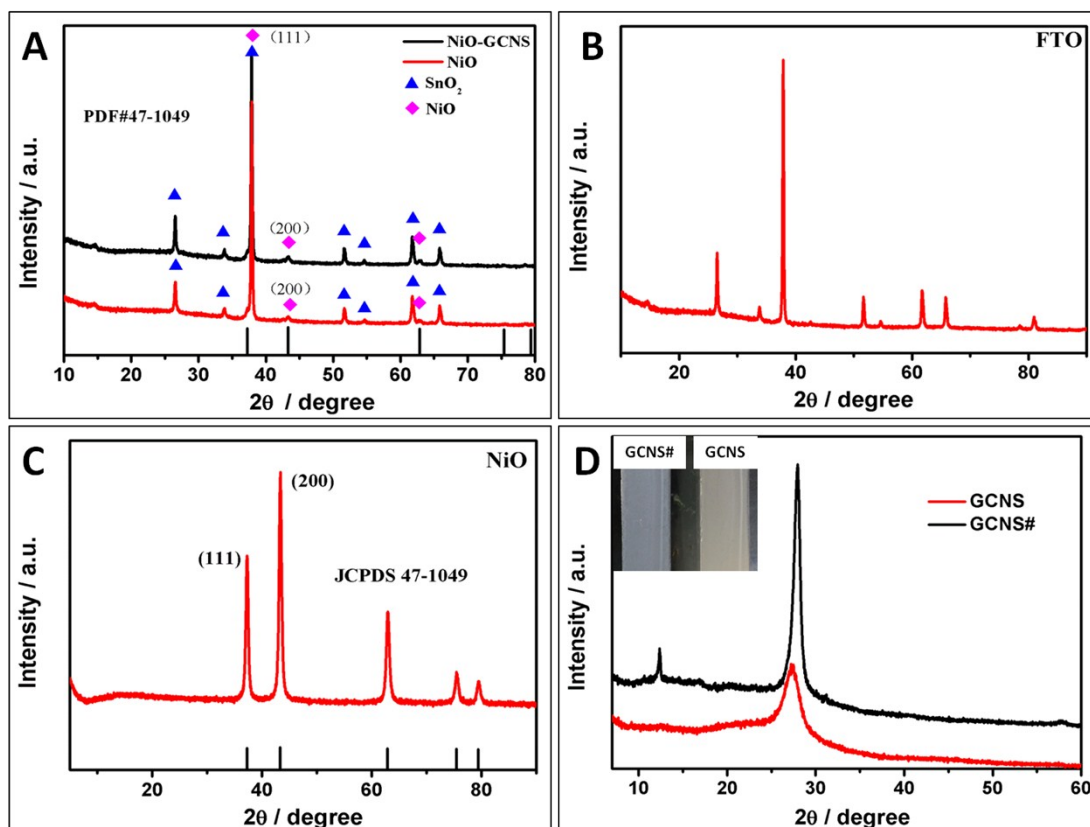


Figure S4. XRD plots of NiO powder (A) and GCNS before (black line) and after calcinations (red line) at 350 °C, inset photograph of the GCNS before (GCNS#) and after (GCNS) sintering at 350 °C.

Results and discussion:

XRD of FTO glass was investigated to illustrate that the XRD peaks of NiO was partly covered by the peaks of FTO. The obtained GCNS remained the same crystal structure except some minor changes. After calcinations at 350 °C, the (002) peak in XRD pattern of GCNS shifted back to 27.4°, which is close to that of bulk GCN sample. More details about the analysis of XRD patterns of GCNS can be derived from the reported reference by our group.

5. Supporting information for XPS.

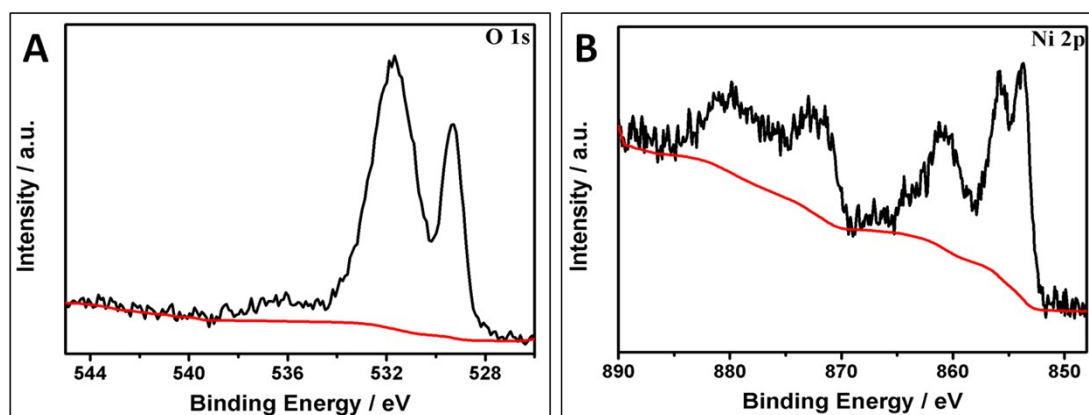


Figure S5. High resolution XPS spectra of (A) O 1s and (B) Ni 2p.

6. Supporting information for FT-IR.

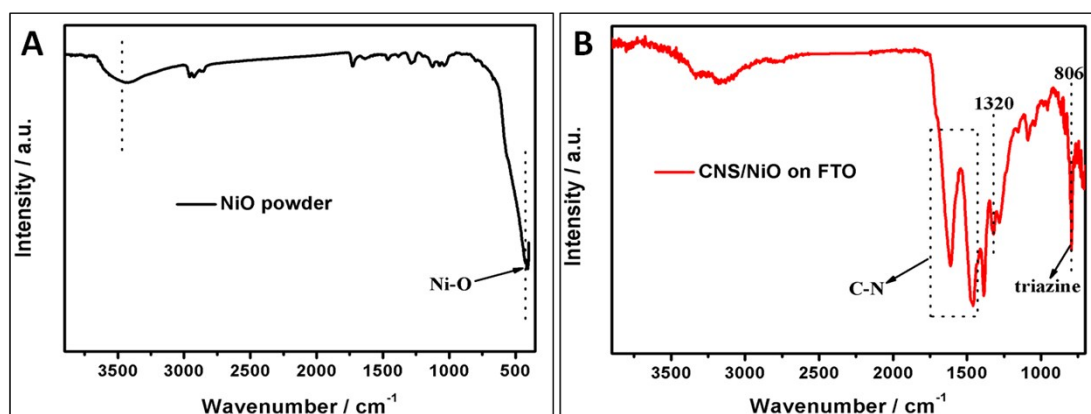


Figure S6. FT-IR spectra of (A) NiO powder and (B) GCNS/NiO on FTO.

Results and discussion:

In Figure S5A, the peaks at 3438 cm⁻¹, 1631cm⁻¹ and 1384 cm⁻¹ are attributed to the adsorbed water on the NiO nanosheets. The peak at 430 cm⁻¹ can be assigned to the Ni-O stretching mode.

7. Supporting information for UV-absorption spectra.

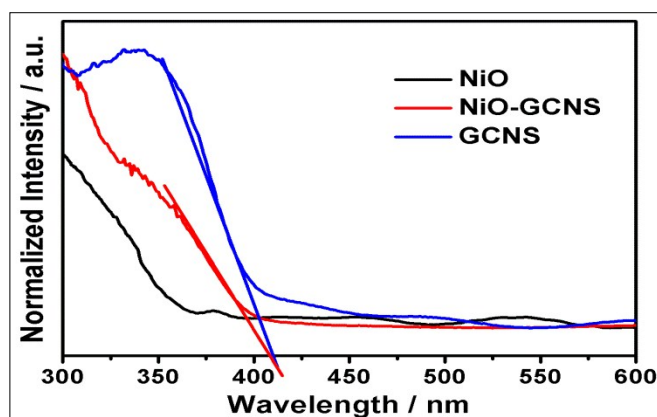


Figure 7. UV-Vis diffusive absorption spectra of NiO, GCNS, and NiO/GCNS.

8. Supporting information for linear sweep voltammograms.

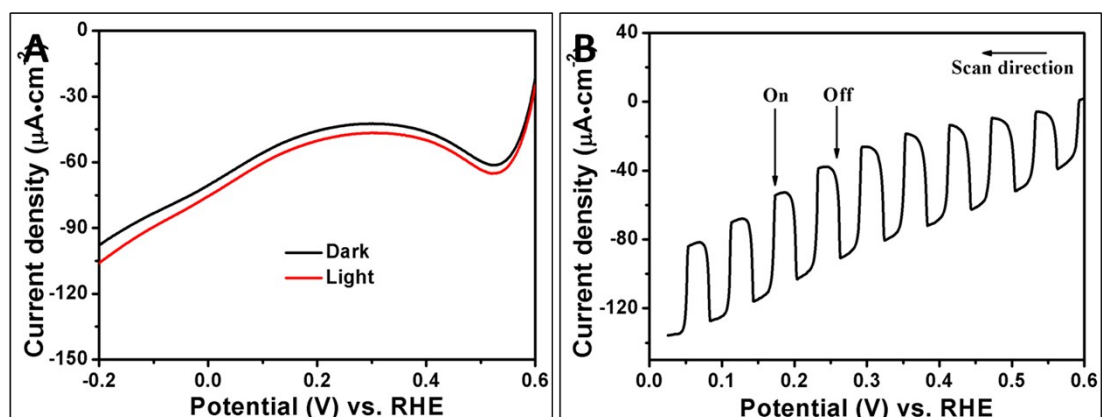


Figure S8. (A) Linear sweep voltammograms from 0.6 to -0.2 V (*vs.* RHE) for NiO with and without visible light illumination, scan rate: 50 mV s^{-1} . (B) Linear sweep voltammograms from 0.6 to -0 V (*vs.* RHE) for NiO/GCNS with light illumination at an interval of 10 s on/off switch, scan rate: 3 mV s^{-1} .

9. Supporting information for $I-t$ curves.

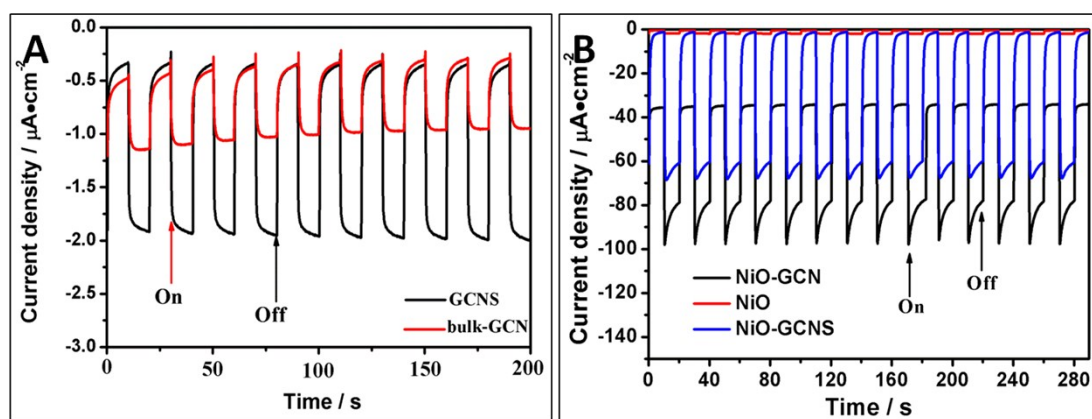


Figure S9. (A) amperometric $I-t$ curves of GCNS and bulk GCN at an applied voltage of 0.42 V *vs.* RHE with 10 s light on/off cycles. (B) amperometric $I-t$ curves of NiO, NiO-GCN, and NiO-GCNS at an applied voltage of 0.42 V *vs.* RHE with 10 s light on/off cycles.

10. Supporting information for XPS valence band spectra.

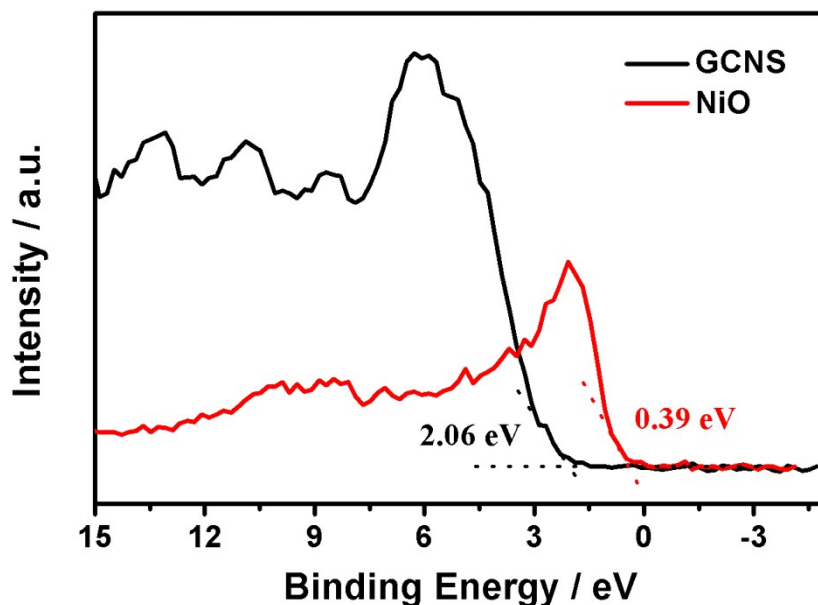


Figure S10. XPS valence band spectra of the GCNS and NiO.

Results and discussion:

XPS valence bands (VB) were performed to determine the band edges. As illustrated in Figure S8, the VB maximum of the GCNS and NiO were 2.06 eV and 0.39 eV, respectively. The VB positions were responded in Scheme 2.

References

1. K. Xu, P. Chen, X. Li, Y. Tong, H. Ding, X. Wu, W. Chu, Z. Peng, C. Wu and Y. Xie, *J. Am. Chem. Soc.*, 2015, **137**, 4119-4125.
2. X. Du, G. Zou, Z. Wang and X. Wang, *Nanoscale*, 2015, **7**, 8701-8706.