Supplementary Information

One step synthesis of zinc oxide containing porous boron nitride carbon sheets for oxygen reduction reaction and degradation of organic dye

A. Yamuna, Aditya Mandalam, R. Karthigaiselvi, M. Balasubramanian, B. Thiruparasakthi, Subbiah Ravichandran and Sundar Mayavan*

Experimental

Graphene oxide (GO) was obtained by the modified Hummers method as described elsewhere.[1] Boron oxide (B_2O_3) (Sigma-Aldrich) was mixed with Graphene oxide (GO), Glycine (Gly) (Sigma-Aldrich) and Zinc nitrate ($ZnNO_3$) (Sigma-Aldrich) at a mass ratio of 1:0.5: 2:2 (B_2O_3: GO: Gly: $ZnNO_3$) in water. The resulting mixture was sonicated for two hours and poured into an alumina crucible. The temperature of the mixture was gradually increased from room temperature to 500°C (at 2º C/min) under argon atmosphere and maintained for 2 hours, resulting in the formation of Zinc oxide containing hexagonal boron nitride carbon nanosheets (ZnO/h-BNC). The final product was collected from the crucible directly. ZnO/BCN sheets was prepared under same experimental condition without GO. Pure ZnO was prepared by thermal treatment of zinc nitrate at 500 ºC under similar experimental conditions.

Instrumentation

X-ray diffraction (XRD) patterns of the samples were measured using Bruker D8 Advance X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) measurement was performed with Sigma probe X-Ray Photoelectron Spectrometer (Thermo VG Scientific) with Al Kα X-ray for excitation. FT-IR spectra were recorded using a Nicolet 380 FTIR instrument having ATR attachment (Thermo USA). The photo luminescence spectra were recorded on a UV580C spectrophotometer. The Field-emission Scanning electron microscopy (FE-SEM) images are done with Carl Zeiss SEM instrument (model number: Supra 55VP/41/46) with an accelerating voltage between 15 kV using SE detector. Energy-dispersive X-ray (EDX) analysis was obtained with an EDX detector installed on the same FE-SEM. A Philips-Tecnai F20 field-emission transmission electron microscopy (FE-TEM) apparatus operated at 200 kV was also used to observe the morphology of as-prepared sample. The samples for TEM measurements were prepared by placing a drop of aqueous dispersion of ZnO/h-BNC on carbon-coated copper grids followed by drying.

Electrocatalytic activity

Voltammetric curves were measured on an electrochemical workstation (Solatron 1287 A) using a conventional three-electrode cell with a platinum counter electrode and a silver chloride reference electrode (SCE) (0.196 V vs reversible hydrogen electrode (RHE)). The working electrode for electrochemical experiment was prepared by thin film electrode method. A polished glassy carbon electrode (GC, 3mm diameter) was used as a substrate. A 10 µl aqueous suspension of ZnO/BCN or ZnO/h-BNC was transferred onto the GC substrate and dried at 80°C to form a catalyst layer. The experiments are carried out in O_2 saturated 0.1 M KOH solution for the oxygen reduction reaction. RDE measurements are conducted at different rotating speeds from 100 to 2500 rpm by using an Pine RDE Model. Koutecky−Levich plots of J −1 vs ω−1/2 at different potentials derived from the RDE measurements. The slopes of their linear fit lines are used to calculate the electron transfer number (n) on the basis of the Koutecky−Levich equation (1).

$$I_L = (0.620)nFAD^{\frac{2}{3}}w^{\frac{1}{2}}v^{\frac{-1}{6}}C \quad \text{.....(1)}$$

Dye degradation

The photo catalytic activity of the sample was evaluated by the photo catalytic degradation of methyl orange in an aqueous solution under UV irradiation. In the experiment, 30 mg of as-prepared ZnO/h-BNC and pure ZnO was added into 15 mL of methyl orange solution (MO) with a concentration of 10 mg/L. Prior to irradiation, the suspensions were sonicated in the dark for 60 min to obtain the saturated absorption of methyl orange onto the catalysts. After irradiation time interval of every 10 min, the suspensions were collected and then centrifuged (5000 rpm, 5 min) to remove the photocatalyst particles. UV-Vis absorption spectra of the supernatant were then measured using a UV-visible spectrophotometer.

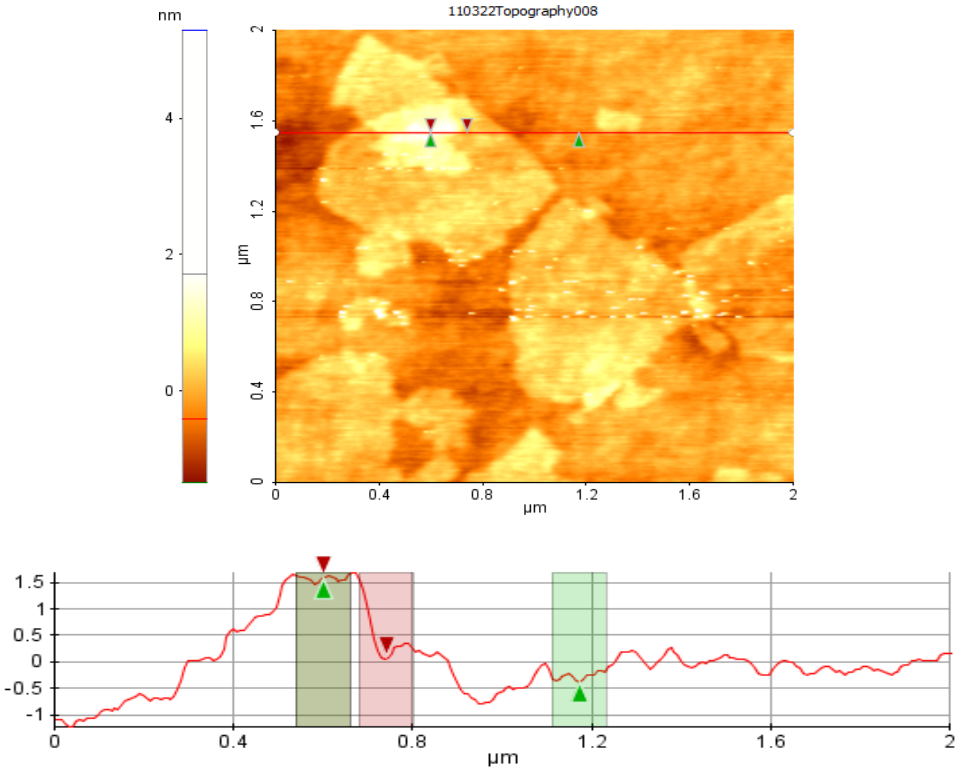

Figure S1. AFM image of GO sheets used in this work

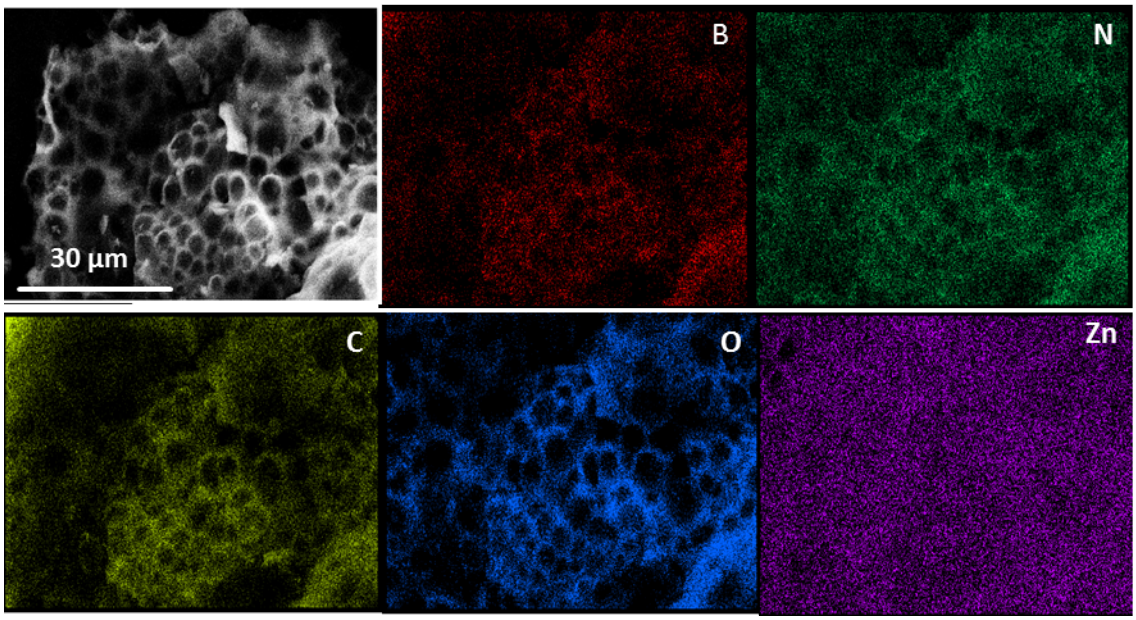

Figure S2. FE-SEM image of (a) ZnO/h-BNC hybrid and the corresponding EDX (b-f) maps of B, N, C, O and Zn.

1. W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc. 1958, 80, 13391. W. Lv, D. M. Tang, Y. B. He, C. H. You, Z. Q Shi, X. C. Chen, C. M. Chen, P. X. Hou, C. Liu and Q. H. Yang, ACS Nano, 2009, 3, 3730