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Porous BN/TiO_2 hybrid nanosheets as highly efficient visible-light-driven photocatalysts

Dan Liu[a,1], Mingwen Zhang[a,1], Wanjie Xie[a], Lu Sun[a,b], Ying Chen[a,*], Weiwei Lei[a,*]

[a] *Institute for Frontier Materials, Deakin University, Victoria 3216, Australia*
[b] *School of Textile Science and Engineering, Wuhan Textile University, Wuhan 430073, China*

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ABSTRACT

Porous boron nitride (BN) nanosheets, which possess extreme large surface areas, high thermal conductivity and special chemical activities, have demonstrated advantages in water cleaning and energy storage. However, they are usually considered as an underachieving catalytic material for photocatalysis and other photovoltaic conversion applications due to their wide bad gap of 5.5 eV. Here, we report a novel porous BN/TiO_2 hybrid nanosheets with the formation of new B—O—Ti bondings between the boron dangling bonds at the open edges of pores of porous BN nanosheets and nanosized TiO_2 particles. Such highly active bondings make the hybrid nanosheets responsive to an extended wavelength range from UV to visible light ($\lambda > 420$ nm) spectrum and also substantially enhance the photocatalytic effect (up to 99%) for degradation of organic molecules. In addition, the porous BN/TiO_2 hybrid nanosheets exhibit excellent cycling stability up to 5 cycles maintaining high visible-light photocatalytic activity (97%). These results provide new insights for design of advanced hybrid photocatalysts with actively chemical bonding species, which can be applied in environmental protection, water splitting, and photo-electrochemical conversion.

1. Introduction

Porous two-dimensional (2D) nanomaterials with unique structural advantages have led to their intriguing properties, attractive applications, as well as industrial and environmental benefits [1–4]. Several porous 2D nanomaterials, including ZnO nanosheets [5], In_2O_3 nanosheets [6], graphene [7], and BN nanosheets [4] were successfully produced and they exhibit significantly new properties in oil adsorption, gas sensing, biological probes, water cleaning, and electrochemical energy storage and conversion. One of the most attractive functionalities of the porous 2D nanomaterials is that they can interact with various organic or inorganic species not only on the surfaces but also at the edges of pores due to a large number of exposed and active radicals [8–10]. Therefore, the design and fabrication of unconventional porous nanosheet structures with highly active edges is an appealing endeavor for new properties and applications.

Among various 2D nanomaterials, boron nitride nanosheets (BNNSs), so—called "white graphene" due to the similarity to graphene, consist of a honeycomb structure of covalently bound boron and nitrogen atoms [11]. It has unique electronic features with a wide bandgap of up to 5.5 eV, and some important applications such as a deep-ultraviolet-light emitter and perfect substrates for graphene based devices [12,13]. Although BNNSs are not commonly considered as a catalytic material for photocatalysis and other photovoltaic conversion applications because of the strong optical absorption within the ultraviolet-visible region, they could be a promising support material for catalysts due to its remarkable properties, including extremely high resistance to oxidation and good chemical inertness, high thermal conductivity, high melting point and high surface area, especially under relatively harsh conditions, as it could avoid the sintering of the supported catalysts on hot spots [14–20]. Besides of the intrinsic properties of BNNSs, porous BNNSs with plentiful pores and large surface areas are showing some innovative applications in hydrogen storage and water cleaning treatment [21–26].

In this work, we demonstrated a rationally design of porous BN/TiO_2 hybrid nanosheets with a large number of new B—O—Ti chemical bonds. The synthesized porous BN/TiO_2 hybrid nanosheets possess much higher photocatalytic activity and regeneration ability for degradation of organic molecules in both UV and

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[*] Corresponding authors.
E-mail addresses: ian.chen@deakin.edu.au (Y. Chen), weiwei.lei@deakin.edu.au (W. Lei).
[1] These authors contributed equally.

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visible light ($\lambda > 420$ nm). A mechanism on their highly efficient visible-light-driven characteristic was also proposed based on the experimental results. All the results implicated the great potentials of the developed porous BN/TiO_2 hybrid nanosheets and inspired the further design of the BN-based photocatalytic materials.

2. Experimental

2.1. Synthesis of samples

Porous boron nitride nanosheets were produced by a dynamic templating approach using boron trioxide and guanidine hydrochloride [4]. In a typical experimental run, boron trioxide and guanidine hydrochloride with 1:5 molar ratio were mixed in 10 mL methanol under stirring to form a clear, colorless solution. After 24 h fast stirring, a white crystalline powder (a complex between the boron trioxide and guanidine chloride) as precursors was formed. After that, the precursors were put into a quartz boat and then heated at a rate of 10 °C/min and kept at 1100 °C for 2 h under nitrogen/hydrogen (15% hydrogen) gas flow. Finally, the sample was obtained. Non-porous boron nitride nanosheets (NP-BNNSs) were described as elsewhere [27]. Typically, boric acid and urea were mixed at a molar ratio of 1:48, followed by being added with distilled water (40 mL) and heated at 65 °C until the water was fully evaporated. The mixture was then heated at 900 °C in a N_2 atmosphere for 5 h to obtain white products.

Commercial P25 (80% anatase and 20% rutile TiO_2, 21 nm particle size) were purchased from Sigma-Aldrich (Australia). TiO_2 precursor solution was used as the starting material and prepared by the following route. In a typical run, 1 mL of tetrabutyl titanate (TBT, $Ti(OC_4H_9)_4$ from Sigma-Aldrich) was dissolved in 5 mL of ethanol using ultrasonic vibration for 5 min, to form a transparent solution. Then 2 mL nitric acid (HNO_3, 73 wt.%) was added drop wise into the ethanol solution with vigorous stirring. The obtained solution was further diluted to 10 mL by ethanol to form a clear TiO_2 precursor.

40 mg porous BNNSs was first dispersed in 20 mL nitric acid (8 M) under ultrasonic treatment for 2 h at room temperature, and then the treated porous BNNSs was obtained after washing repeatedly with ethanol and separating by centrifugation. The treated porous BNNSs was dispersed into 20 mL ethanol by ultrasonic vibration for 10 min, then TiO_2 precursor solution was added into the dispersion under vigorous stirring. After stirring for 30 min, the obtained dispersion was further diluted to 25 mL by ethanol and transferred to a 50 mL stain steel autoclave. The thermal recrystallization treatments were carried out at 180 °C for 20 h. After that, the autoclave was allowed to cool down naturally. Brown precipitates of porous BN/TiO_2 hybrid nanosheets were collected and washed with ethanol three times to remove impurities. Finally, the precipitates were dried at room temperature overnight. The TiO_2 nanoparticles and porous BN/TiO_2 hybrid nanosheets with different ratio of TiO_2 were prepared using the same method. 40 mg of porous BNNSs was added to the calculated amount of the above reaction system to prepare 18 wt%, 38 wt% and 51 wt% porous BN/TiO_2 hybrid nanosheets catalysts with different weight addition ratios of TiO_2 in porous BN/TiO_2 hybrid nanosheets. 18 wt%, 38 wt% and 51 wt% were the weight of TiO_2 over that of porous BN/TiO_2 nanosheets. Similar to the preparation method for porous BN/TiO_2 hybrid nanosheets, non-porous BN/TiO_2 hybrid nanosheets were obtained by replacing porous BNNSs with non-porous BNNSs.

2.2. Materials characterization

The crystallite structures were determined on a Panalytical X'Pert PRO X-ray powder diffraction (XRD) using Cu Kα radiation in a 2θ range from 15° to 80° at room temperature. Fourier transform infrared spectroscopy (FTIR) data were determined from a Bruker FTIR Spectrophotometer in transmission mode, with accumulation of 32 scans at 4 cm^{-1} resolution. Transmission electron microscopy (TEM) was performed on a JEOL 2100F high resolution mode operating at 110 kV apparatus. The surface areas of samples were determined from nitrogen adsorption and desorption isotherms using a Tristar 3000 apparatus at 77 K.

2.3. Photocatalytic experiments

The photocatalytic activities of products were evaluated of the degradation of rhodamine B (RhB) under simulated solar and visible light ($\lambda > 420$ nm) irradiation, respectively. In a typical procedure for RhB photocatalytic reaction, the weight of TiO_2 content in different photocatalysts (commercial P25, synthesized TiO_2 nanoparticles, and porous BN/TiO_2 hybrid nanosheets) used for each experiment was kept at 5 mg. The photocatalyst were added into a 100 mL quartz photo-reactor containing 50 mL RhB solution (150 mg L^{-1}) for simulated solar light irradiation. The suspension was first ultrasonicated for 10 min, and then stirred in the dark for 1 h to ensure absorption–desorption equilibrium. Subsequently, it was irradiated under the simulated solar light using an Atlas Suntest CPS1 instrument (Ametek, United States) equipped with 1500 W air cooled xenon arc lamp (light range 300–800 nm wavelengths). The suspensions were stirred constantly during the photocatalytic processes to ensure the uniform dispersion of porous BN/TiO_2 hybrid nanosheets. Filter B was chosen, the temperature inside the box was 35 °C, and the dose was 350 W/m^2.

For visible light-induced photocatalytic activity tests, both RhB and phenol degradations were carried out by adding the RhB (50 mg L^{-1}) and phenol (30 mg L^{-1}) solutions with the porous BN/TiO_2 nanosheets (38 wt%), followed by irradiating the suspensions in the same solar simulator through a GG420 cutting filter. The RhB and phenol concentrations were indicated by the absorbance at 554 nm and 269 nm, respectively. The change of their concentrations under simulated visible light irradiation could be used as a measure of the photocatalytic activity. At the given time intervals, 3 mL of the suspension was extracted and then centrifuged to separate the photocatalysts from the supernatant solution. UV–vis absorption spectra of the supernatant was measured using the Varian Cary 3E UV/Vis spectrophotometer. Commercial P25 was also applied in the same conditions for the comparison with porous BN/TiO_2 hybrid nanosheets (38 wt%). TiO_2 content in both porous BN/TiO_2 hybrid nanosheets and commercial P25 was kept at 5 mg and 7.6 mg for RhB and phenol degradation, respectively.

2.4. Photocurrent measurements

The photocurrents were measured using an electrochemical workstation (Solartron 1470E) in a standard three electrode system with as-prepared samples (synthesized TiO_2 and porous BN/TiO_2 hybrid nanosheets (38 wt%)) deposited on 1 cm × 1 cm ITO substrate as the working electrode, a Ag/AgCl electrode as reference, and a Pt wire parallel to the working electrode as a counter electrode. The light source employed was a Newport 300W xenon light source, controlled by a Newport Digital Exposure Controller, which simulates the solar light.

2.5. Photo-induced chemiluminescence measurements

To compare the free radical populations and decay rates following irradiation on synthesized TiO_2 (6 mg) and porous BN/TiO_2 hybrid nanosheets (38 wt%) (6 mg), a Lumipol 3 chemiluminescence instrument (Polymer Institute, Slovak Academy of Sciences, Bratislava), modified to allow in situ irradiation with selected wavelengths from a medium-pressure mercury arc (Lumatec SUV-