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Research Paper

Bismuth spheres assembled on graphene oxide: Directional charge transfer enhances plasmonic photocatalysis and *in situ* DRIFTS studies

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ABSTRACT

This work reports a facile approach to monodisperse bismuth nanospheres (Bi-NPs), which are then evenly assembled on graphene oxide (GO) via a solution-based sonication method. The resultant Bi-NPs@GO composite can serve as a robust direct plasmonic photocatalyst to remove 42.3% of ppb-level NO from a continuous flow under UV illumination. Localized surface plasmon resonance (LSPR) of Bi nanospheres were confirmed by a numerical simulations and the intense LSPR on Bi nanospheres under UV illumination accounts for the generation of energetic hot electron/hole pairs for NO removal. Experimental results combined with the density functional theory calculation analysis indicate that the abundant carboxyl groups on GO play crucial roles in whole photocatalysis: (i) form a directional carrier deliver channel: $Bi \rightarrow C_{graphene} \rightarrow C_{COOH} \rightarrow O_{COOH}$, facilitating the hot electrons transfer from the plasmonic Bi nanospheres to carboxyl groups and encouraging the carrier separation efficiency, (ii) enrich the reactant concentrations (O_2 and NO) around catalyst surface by adsorption, promoting the generation of active radicals $\cdot O_2^-$ and the sequent oxidation of NO. Further examination of the photocatalytic NO oxidation by *in situ* DRIFT confirms the key roles of carboxyl groups as adsorption/reaction centers for photocatalytic NO oxidation, as well as the pathway of NO oxidation to nontoxic nitrate on the catalyst.

1. Introduction

Photocatalysis constitutes one of the most active branches of heterogeneous catalysis and the designed synthesis of high-efficient photocatalyst is highly desired [1–3]. Plasmonic metals, featured by their unique localized surface plasmon resonance (LSPR) property, have emerged as one appealing class of photocatalysts with wide applications in environmental remediation [4,5]. In this LSPR-directed photocatalysis, the surface electrons of the plasmonic metals will easily oscillate resonated with the incident photon at an appropriate frequency, giving rise to a local electromagnetic field, the non-radiative decay of which will then trigger the generation of numbers of hot carriers for catalytic redox reactions [6–8]. The direct plasmonic photocatalysis is usually operated under a low-intense wave photon illumination, which enables a significant enhancement in kinetics of reactions [9]. However, current SPR-directed photocatalysis are limited to the noble metal, such as Au and Ag [10–13], which restrict their practical application.

In our previous work, we found that the earth-abundant bismuth metal (Bi) also has a unique LSPR property, and more importantly, can serve as a direct plasmonic photocatalyst in ppb-level NO removal from a gas flow under UV illumination [14]. However, bare Bi particles usually suffer from a poor chemical stability, which hampers their use for SPR response. Moreover, the hot carriers produced via LSPR in Bi metal cannot travel over distances longer than tens of nanometers before losing their energy by radiative scattering [15]. As a result, a poor photocatalytic activity was achieved.

To improve the performance of Bi metals, two strategies were proposed in this work: (i) control the metallic Bi into the shape of uniform nanospheres (denoted as Bi-NPs), considering that Bi-NPs with a uniform shape and a large specific surface area have a much enhanced LSPR in the wavenumber range of 220–280 nm [16], and (ii) introduce

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graphene oxide (GO) as the support for Bi-NPs. As we know, the 2D material GO has been widely used as a support for many photocatalysts, such as ZnO [17], TiO_2 [18], Ag_3PO_4 [19] and g-C_3N_4 [20]. The introduce of GO could usually increase both the dispersion of the photocatalyst and the photocarrier separation efficiency [21]. However, our work found that the abundant carboxyl groups on GO actually play more crucial roles: (i) form a unique channel: Bi-graphene-carboxyl group, facilitating the hot electrons transfer from the plasmonic Bi-NPs to carboxyl groups and encouraging the carrier transfer efficiency, (ii) enrich the reactant concentrations (such as O_2 and NO) around catalyst surface by adsorption, promoting the generation of active radicals $\cdot O_2^-$ and the sequent oxidation of NO. To our knowledge, these new functions of GO have never been reported.

Here, the Bi-NPs with uniform size and morphology were fabricated by a wet-chemical reduction method, which were then evenly assembled onto GO sheets under the assistant of intense sonication. The resultant composite (denoted as Bi-NPs@GO) is a robust plasmonic photocatalyst and could remove 42.3% NO removal in a continuous flow under UV illumination. LSPR feature of Bi nanospheres was presented by numerical simulations, and the function of GO was studied by the combination of experimental analysis and density functional theory calculations (DFT calculations). *In situ* Diffuse Reflectance Infrared Fourier-transform Spectroscopy (*in situ* DRIFTS) was applied to track the pathway of pollutant removal during the photocatalytic oxidation. Our results represent an important step in demonstrating the potential of Bi metal as a new direct plasmonic photocatalyst for achieving efficient solar energy conversion and environmental remediation systems.

2. Experimental

2.1. Materials

Bismuth chloride, PVP (Polyvinyl pyrrolidone), hydrazine hydrate, ethylene glycol, sodium hydroxide and ethyl alcohol were purchased from Sigma-Aldrich. GO with a BET surface area of 206.0 m^2/g was purchased from Nanjing Xianfeng Nano Company. All chemicals were analytical grade and used without further purification.

2.2. Sample preparations

In a typical synthesis, 0.158 g of bismuth chloride, 0.1 g sodium hydroxide, 276 mg PVP and 25 mL of ethylene glycol were mixed into a 50 mL three-neck flask and magnetically stirred under a N_2 atmosphere till a transparent light white solution was obtained. The resultant mixture was heated from room temperature to 190 °C, and then kept for a certain time. The reaction time was controlled for 0.5 h, 1.0 h and 2.0 h, respectively (the obtained samples were labeled as Bi-NPs-0.5, Bi-NPs-1 and Bi-NPs-2). Once cooled down to room temperature, Bi-NPs were collected by adding ethanol and centrifugation (5500 rpm, 3 min), and further purified with hydrazine monohydrate/ethanol to remove the surfactant [22], which was labeled as Bi-NPs-HW. The as-prepared Bi nanospheres powders and 0.05 g graphene oxide were dispersed in 5 mL and 50 mL ethanol by ultrasonication, respectively. The GO suspension was dropwise added into Bi NP solution and stirred for 60 min to obtain Bi-NPs@GO composite. The composite was collected by centrifugation and further subjected to a hydrazine-washing to remove the surfactant. The as-prepared samples were labeled as Bi-NPs@GO. The process is illustrated in Fig. 1.

2.3. Characterization

The crystal phases of the sample were analyzed by X-ray diffraction (XRD) with Cu Kα radiation (model D/max RA, Rigaku Co., Japan). Fouriertransform infrared (FT-IR) spectra were recorded on a Nicolet Nexusspectrometer on samples embedded in KBr pellets. Scanning electron microscopy (SEM; model JSM-6490, JEOL, Japan) and transmission electron microscopy (TEM; JEM-2010, Japan) were used to characterize the morphology and structure of the obtained products. The UV–vis diffuse-reflectance spectrometry (DRS) spectra were obtained for the dry-pressed disk samples using a Scan UV–vis spectrophotometer (TU-1901, China) equipped with an integrating sphere assembly, using 100% $BaSO_4$ as the reflectance sample. Nitrogen adsorption–desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA). All the samples were degassed at 100 °C prior to measurements. The sample for electron spin resonance (ESR) measurement was prepared by mixingBi-NPs@GO in a 50 mL DMPO solution tank, respectively (aqueous dispersion for DMPO-$\cdot$OH and methanol dispersion for DMPO-$\cdot O_2^-$). The photocurrent response measurements were performed in three-electrode quartz cells with a 0.1 M Na_2SO_4 electrolyte solution. Platinum wire was used as the counter electrode, and saturated calomel electrodes were used as the reference electrodes. Bi-NPsand Bi-NPs@GO film electrodes on ITO served as the working electrode, separately. The photoelectrochemical experiment results were recorded using an electrochemical system (CHI-660B, China).

2.4. Evaluation of photocatalytic activity

The photocatalytic activity was evaluated by measuring its efficiency for ppb-level NO removal in a continuous flow reactor at room temperature. The rectangular reactor, made of stainless steel and covered with Saint-Glass, has a volume capacity of 4.5 L (30 cm × 15 cm × 10 cm). A 15 W UV lamp with wavelength range of 280–320 nm is vertically placed on top of the reactor. The photocatalyst (0.2 g) was dispersed into 15 mL of ethanol via the sonication and then painted onto the bottom of two culture dishes (made of glass, 12.0 cm in diameter). Then, the dishes are vacuum dried and placed at the center of the reactor. NO gas is supplied by a compressed gas cylinder with a concentration of 100 ppm (N_2 balance), which is further diluted to 500 ppb by the air stream. The desired relative humidity level in NO flow was controlled at 50% by passing the zero air streams through a humidification chamber. A gas blender premixed the gas streams completely, and a mass flow controller was used to control the flow rate at 2.4 L min^{-1}. The lamp was turned on once the adsorption-desorption equilibrium was achieved. One chemiluminescence NO analyzer (Thermo Environmental Instruments Inc., 42i-TL) continuously measured the NO concentration at a sampling rate of 1.0 L min^{-1}. The removal efficiency (η) was calculated as η (%) = $(1 - C/C_0) \times 100\%$, where C and C_0 are the NO concentrations in the outlet and feeding stream, respectively.

2.5. In situ DRIFTS investigation on photocatalytic NO oxidation

In situ DRIFTS measurements were conducted using the TENSOR II FT-IR spectrometer (Bruker) equipped with an *in situ* diffuse-reflectance cell (Harrick) and a high temperature reaction chamber (HVC). The reaction chamber equipped with three gas ports and two coolant ports. High-purity He, high-purity O_2 and 100 ppm of NO (in He) mixture can be fed into the reaction system and a three-way ball valve is used to switch the target gas (NO) and purge gas (He). The total gas flow rate was 100 mL min^{-1} and the concentration of NO is 50 ppm by the dilution of O_2. The chamber is enclosed with a dome with three windows, two for IR light entrance and detection, and one for illuminating of the photocatalyst. The observation window is UV quartz and ZnSe for the other two windows. And High Pressure Mercury lamp (MVL-210, Optpe, Japan) was used for UV light source.

2.6. DFT calculations

Spin-polarized DFT-D2 [23] calculations were carried out utilizing the “Vienna ab initio simulation package” (code VASP5.4) [24,25], which uses a generalized gradient correlation functional [26]. A plane-