Electronic Supplementary Information for

Enhanced Plasmonic Photocatalytic Disinfection on Noble-Metal Free Bismuth nanospheres/Graphene Nanocomposites

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● Experimental Section

1.1. Preparation of photocatalysts

0.973 g of Bi $(NO_3)_3$.$5H_2O$ and 10 mL of 1-dodecanethiol were added into a three-necked-flask placed on a magnetic stirrer. Under the protection of nitrogen flow, the light yellow mixture was programmed heated to 178℃ with electric jacket.[1] The solution changed from red to dark brown at about 172℃. When the mixture cooled to 40℃, the Bi nanospheres were obtained by centrifugation. During the entire reaction, nitrogen must be kept in the three-necked-flask to prevent oxidation. The product was washed with a mixture of tetrahydrofuran and acetone by centrifugation for 3 times until the supernatant was clear enough to ensure all possible residues been removed.

0.009g of graphene was added into an appropriate amount of n-hexane according to a ratio of 100:3. The Erlenmeyer flask was placed in ultrasonic vibrator to make graphene uniformly distributed on n-hexane. Later the prepared bismuth sample was slowly added into the flask along with the ultrasonic treatment for 1.5 hours. Then the Bi nanospheres/graphene nanocomposites were obtained by centrifugation after washed by a mixture of hydrazine hydrate and ethanol (1:2) for 3 times to remove any possible residues. The sample is dried under temperature lower than 60℃ to obtain Bi@graphene nanocomposites.

1.2. 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). X-ray photoelectron spec- troscopy (XPS) with Al Kα X-rays (hv = 1486.6 eV) radiation operated at 150W (Thermo ESCALAB 250, USA) was used to investigate the surface properties. 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 reflection spectra were obtained for the dry-pressed disk samples using a Scan UV–vis spectrophotometer (UV–vis DRS: TU-1901, China) equipped with an integrating sphere assembly, using 100% BaSO4 as reflectance sample. The sample for electron spin resonance (ESR) measurement was

prepared by mixing Bi and Bi@graphene nanospheres in a 50 ml DMPO solution tank, respectively (aqueous dispersion for DMPO-•OH and methanol dispersion for DMPO-•O_2^-).

1.3. Evaluation of antibacterial activity

The photocatalysts were added to the 0.9% saline solution in volumetric flasks and homogenized by sonication. All solid or liquid materials have been sterilized by autoclaving at 121℃ for 20 min. The bacterial cells were resuspended and diluted to a suspension with concentration of 1×10^7 cfu/ml and mixed with the prepared photocatalyst suspension to the use for photocatalytic inactivation[2]. The final photocatalyst concentration was adjusted to 0.2 mg/ml. The suspensions were irradiated by a 15W UV lamp with wavelength of 280 nm. A bacterial suspension without photocatalyst was irradiated as a control. The reaction mixture was immediately diluted on nutrient agar. Each set of experiment was performed in duplicate. The colonies were counted after incubation at 37℃ for 14 h.

● DFT calculation section

Spin-polarized DFT-D2 calculations were carried out utilizing the "Vienna ab initio simulation package" (code VASP5.4), which uses a generalized gradient correlation functional. A plane-wave basis set with energy cut off at 400 eV with the framework of the projector-augmented wave method was conducted, setting the Gaussian smearing width to 0.2 eV. The k-points of Brillouin zone was sampled with a 3 × 3 × 1. The lattice parameters were set to 15 x 13 x 14 Å with a vacuum region of 10 Å. All atoms were allowed to converge to 0.01 eV $Å^{-1}$. A 1 × 1× 1 supercell containing 1 bismuth atom and 70 carbon atoms was employed first, in which the carbon atom at the center of graphene layer was removed to create a 5-8-5 vacancy to provide an anchoring site for single bismuth atom.[3] In order to simulate the generation of ROS, 1 oxygen atom along with 2 hydrogen atoms and 2 oxygen atoms were then added above, respectively.

Reference

1 B. Wei, X. Zhang, C. Zhang, Y. Jiang, Y. Y. Fu, C. Yu, S. K. Sun and X. P. Yan, *ACS Appl. Mater. Interfaces*, 2016, **8**, 12720–12726.

2 J. C. Yu, W. Ho, J. Yu, H. Yip, K. W. Po and J. Zhao, *Environ. Sci. Technol.*, 2005, **39**, 1175–1179.

3 J. Li, M. Hou, Y. Chen, W. Cen, Y. Chu and S. Yin, *Appl. Surf. Sci.*, 2017, **399**, 420–425.

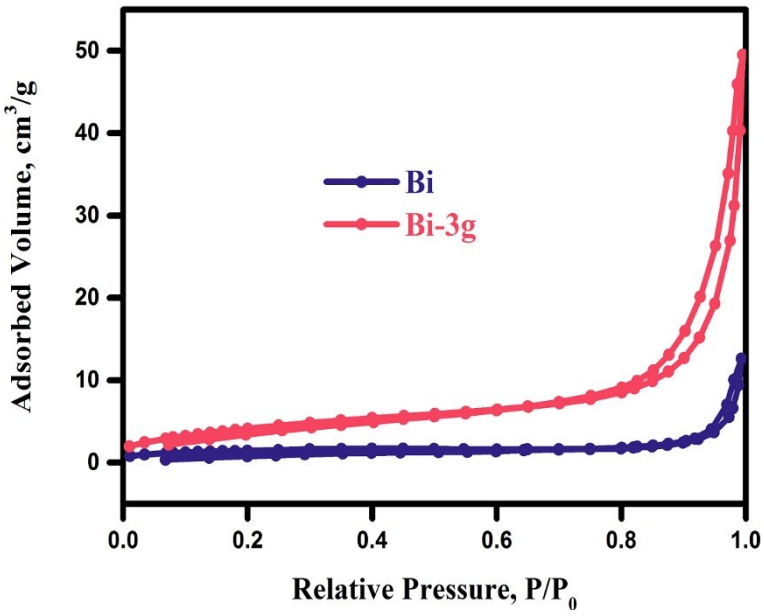

Figure 1 N2 adsorption-desorption isotherm

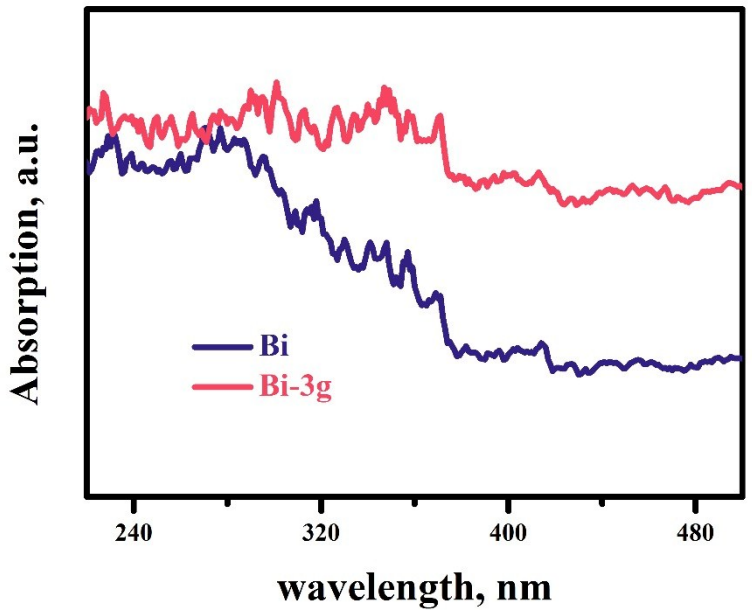

Figure 2 UV spectra of Bi and Bi@graphene

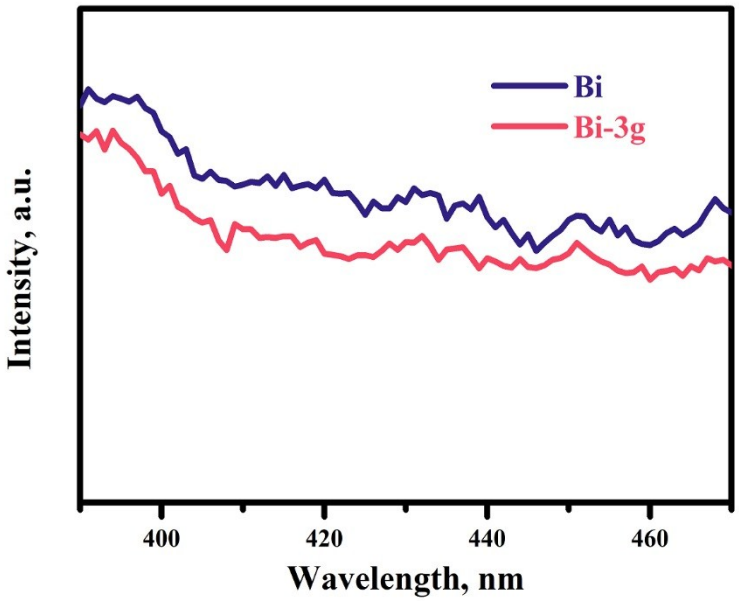

Figure 3. PL spectra of Bi and Bi@graphene

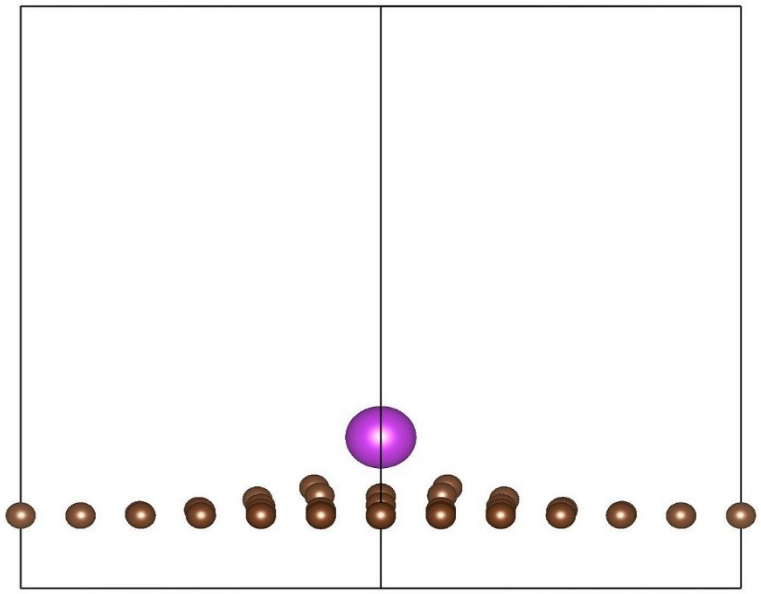

Figure 4 the original structure of Bi@graphene for theory calculation