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# Supplementary Information

## Preparation of three-dimensional inverse opal $SnO_2$/graphene composite microspheres and their enhanced photocatalytic activities

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## Part I. Preparation of GO

*Materials*

Graphite flakes (325 mesh) were supplied by Beijing Jixing Sheng'an industry & trade Co., Ltd. Analytical reagents including 98% $H_2SO_4$, $KMnO_4$ and $H_2O_2$ (30 wt%) were all purchased from Shanghai Chemical Reagents Co., Ltd. Distilled water was used in all the experiments.

*Method*

Graphite (2 g) was added slowly into 140 mL of concentrated sulfuric acid in an ice bath. $KMnO_4$ (20 g) was subsequently added into the mixture slowly at a temperature below 20 °C. After mechanically stirred in an ice bath for 1 h, the mixture was placed into a water bath of 40 °C with continuous stirring for 1 h. Then it was put back into the ice bath and added with 160 mL of water slowly. The system was heated to 95 °C in an oil bath and stirred for 1 h. Then, a certain amount of $H_2O_2$ (30 wt%) was added until the color of the above system turned to golden brown. Finally, the brown suspension was dialyzed against water until the pH of the suspension became 7. The aqueous suspension in dialysis bag was air-dried in an oven at 50 °C. The dried products, GO, were collected.

*Characterization*

The morphology of the above prepared GO was investigated by transmission electron microscopy (TEM, JEOL H-7650, 100 kV), as shown in Fig. S1. It can be observed that the GO sheets appear wrinkled, and the size is around 450 nm.

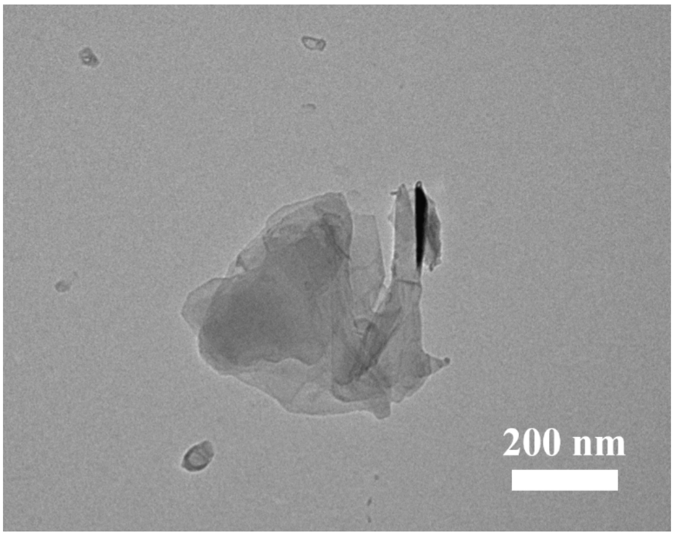

**Fig. S1.** TEM image of GO.

UV-vis spectrum of the aqueous dispersion of GO was obtained using UV-2600, as displayed in the following Fig.S2. The sharp absorption peak around 230 nm and the shoulder peak of GO around 290 nm are attributed to $\pi \rightarrow \pi^*$ transition of aromatic C–C bonds and $n \rightarrow \pi^*$ transition of C=O bonds, respectively[1].

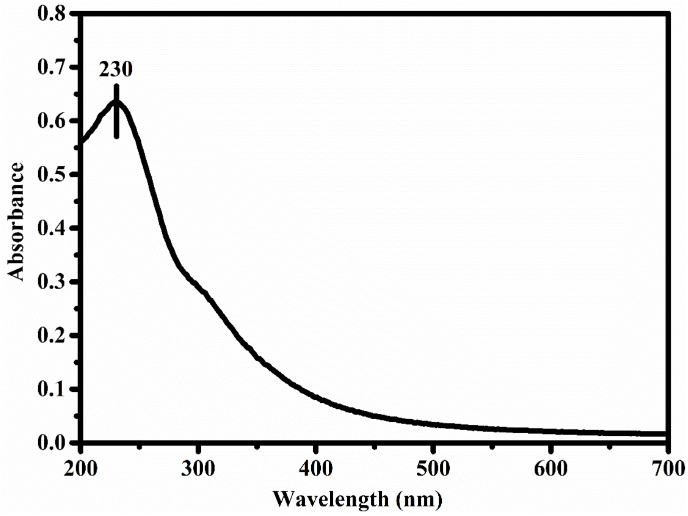

**Fig. S2.** UV-vis spectrum of the aqueous dispersion of GO.

## Part II. XRD spectra of IO-$SnO_2$/Graphene composite microspheres

X-ray diffraction spectra were operated on Rigaku SmartLab high resolution X-ray diffraction system using Cu K$\alpha$ radiation at a wavelength of 1.541 Å, as shown in Fig. S3. It shows clearly that there is no crystals in the dried PS colloidal crystal balls infiltrated with $SnO_2$ precursor (PS/$SnO_2$ precursor) before calcination. After the samples were calcinated at 400 $^oC$ in Ar atmosphere for 3 h (the samples termed as IO-$SnO_2$/G-0.15-Ar and IO-$SnO_2$-Ar), evident diffraction peaks of $SnO_2$ crystals (located at 26.4$^o$, 33.8$^o$, 37.9$^o$, 51.6$^o$ and 54.7$^o$, which are ascribed to (110), (101), (200), (211) and (220).) could be detected, indicating the formation of $SnO_2$ crystal. However, a part of SnO are produced in the presence of GO since there are a lot of weak diffraction peaks belong to SnO crystal (located at 31.2$^o$, 32.1$^o$ and 35.9$^o$, JCPDS NO. 13-0111) appearing on the XRD curve of the sample IO-$SnO_2$/G-0.15-Ar. This phenomenon is in accord with the other results about the preparation of MnO/graphene composite in the literature[2]. But these SnO crystals will transform into $SnO_2$ crystals during the following calcination at 450 $^oC$ in air for 2 h, i.e., the final product IO-$SnO_2$/G-0.15, because all of the diffraction peaks of SnO crystals disappeared on the XRD curve of IO-$SnO_2$/G-0.15.

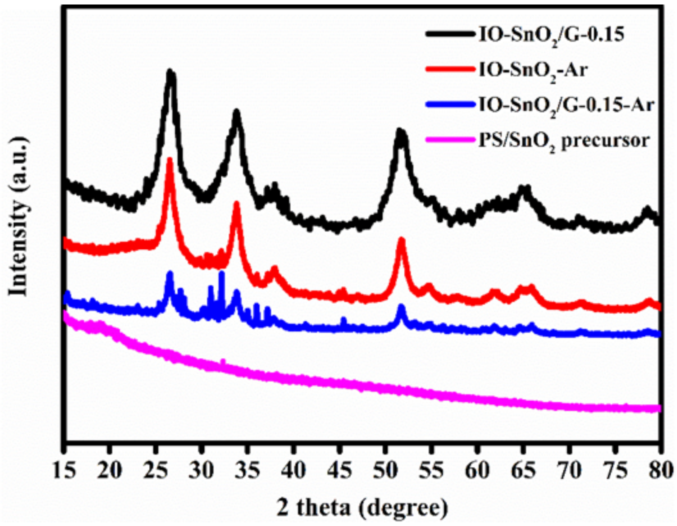

**Fig. S3.** The XRD spectra of dried PS/SnO$_2$ precursor; IO-SnO$_2$/G-0.15-Ar and IO-SnO$_2$-Ar which is calcinated at 400 °C in Ar atmosphere for 3 h; and IO-SnO$_2$/G-0.15 which is calcinated at 400 °C in Ar atmosphere for 3 h, followed by calcination at 450 °C in air for 2 h.

## Part III. XPS, XRD and Raman spectroscopy of GO after the heat treatment

### *The heat treatment process*

The GO sample was sealed in a quartz tube and put in a horizontal tube furnace. The furnace was heated to 400 °C at a rate of 3 $°C\cdot min^{-1}$ under a gas flow of argon and kept for 3 h.

### *Characterization*

X-ray photoelectron spectroscopy (XPS) was carried out on Thermo ESCALAB 250 using monochromatic Al K$\alpha$ radiation, as shown in Fig. S4. For GO sample (Fig. S4a), the main peak positioned at 284.6 eV originates from sp$^2$ carbon atoms. The peaks centered at 287.2 eV and 289.1 eV are due to C-O and C=O, respectively[3]. In Fig. S4b, the sample of GO after calcinated at 400 °C for 3 h shows the disappearance of the C=O groups and the relatively low intensity of peaks assigned to C-OH groups when compared with GO. This indicates that GO has been reduced during the heat treatment.

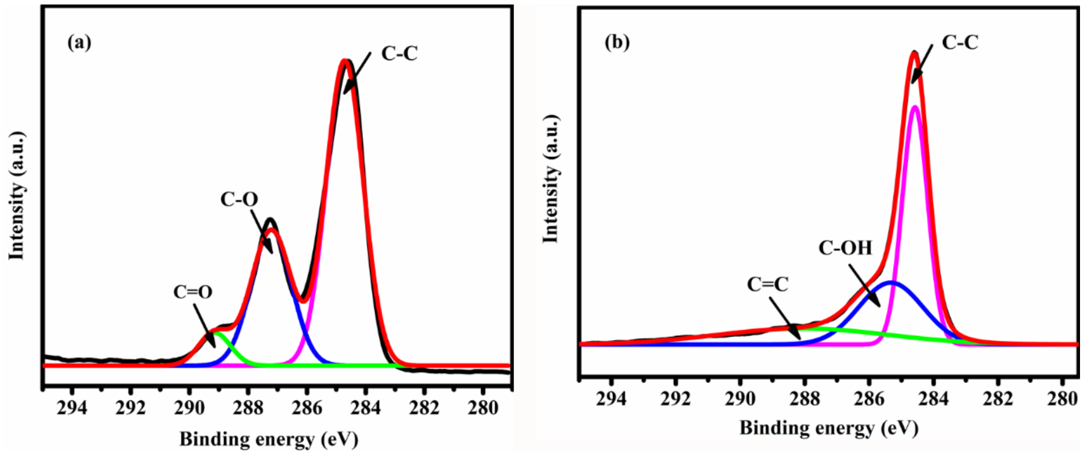

**Fig. S4.** The XPS spectra of GO before (a) and after calcinated at 400 °C in Ar atmosphere for 3 h (b).

X-ray diffraction spectra were operated on Rigaku SmartLab high resolution X-ray diffraction system using Cu K$\alpha$ radiation at a wavelength of 1.541 Å, as shown in Fig. S5. It shows the crystalline structure of the GO before and after the heat treatment. It can be observed that the characteristic diffraction peak located at 11.8° of GO disappears nearly after the heat treatment. Instead, the characteristic diffraction peak of graphite at 26.3° appears. It implies that GO had been reduced to graphene, here termed as rGO, during the calcination at 400 °C for 3 h.

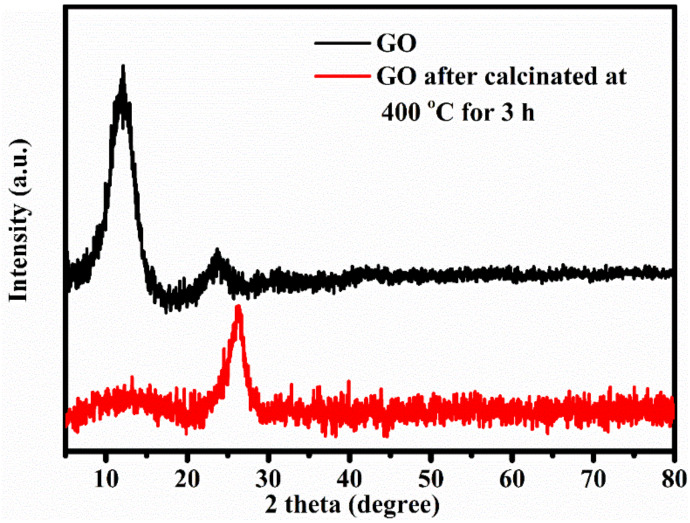

**Fig. S5.** XRD spectra of GO before and after calcinated at 400 °C in Ar atmosphere for 3 h.

The structural evolution of GO during the heat treatment was investigated by Raman spectroscopy (LABRAM-HR, 514 nm of the excitation laser irradiation), as shown in Fig. S6. According to the previous work[4], the strong peaks at 1347 $cm^{-1}$, i.e., D band, indicates a disordered structure of GO sheets. Another strong peak at 1594 $cm^{-1}$ is assigned as G band, which is associated with the $sp^2$ bonded carbon domains. The ratio of $I_D/I_G$ of GO decreased from 0.92 to 0.75 after the calcination, which can be ascribed to the improved crystallinity of rGO after the heat treatment at high temperature[4].

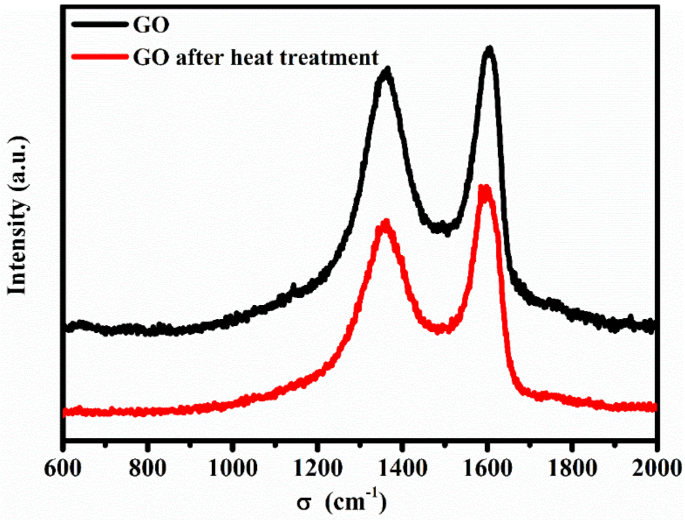

**Fig. S6.** Raman spectra of GO before and after calcinated at 400 °C in Ar atmosphere for 3 h.

## Part IV. TGA analysis of GO, rGO and PS microspheres

Thermo-gravimetric analysis (TGA) was operated on TGA Q5000IR in air at a heating rate of 10 °C·$min^{-1}$. The results are shown in Fig. S7. As for GO, the mass loss before 211 °C should be ascribed to the loss of water and impurities[5, 6]. The oxygen-containing groups and the carbon skeleton of GO decompose mainly at 523 °C. Different from GO, there is nearly no mass loss of rGO before 384 °C, which implies that the most oxygen-containing groups have been burned out during the calcination at 400 °C. However, when the temperature is above 450 °C, a rapid mass loss of rGO appears, which is due to the decomposition of carbon skeleton. PS microspheres decompose completely when the temperature exceeds 400 °C. Therefore, it could be inferred that 450 °C is a suitable calcination temperature for the PS colloid crystals infiltrated with the sol precursor of $SnO_2$ and GO to remove PS microspheres but not destroy rGO.

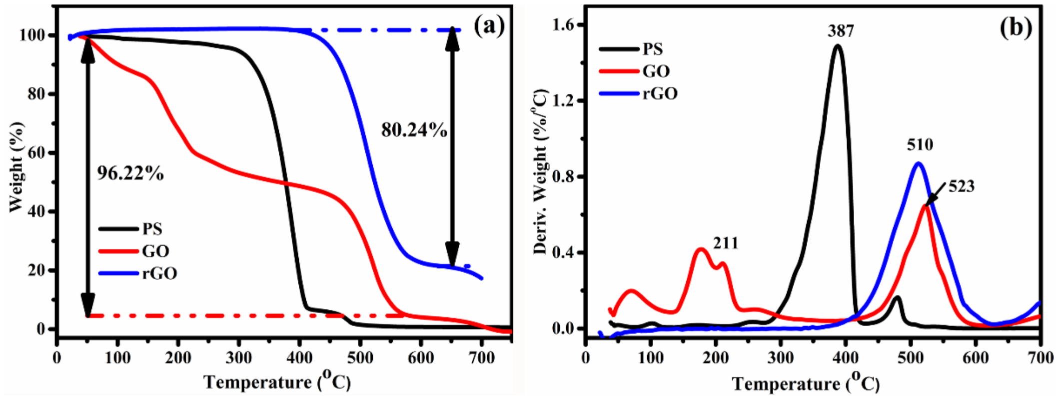

**Fig. S7.** (a) TG and (b) DTG curves of GO, rGO and PS.

## References

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