Supporting Information

Inverse Opal TiO₂/g-C₃N₄ Composite With Heterojunction Construction for Enhanced Visible Light-driven Photocatalytic Activity

Experimental section Preparation of ordered silica PCs

Monodispersed SiO₂ microspheres with a size of ~400 nm were prepared by the Stöber method. Briefly, TEOS (8 mL) was added to ethanol (92 mL) and the mixed solution was stirred to form solution A. Meanwhile, ethanol (56.6 mL), deionized water (29.4 mL) and ammonium hydroxide (14 mL) were added to a round bottom flask (250 mL) to form solution B. Solution A was quickly added to Solution B and then the round bottom flask was sealed with a frosted hollow plug. After vigorous stirring for 1 min, the mixture was decelerated to bubble-free stirring. After that, the mixture was kept stirring for 24 h under an oil bath at 25°C. After the reaction, the prepared silica spheres were washed with water by centrifugation three times to remove unreacted residues. Later, the obtained silica spheres, which dispersed in water with a concentration of 5 wt%, were allotted into 10 mL vials. The silica PCs self-assembled on the wall of the vials at 110 °C, with little sediment at the bottom.

Preparation of inverse opal TiO₂ (IO TiO₂) and pristine TiO₂

IO TiO₂ was prepared according to previous reports¹.

Preparation of inverse opal g-C₃N₄ (IO g-C₃N₄) and bulk g-C₃N₄

Dicyandiamide (0.6 g) was mixed with silica PCs (1.0 g), and calcined in Ar at 520 °C with a ramp of 2 °C \cdot min⁻¹ for 2 h. Afterward, the product was further heated to 550 °C with a ramp of 4 °C min⁻¹ and kept at 550 °C for another 2 h. The as-obtained product was etched using 4 M NH₄HF₂ aqueous solution for 48 h to remove the silica templates completely, washed with deionized water several times and dried at 60 °C in a vacuum drying oven overnight. The obtained catalyst was designated as IO g-C₃N₄.

The preparation of bulk $g-C_3N_4$ is similar to that of IO $g-C_3N_4$ except that silica PCs were not introduced into samples.

Preparation of inverse opal TiO₂/g-C₃N₄ (IO TiO₂/g-C₃N₄) and TiO₂/g-C₃N₄

Dicyandiamide (0.6 g) was mixed with silica PCs (1.0 g) and placed in a porcelain boat. TiO₂ precursor perfusate is prepared as follows: anhydrous ethanol (26 mL), acetylacetone (0.25 mL), isopropyl titanate (1.4 mL), hydrochloric acid (220 μ L) and deionized water (1.2 mL) were mixed and stirred on a magnetic stirrer for 2 h to form a clear yellow solution. 1 mL of the prepared perfusate was instilled into the porcelain boat filled with mixed powder and then the solution was stirred to make the powder immersed by the solution sufficiently. The sample was dried at room temperature overnight eventually.

The dried sample was calcined in Ar at 520 °C with a ramp of 2 °C·min⁻¹ for 2 h. Afterward, the product was further heated to 550 °C with a ramp of 4 °C·min⁻¹ and kept at 550 °C for another 2 h. In order to remove the carbonized material produced by calcination under an inert atmosphere, the calcined product was calcined at 450 °C with a ramp of 2 °C·min⁻¹ for 4 h. The as-obtained product was etched using 4 M NH₄HF₂ aqueous solution for 48 h to remove the silica templates

completely, washed with deionized water several times and dried at 60 °C in a vacuum drying oven overnight, and named as ITC-1. The catalysts ITC-2, ITC-3, ITC-4 were obtained by reducing the volume of precursor perfusate to 1/2,1/3 and 1/4 respectively.

The preparation of $TiO_2/g-C_3N_4$ was similar to that of IO $TiO_2/g-C_3N_4$ except that silica PCs were not introduced into samples. The as-prepared catalyst TC-4 was obtained by reducing the volume of precursor perfusate to 1/4.



Fig. S1. SEM image of TC-4



Fig. S2. HRTEM image of TC-4



Fig. S3. High-resolution XPS spectra of g-C₃N₄ (A) C 1s and (B) N 1s

 $\begin{tabular}{|c|c|c|c|c|c|c|} \hline Sample & S_{BET} (m^2 / g) \\ \hline ITC-4 & 34.1375 \\ TC-4 & 18.2873 \\ IO TiO_2 & 35.7634 \\ g-C_3N_4 & 7.3467 \\ \hline \end{tabular}$

Table S1. BET surface area of ITC-4, TC-4, IO TiO_2 and $g\text{-}C_3N_4$

References

 L. González-Urbina, K. Baert, B. Kolaric, J. Pérez-Moreno and K. Clays, *Chemical Reviews*, 2012, 112, 2268-2285.