Supporting Information

**Rationally designed 1D Ag@AgVO$_3$ nanowires/graphene/protonated g-C$_3$N$_4$ nanosheets heterojunctions for enhanced photocatalysis via electrostatic self-assembly and photochemical reduction methods**

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1 Experimental Section

1.1 Preparation of photocatalysts

Preparation of GO

Graphene oxide was prepared using modified Hummers method from flake graphite with an average particle diameter of 325 mesh. Briefly, a mixture of 5.0 g graphite and 3.75 g NaNO$_3$ were placed in an ice-cooled flask. 375 mL H$_2$SO$_4$ was added slowly with stirring, followed with 22.5 g KMnO$_4$ within about 1 h. This solution was stirred 2 more hours with an ice bath before warming up to r.t. and stirred vigorously for 5 days. 700 mL 5 wt% H$_2$SO$_4$ aqueous solution was added in the solution within about 1 h and the temperature was kept at 98 °C for 2 h. After cooling to 60 °C, 15 mL H$_2$O$_2$ (30 wt%) solution was added, and the mixture was stirred for 2 h at room temperature. The resultant mixture was centrifuged and washed with 1:10 HCl aqueous solution to remove any possible metal ions followed by plenty of deionized water to remove the acid. After that, the mixture was dialyzed for a week to obtain the final GO sample. The concentration of the GO nanosheets dispersion was determined by evaporating water to weigh the residual solid.

Synthesis of PCN

Bulk g-C$_3$N$_4$ was prepared by heating melamine from room temperature to 550 °C with a ramp rate of ~2.5 °C/min and kept at this temperature for 4 h. 1.0 g of obtained bulk g-C$_3$N$_4$ was vigorously stirred in 100 mL 10 M HCl solution for 10 h at room temperature for its protonation. The mixture was filtrated, washed with water repeatedly to remove the superfluous HCl. Then 50 mg of the protonated solids was
dispersed in 100 mL deionized water, followed by sonication for ~10 h. The mixture was centrifuged at 3000 rpm to remove unexfoliated aggregates, leaving a homogenous aqueous dispersion of PCN nanosheets. The concentration of the PCN nanosheets dispersion was determined by evaporating water to weigh the residual solid.

**Preparation of Ag@AgVO$_3$ nanowires**

Ag@AgVO$_3$ nanowires were prepared by the hydrothermal method. In a typical synthesis, 0.30 g NH$_4$VO$_3$ and 0.50 g P123 were dissolved in a mixture solution of 30 mL DI water and 2 mL 1.0 M HNO$_3$. This solution was stirred at room temperature for 7 h before adding 1.1 g of AgNO$_3$. After stirring for 1 h, the mixture was transferred to a 50 mL Teflon-lined autoclave and heated to 120 °C for 24 h. The resulting precipitate was collected, rinsed with DI water and acetone.

**Synthesis of Ag@AgVO$_3$/rGO/PCN heterojunctions via electrostatic self-assembly and photochemical reduction methods**

30 mg GO was well dispersed in 30 mL deionized water with the aid of ultrasonication to obtain Solution A. 180 mg PCN nanosheets was dispersed in 90 mL deionized water to make Solution B. 80 mg Ag@AgVO$_3$ nanowires was dispersed in 80 mL deionized water under vigorous stirring for 5 h to obtain Solution C. Solutions A, B and C were mixed and stirred for 5 h. Then, it was centrifuged and redispersed in a mixture solution of deionized water and ethanol (v/v = 1). Under stirring, this solution was irradiated under 300 W xenon lamp for 5 h, during which the solution changed its color from orange to taupe, indicating that PCN and Ag@AgVO$_3$ were
the photocatalysts for GO reduction and ethanol was the vacancy sacrificial reagent. The Ag@AgVO$_3$/rGO/PCN heteroconjugates were obtained by washing with deionized water. For comparison, rGO/PCN, Ag@AgVO$_3$/rGO and Ag@AgVO$_3$/PCN were also prepared using similar methods without the presence of Ag@AgVO$_3$, PCN and GO, respectively.

1.2 Characterization

Powder X-ray diffraction (XRD) data were collected using a D/MAX2500V diffractometer using Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å). The structural information of samples were measured by a Fourier transform spectrophotometer (FT-IR, Avatar 370, Thermo Nicolet) using the standard KBr disk method. X-ray photoelectron spectroscopy (XPS) was performed using ESCALAB250 with Mg K$\alpha$ as the source and the C 1s peak at 284.6 eV as an internal standard. The zeta-potential was measured by using a ZETASIZER 3000 HSA system. The UV-vis absorption spectra were obtained by a Shimadzu UV-2500 spectrophotometer using BaSO$_4$ as the background. Photoluminescence (PL) spectra were obtained on a FLUOROLOG-3-TAU. All the spectra were taken at room temperature with an excitation wavelength of 365 nm. Raman spectra were taken using a Raman spectrometer with a 633 nm laser excitation (Renishaw 1000B). The Brunauer-Emmett-Teller (BET) surface area of the photocatalysts was determined by a multi-point BET method. Electrochemical impedance spectroscopy (EIS) and Cyclic voltammograms (CV) measurements were obtained using a CHI660C electrochemical workstation (Chenhua Instruments, Shanghai, China). The measurement was conducted in a conventional three-electrode
cell system. The morphologies and compositions of the Ag@AgVO$_3$/rGO/PCN heteroconjugates were characterized using a JEOL JSM-6330F scanning electron microscopy (SEM) instrument operated at a JEOL-2100 field emission transmission electron microscope (FETEM) at an accelerating voltage of 200 kV.

1.3 Photocatalytic tests

Methylene blue (MB), methyl orange (MO) and colorless phenol were selected as model pollutants for degradation experiments under visible light irradiation. The visible light was obtained from a 300W Xe lamp, equipped with a super cold filter, which provided the visible light region from 400 to 700 nm. The distance between the light source and the reactor was ~5 cm. The aqueous suspensions were irradiated in 150 mL open cylindrical reactor whose base contained an optical window with a surface area of ~100 cm$^2$ and an average light intensity of ~90 mW/cm$^2$. The photocatalytic activities of the photocatalysts (25 mg) were examined by monitoring the degradation of dyes (10 mg/L, 100 mL) in a beaker under stirring condition (400 rpm/min) at room temperature. The mixtures were pre-stirred for ~120 min in the dark to ensure adsorption-desorption equilibrium. MB concentrations at different time intervals were determined quantitatively by the absorption peak generated using the UV-Vis spectrophotometer (UV-2550, Shimadzu).
Figure S1. AFM images of GO nanosheets on mica and its section analysis (A, B), TEM image of PCN nanosheets (C).
Figure S2. The zeta potentials ($\xi$) of GO nanosheets, PCN and Ag@AgVO$_3$ in deionized water.
**Figure S3.** Elemental mapping of the homogenous dispersion of C and N elements in the rGO/PCN.

**Figure S4.** The HRTEM image of the Ag@AgVO$_3$/rGO/PCN heterojunction.
Figure S5. The XRD pattern and UV-vis diffuse reflectance spectra of bulk g-C$_3$N$_4$.

Figure S6. N$_2$ adsorption-desorption isotherms of the as-prepared photocatalysts.
**Figure S7.** The TEM image of the Ag@AgVO$_3$/rGO/PCN after photocatalytic reaction.
Table S1. Summary of surface areas and the photocatalytic activities of rGO/PCN and Ag@AgVO$_3$/rGO/PCN photocatalysts as well as the photocatalytic activity enhancement times.

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>K (min$^{-1}$)</th>
<th>K’ (g/(min·m$^2$))</th>
</tr>
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<tr>
<td>rGO/PCN</td>
<td>96.3</td>
<td>0.0149</td>
<td>1.54×10$^{-4}$</td>
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<tr>
<td>Ag@AgVO$_3$/rGO/PCN</td>
<td>157.6</td>
<td>0.2377</td>
<td>1.51×10$^{-3}$</td>
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<td>Enhancement times</td>
<td>1.64</td>
<td>15.95</td>
<td>9.75</td>
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