

# **Ag<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/C<sub>3</sub>N<sub>4</sub> nanocomposites as efficient photocatalyst for hydrocarbon selective oxidation**

## **(Supporting Information)**

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### **1. Experimental section**

#### **1.1 Synthesis of g-C<sub>3</sub>N<sub>4</sub>**

All chemicals were purchased from Sigma–Aldrich and used as received without further purification.

We produced g-C<sub>3</sub>N<sub>4</sub> on a large scale by the simple pyrolysis of urea under ambient pressure and pyrolysis-generated self-supporting atmosphere. In a typical synthesis, 10 g of urea powder was put into a covered crucible. The crucible was heated to 550 °C at the rate of 1 °C/min, and then maintained for 3 h.

#### **1.2 Synthesis of pg-C<sub>3</sub>N<sub>4</sub>**

10 g of urea powder was mixed with 1 mL, 3 mL and 5 mL ammonium hydroxide respectively with a glass rod and then put in covered crucibles. The pg-C<sub>3</sub>N<sub>4</sub> was synthesized by heating the above mixture in a muffle furnace at 550 °C for 3 h, where the heating rate is 1 °C/min.

#### **1.3 Synthesis of Ag<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/C<sub>3</sub>N<sub>4</sub>**

0.2 g as-synthesized g-/pg-C<sub>3</sub>N<sub>4</sub> were added in 10 mL 30 mM AgNO<sub>3</sub> aqueous solution with magnetic stirring for 12 h under dark. Then adding 100 mL 1 mM H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> aqueous solution into the mixture solution with stirring for one hour. The desired Ag<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/C<sub>3</sub>N<sub>4</sub> nanocomposites can be obtained by centrifugation with a speed of 12000 rpm. The solid powder was washed by ultrapure water for three times. Afterwards the final catalyst was dried at 60 °C.

#### **1.4 Photocatalyst Characterization.**

The crystal structure of the resultant products was characterized by X-ray diffraction (XRD) using an X'Pert-ProMPD (Holand) D/max-γAX-ray diffractometer with Cu Kα radiation (λ=0.154178 nm). Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDS) spectroscopy were performed by a FEI-quanta 200 scanning electron microscope with an acceleration voltage of 20 kV. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images were obtained with a FEI-Tecnai F20 (200 kV), respectively. The TEM samples were prepared by dropping the solution onto a copper grid with polyvinyl supporting film and dried in air. Room temperature UV–Vis absorption was recorded using a Lambda 750 (Perking Elmer) spectrophotometer in the wavelength range of 300–800 nm. X-ray photoelectron spectroscopy (XPS) measurement was conducted to figure out the sample compositions with the PHI 5000 VersaProbe (Ulvac-phi company, Japan). Conversion was determined by GC analysis; the variance of values is estimated to be less than ±2%. For analysis the production of cyclohexane, the gas chromatograph (GC) were performed in a Varian 3400 GC column with a cross-linked 5 % PhMe silicone column (25 m × 0.20 mm × 0.33 μm) and a FID detector under the following conditions: carrier gas (N<sub>2</sub>) at 140 K; temperature program 60 °C, 1 min, 15 °C/min, 180 °C, 15 min; split ratio, 6:1; injector, 280 °C; detector, 280 °C. For detection the production of cyclooctene, the temperature program 60 °C, 1 min, 15 °C/min, 180 °C, 15 min; split ratio, 10 : 1;

injector, 300 °C; detector, 300 °C. The electro-catalysis actions were tested by a Model CHI 660C workstation (CH Instruments, Chenhua, Shanghai, China).

### 1.5 Photocatalysis activity test

The photocatalytic reactions were carried out in a quite mild condition. The reaction mixture of 0.5 g catalyst, 20 mL ultrapure water and 5 mL cyclooctene (cyclohexane) were magnetically stirred at 60 °C in a round bottom flask with a condenser pipe in oil bath for 6-48 h. Before photocatalysis experiment, the air was removed by bubbling nitrogen for 30 min. After that the top of condenser pipe was sealed with a rubber plug. The reaction was carried out under visible light (a cutoff filter was used to remove  $\lambda < 400$  nm light from the 300 W Xenon lamp). After reaction, the catalyst was separated by centrifugation and products were directly analyzed by GC and GC-MS.

### 1.6 Determination of electron transfer number.

The electron transfer number was studied by rotating Pt disk-Pt ring electrodes (RRDE). The  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}/\text{C}_3\text{N}_4$  modified glassy carbon electrode at a rotating speed of 1600 rpm in  $\text{N}_2$ -saturated ultrapure water. The disk potential was set at open circuit voltage under light irradiation ( $\lambda > 400$  nm). The ring potential was set at 0.9 V vs. SCE. A 300 W Xenon lamp was used as the light source with a cutoff filter to achieve  $\lambda > 400$  nm and positioned 3 cm away from the bottom of the RRDE.

The electron-transfer number (n) is calculated as follows:

$$n = \frac{4I_{\text{disk}}}{I_{\text{disk}} + I_{\text{ring}} / N}$$

Here N is the RRDE collection efficiency, measured to be 0.24.

### 1.7 Turnover frequency calculation.

Typically, for oxidation of water, the TON is expressed as the number of moles of oxidized cyclooctene (cyclohexane) per mole of active catalyst. The TON and TOF (turnover frequency, the number of molecules formed per active site per second) are calculated as follows (taking the situation of  $1.6 \times 10^{-5} \text{ g}_{\text{CDots}}/\text{g}_{\text{catalyst}}$  for example):

For the oxidation of cyclooctene,

$$\begin{aligned} \text{TON}_{\text{cyclooctene}} &= \frac{n_{\text{production}}}{n_{\text{Ag}_3\text{PW}_{12}\text{O}_{40}}} = \frac{n_{\text{oxidized cyclooctene}}}{\frac{m_{\text{Ag}_3\text{PW}_{12}\text{O}_{40}}}{3200.7}} = \frac{41.26\% \times 5 \times 0.848 / 110.2}{\frac{0.4}{3200.7}} \\ &= 127.03 \quad (1) \end{aligned}$$

$$\text{TOF}_{\text{cyclooctene}} (\text{h}^{-1}) = \frac{\text{TON}}{\tau} = \frac{127.03}{48} = 2.65 \quad (2)$$

For the oxidation of cyclohexane,

$$\begin{aligned} \text{TON}_{\text{cyclohexane}} &= \frac{n_{\text{production}}}{n_{\text{Ag}_3\text{PW}_{12}\text{O}_{40}}} = \frac{n_{\text{oxidized cyclohexane}}}{\frac{m_{\text{Ag}_3\text{PW}_{12}\text{O}_{40}}}{3200.7}} = \frac{8.62\% \times 5 \times 0.779 / 84.16}{\frac{0.4}{3200.7}} \\ &= 31.92 \quad (3) \end{aligned}$$

$$\text{TOF}_{\text{cyclohexane}} (\text{h}^{-1}) = \frac{\text{TON}}{\tau} = \frac{31.92}{48} = 0.67 \quad (4)$$

Table S1.  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}/\text{C}_3\text{N}_4$  catalyst for photocatalysis oxidation of cyclooctene under visible light (300 W Xenon lamp with a cutoff filter to achieve  $\lambda > 400$  nm).

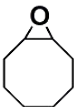
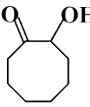
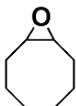
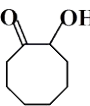
Reaction time (h)	Conversion (%)	Product selectivity (%)		Selectivity (%) $\sum_{\text{sel}}\text{C}_8$
				
0	0	0	0	0
6	9.29	58.6	41.3	99.9
12	18.39	62.5	37.1	99.6
24	27.67	68.1	31.1	99.2
36	34.81	73.3	25.6	98.9
48	41.26	77.2	21.4	98.6
Without catalyst	0	0	0	0

Table S2. Different catalyst for photocatalysis oxidation of cyclooctene.

Catalyst	Light	Conversion (%)	Product Selectivity (%)		Selectivity (%) $\sum_{\text{sel}}\text{C}_8$
					
$\text{Ag}_3\text{PW}_{12}\text{O}_{40}/\text{C}_3\text{N}_4$	Light	41.26	77.2	21.4	98.6
$\text{Ag}_3\text{PW}_{12}\text{O}_{40}/\text{C}_3\text{N}_4$	Dark	2.03	76.3	21.1	97.4
$\text{Ag}_3\text{PW}_{12}\text{O}_{40}$	Light	0.97	74.5	24.6	99.1
$\text{Ag}_3\text{PW}_{12}\text{O}_{40}$	Dark	0.89	72.6	26.3	98.9
$\text{C}_3\text{N}_4$	Light	9.25	78.1	21.7	99.8
$\text{C}_3\text{N}_4$	Dark	0.68	76.8	22.9	99.7

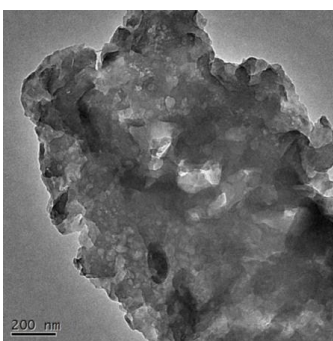
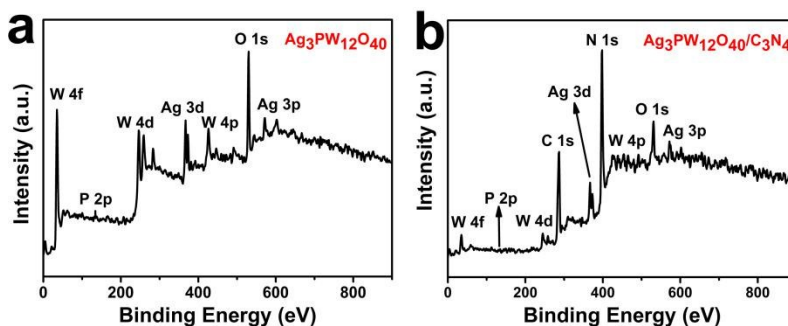
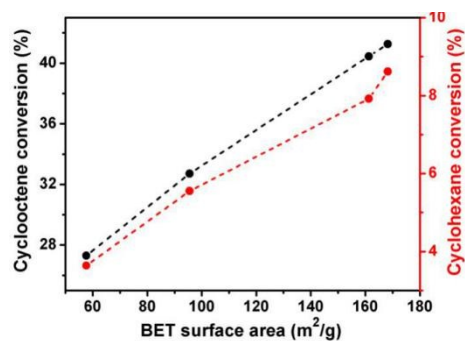


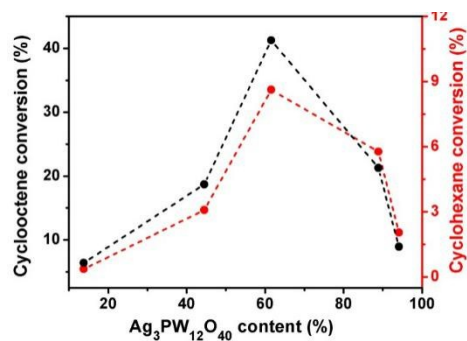
Figure S1. TEM image of  $\text{C}_3\text{N}_4$ .



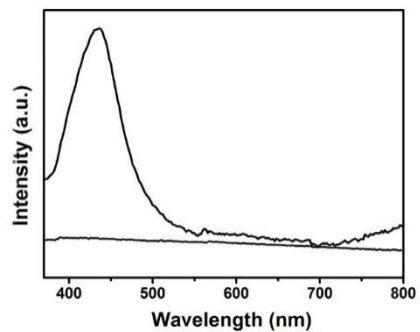
**Figure S2.** (a) XPS full spectrum of  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$  and (b)  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}/\text{C}_3\text{N}_4$ .



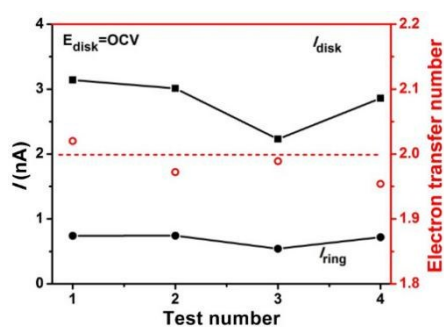
**Figure S3.** Conversion of cyclooctene and cyclohexane for  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}/\text{C}_3\text{N}_4$  with different BET surface area (the mass ratio of  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$  in the catalyst is 61.54 %).



**Figure S4.** Conversion of cyclooctene and cyclohexane for different content of  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$  to the catalyst (the mass ratio of  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$  to  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}/\text{C}_3\text{N}_4$ ). The data were derived by using an optimized  $\text{C}_3\text{N}_4$  (BET surface area is  $168.25 \text{ m}^2/\text{g}$ ) catalyst.



**Figure S5.** The UV-Vis absorption spectra of  $C_3N_4$  (the top line) and  $Ag_3PW_{12}O_{40}/C_3N_4$  (the bottom line) under light ( $\lambda > 400$  nm) respectively.



**Figure S6.** Pt disk-Pt ring electrodes (RRDE) measurements applying a rotation rate of 1600 rpm. The disk electrode is under  $\lambda > 400$  nm irradiation with potential kept at the open circuit voltage. The Pt ring was biased at 0.9 V vs. SCE. Note that the average charge transfer number of 2 (pointing to a  $2e^-$  process) was obtained.