Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Hybrid Catalysts of Molybdovanadophosphoric Acid and *g*-C_3N_4 with Tunable Bandgaps

Linkun Cai, Jie Hu, Mu Li and Panchao Yin [a]*

Experimental Section

General Method and Materials

All the reagents are commercially available and used without further purification. Fourier transform infrared spectroscopy (FTIR) tests were taken on VERTEX 70 infrared spectroscope. Thermogravimetric analyses (TGA) were obtained under a N_2 atmosphere on a NETZSCH TG 209 F1 Libra apparatu with the heating rate of 10°C·min^{-1} from 25 to 800 °C. Transmission electron microscope (TEM) images were taken on JEOL JEM-1400plus electron microscope equipped with German Bruker Electric Refrigeration Spectrometer Quantax 200 and XFlash 5030 T detector. WAXS were measured on a Xenocs Xeuss 2.0 HR SAXS/WAXS instrument with a MetalJet-D2 X-ray source and Pilatus3R detector. The scattering vector scale was calibrated using a silver behenate standard. The solid diffuse reflectance UV-vis spectra were recorded on a Varian Cary 5000 UV-vis spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD spectrometer. Binding energies were calibrated using a C 1s band (BE = 284.6 eV).

Catalyst Preparation.

As a hypothetical two-dimensional analog of graphene based on tri-*s*-triazine tectonic moieties, graphitic carbon nitride type materials are rich in the inherent ligands of NH_2/NH/=N, and direct protonation followed by adding a target counterion is a very convenient modification method[10]. The scheme shows the procedures for the surface modification of C_3N_4 and the subsequent immobilization of $PMo_{12-x}V_xO_{40}$ type heteropolyacids on the carbon nitride support. $H_3PMo_{12}O_{40}$ (PMo_{12}) was purchased from aladin company. $H_4PMo_{11}V_1O_{40}$ ($PMo_{11}V_1$), $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$), and $H_6PMo_9V_3O_{40}$ (PMo_9V_3) are prepared according to the previous report. Pristine g-C_3N_4 was prepared by thermally decomposing urea at 550 °C in an a porcelain crucible with a cover for 4 h in air with a ramp rate of 5 °C min^{-1}. g-C_3N_4 was received after cooling down to 25 °C. The protonation process was using a chemical exfoliation method.[12] The as prepared bulk g-C_3N_4 (1g) was mixed with 10ml of H_2SO_4(98 wt%) in a 20 ml flask and stirred for 10 h at room temperature. Then the mixture was slowly poured into 100 ml of deionized water and sonicated with 8h for exfoliation. After that, the above compound was centrifuged, and the deposition was washed by deionized water again and again. As most of the deposition could not be separated from the suspension by centrifugation, we obtained a stable colloidal suspension of p-C_3N_4 nanosheets. The concentration of p-C_3N_4 NSs was determined by drying specific volume liquor. Then the p-C_3N_4/ $PMo_{12-x}V_x$ nanocomposites were prepared by the electrostatic interaction of $[PMo_{12-x}V_x]^{-3-x}$ and p-C_3N_4 in acidic situation. The solution of $H_{3+x}PMo_{12-x}V_xO_{40}$ was dropwise added into the p-C_3N_4 NSs suspension (1mg ml^{-1}). The suspension was left for 1h stirring. All of p-C_3N_4 NSs was flocculated, the sediment was filtered, followed by washing with water and ethanol and finally dried in vacuum overnight.

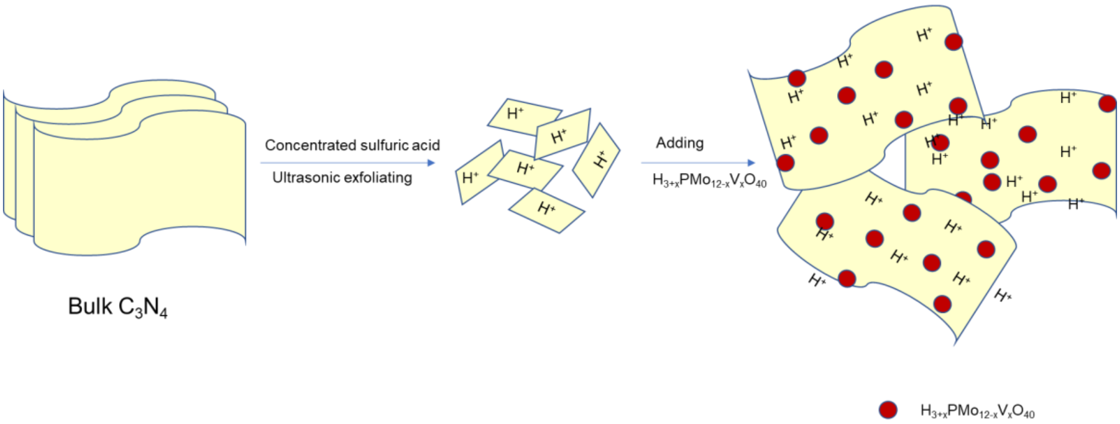
Catalytic Experiments

The catalytic performance of p-C_3N_4 and $PMo_{12-x}V_x$@C_3N_4 has been investigated in this study. We have selected the oxidation of methyl p-tolylsulfide with H_2O_2(35%) in CH_3CN (Scheme 1) as the target reaction to evaluate the catalytic efficiency of the hybrid catalysts. tert-Toyl sulfide (260 µL), H_2O_2 (30%, wt; 600µL), octane (130µL) and the catalysts, p-C_3N_4 or different loading types of $PMo_{12-x}V_x$@C_3N_4, were mixed in acetonitrile (6 mL). The reaction solution was kept at 40 °C using an oil bath, with stirring at 1000 rpm. GC-MS (CEAulight GC-7920) was used to monitor the reactions. Octane was used as standard to measure the relative concentration of reactant and products. Relative concentration of certain species was calculated as $c = (I_t/I_{octane,t})/(I_{sulfide,0}/I_{octane,0})$. The hybrid catalysts were recycled through centrifugation and washed with acetonitrile.

Electrochemical Studies

The cyclic voltammetry and the AC impedance measurements were performed using a three-electrode cell connected to an electrochemistry CHI 660 E workstation. The cell setup consisted of a saturated calomel electrode (SCE), a Pt wire, a carbon cloth electrode coated with the sample as reference, counter electrode and working electrode, and 1 M H_2SO_4 solution as the electrolyte. The working electrode was prepared as follows: active material sample (5 mg), conductive carbon black and polytetrafluoroethylene solution (60% in H_2O) were mixed in 1 mL ethanol with weight proportion of 85:10:5. After sonication for 10 minutes, a certain amount of suspension was drop-cast onto a carbon cloth substrate with an area of 1 cm^2 using a micropipette.

Mott-Schottky plots were measured in a different experimental setup. The samples were coated onto the ITO conductive glass by a casting method. The experiments were conducted in 0.05 M Na_2SO_4 solution in the dark at 1 kHz, 1.5 kHz and 2 kHz. The PH of the solution was measured after each test. The voltages measured were converted to reversible hydrogen electrode based on Nernst equation.



Scheme S1 Synthetic route of the hybrids.

Supplementary Physical and Chemical Characterizations

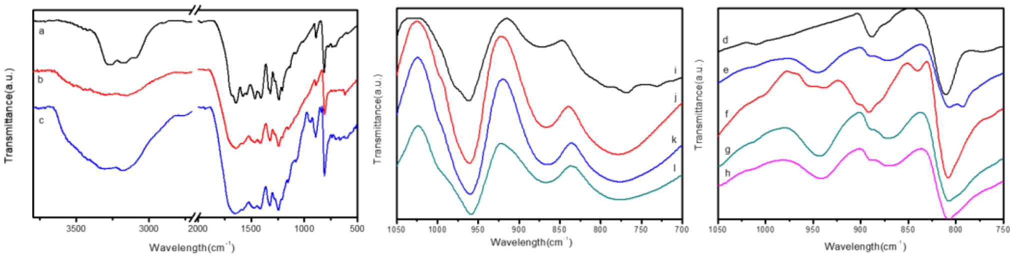


Fig. S1. FT-IR spectrum of the samples: pCN (a) (i) (d), V_0-CN (e), V_1-CN (f), V_2-CN (g), V_3-CN (h), PMo_{12} (i), $PMo_{11}V_1$ (j), $PMo_{11}V_1$ (k) $PMo_{11}V_1$ (l).

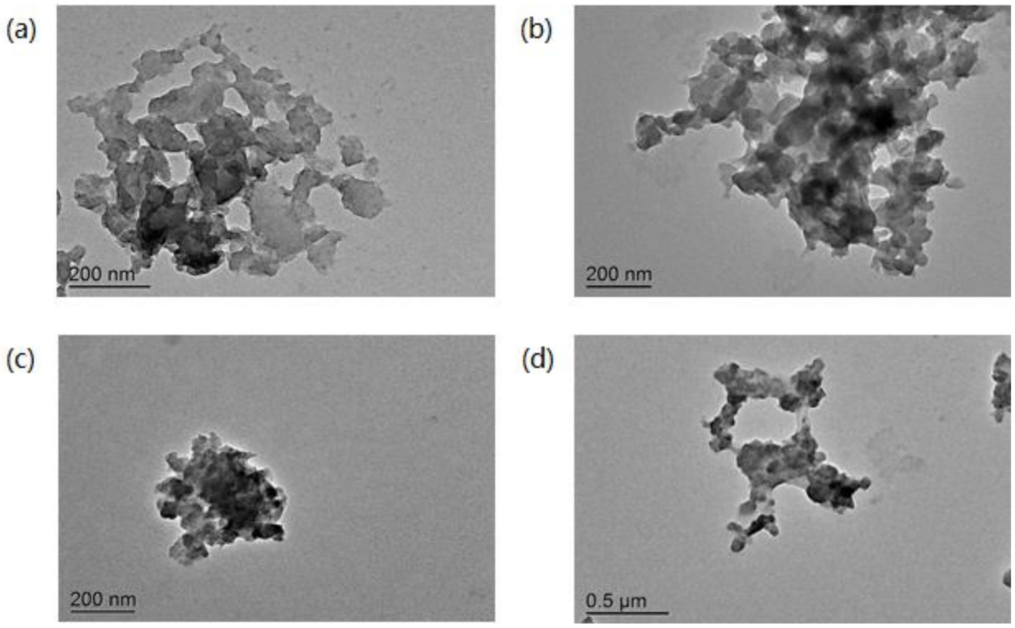


Fig. S2. TEM images of the V_0-CN (a), V_1-CN (b), V_2-CN (c), V_3-CN (d).

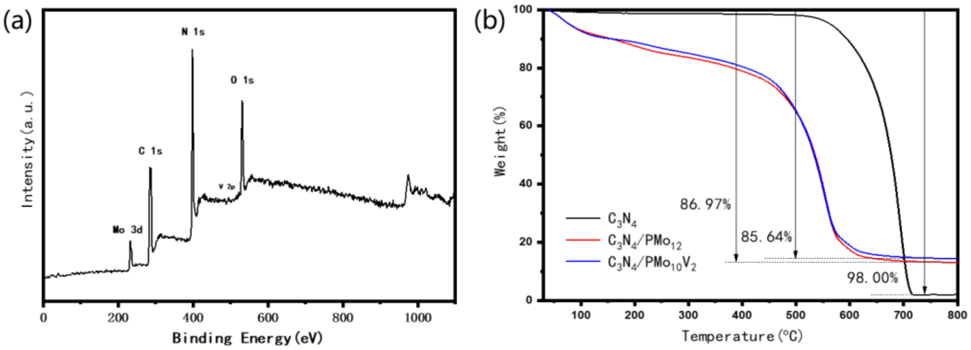


Fig. S3. XPS survey spectrum of V_3-CN; F) TGA curves of pCN, V_0-CN and V_2-CN.

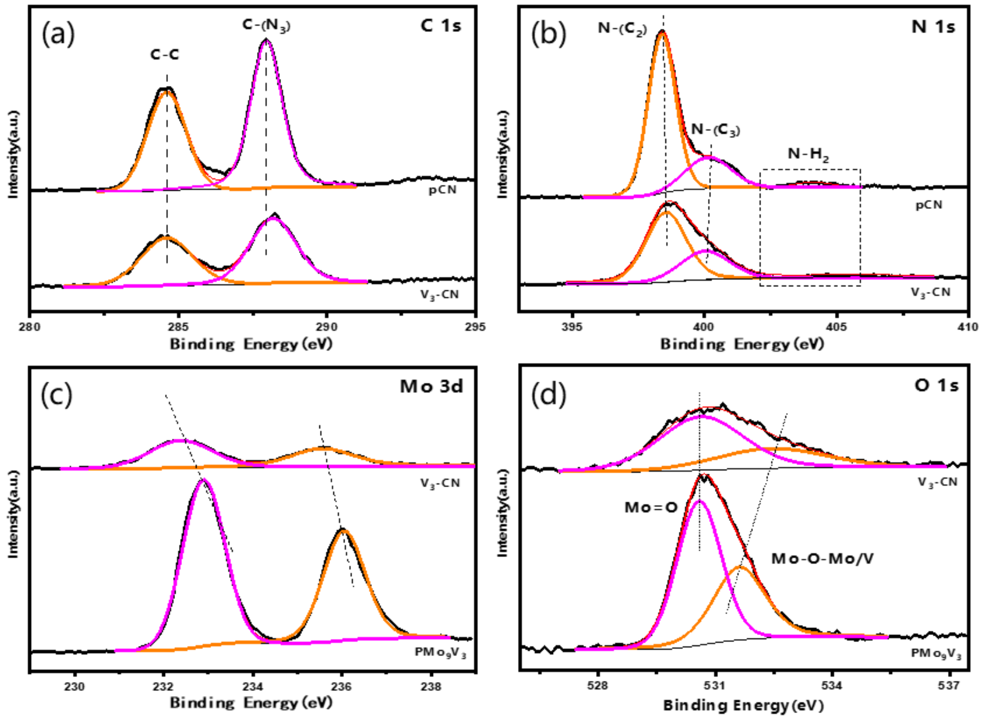


Fig. S4. a) C 1s and b) N 1s XPS spectra of unsupported pCN and the hybrid V_3-CN nanocomposite; c) Mo 3d and d) O 1s XPS spectra of pCN and V_3-CN.

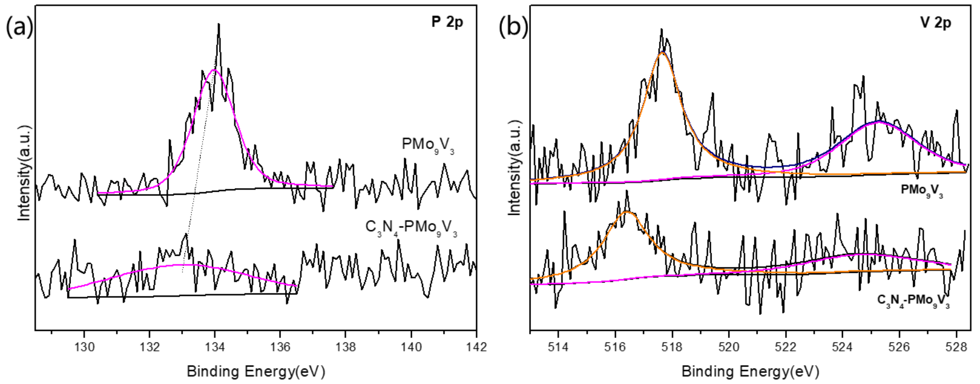


Fig. S5. (a) P 2p and XPS spectra of pCN and V_3-CN.

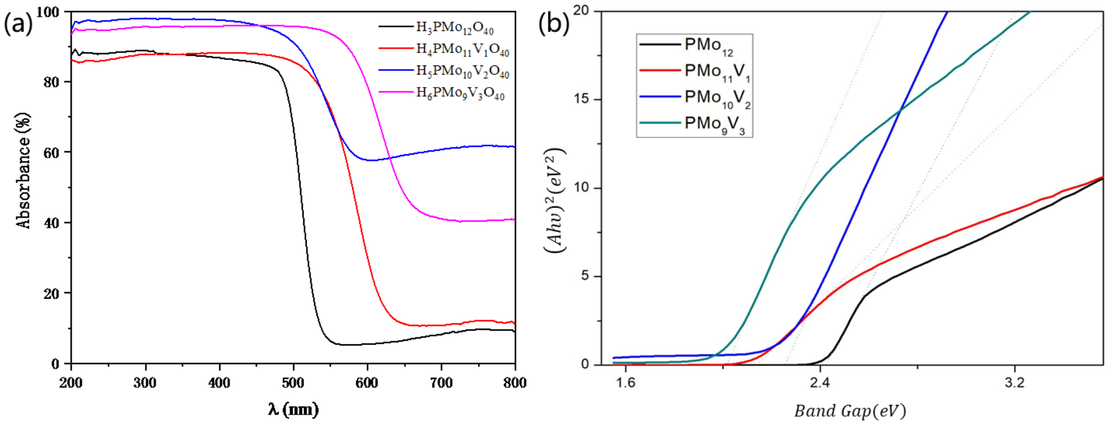


Fig. S6. DRS spectra and Tauc plot of the phosphovanadomolybdates ($H_{3+x}PMo_{12-x}V_xO_{40}$, x = 0~3).

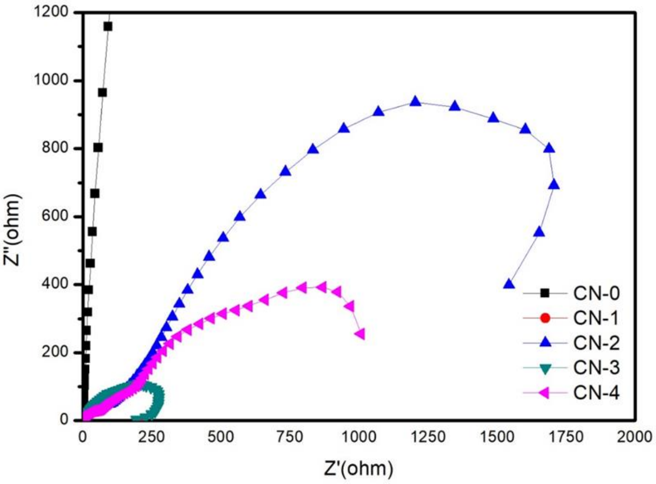


Fig. S7. Electrochemical impedance spectroscopy response for pCN, V_0-CN, V_1-CN, V_2-CN and V_3-CN, denoted as CN-0, CN-1, CN-2, CN-3, CN-4

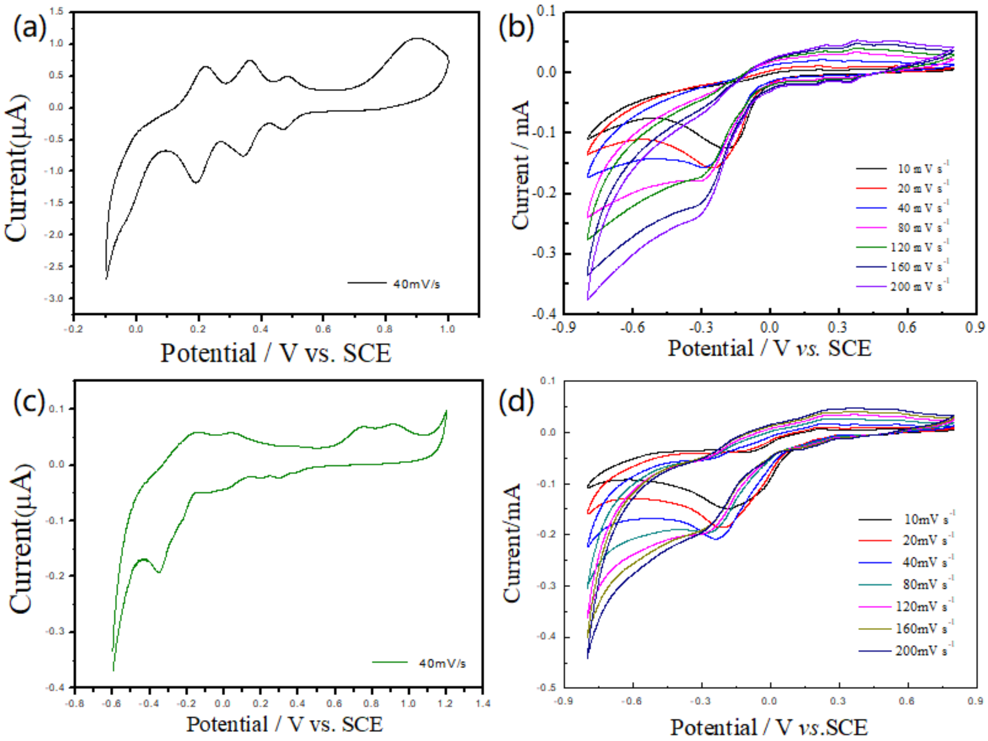


Fig. S8. Cyclic Voltammograms of V_0-CN (a), PMo_{12} (b), V_1-CN (c), $PMo_{11}V_1$ (d).

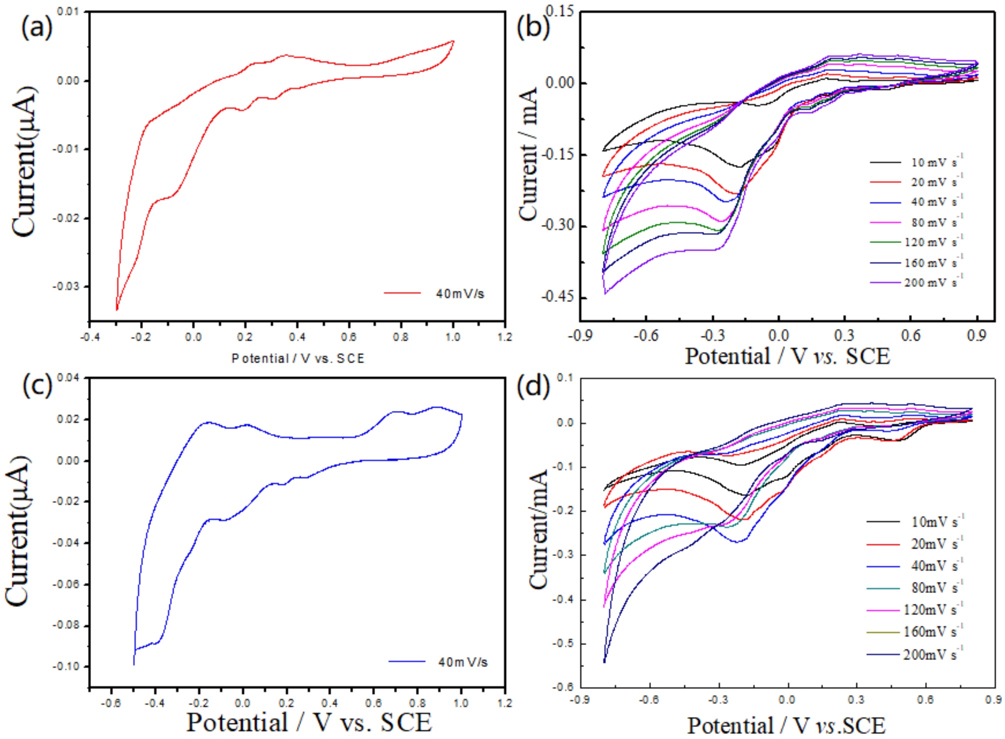


Fig. S9. Cyclic Voltammograms of V_0-CN (a), PMo_{12} (b), V_1-CN (c), $PMo_{11}V_1$ (d).

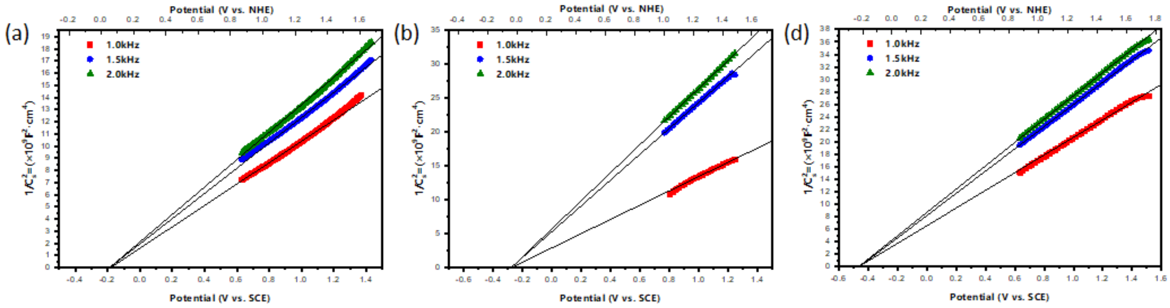


Fig. S10. Mott-Schottky plots of V_0-CN (a), V_1-CN (b), V_2-CN (c).

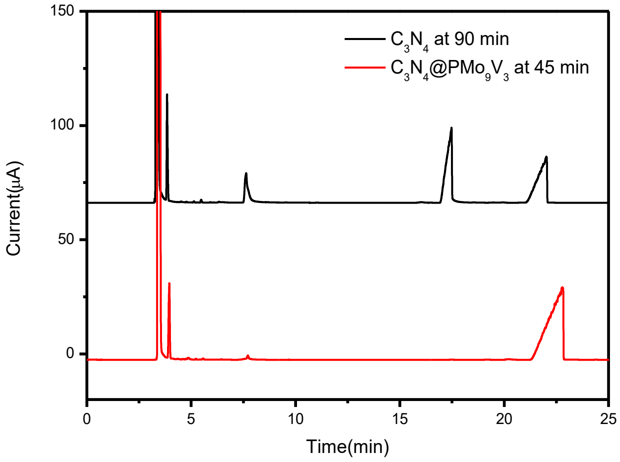


Fig. S11. Gas chromatography results of the catalytic experiments.

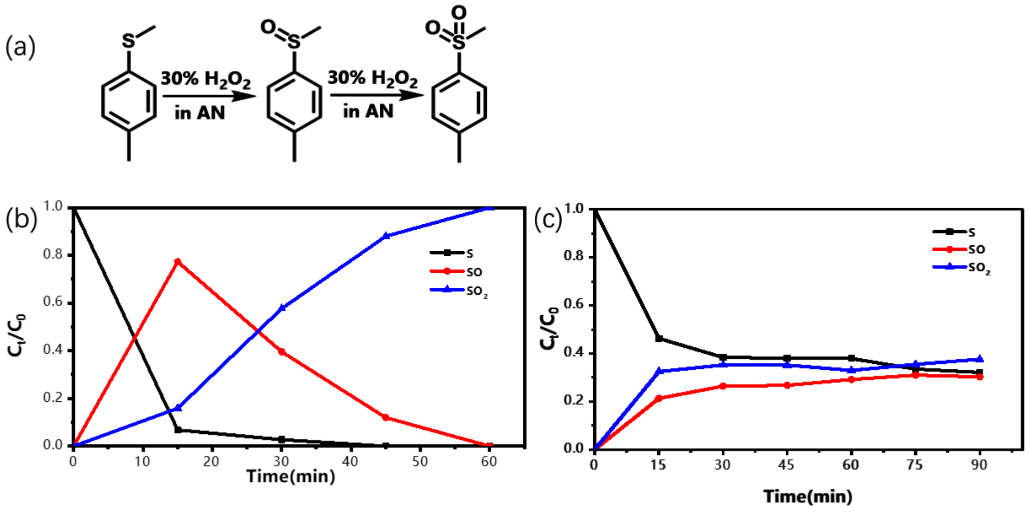


Fig. S12. Reaction scheme for the oxidation of sulfide catalyzed by the nanosheets (a); Kinetic curves of the concentrations of reactant and products in the reaction catalyzed by 10 mg pCN nanosheets (b) and V_3-C_3N_4 nanosheets (c) (S, P-tolysulfide; SO, sulfide monoxide; SO_2, sulfone)

Table S1 Catalytic results of the catalytic experiments in 90 min.

catalysts	Conversion rate of sulfide	Yield%
pCN	63%	36%
V_1-CN	95%	90%
V_2-CN	96%	92%
V_3-CN	99%	99%