

Construction of sp-C~O-V Interface for Selective Conversion of Methane to Methyl Hydroperoxide Under Mild Conditions

Fanle Bu, Jiayu Yan, Yurui Xue*

Shandong Provincial Key Laboratory for Science of Material Creation and Energy Conversion, Science Center for Material Creation and Energy Conversion, School of Chemistry and Chemical Engineering, Shandong University, Qingdao 266237, China.

*Corresponding author. Email: yrxue@sdu.edu.cn

Experimental method

Synthesis of V₂O₅/GDY

The monomer of hexaethynylbenzene was synthesized in good yield (62%) by addition of tetrabutylammonium fluoride to a tetrahydrofuran solution of hexakis-[(trimethylsilyl)ethynyl] benzene for 8 min at 0 °C. The graphdiyne (GDY) nanosheets was successfully on the surface of the copper foil in the presence of pyridine by a cross-coupling reaction of the monomer of hexaethynylbenzene for 72 h at 110 °C under a nitrogen atmosphere. After the reaction completed, the GDY powders were then removed from the copper foil ultrasonically and washed in turn with hot N, N-Dimethylformamide (DMF), hot acetone, 4M HCl, 2M aqueous NaOH, water and acetone. After drying under vacuum, GDY nanosheets powder was obtained.

6 mg of sodium metavanadate and 150 mg of GDY powder were added to 100 mL of deionized water, and the resulting mixture was subjected to ultrasonic treatment for 1 hour. Subsequently, the mixture was stirred at room temperature for 6 hours. Following this, the water was completely evaporated using a rotary evaporator. The resultant product was dried at 60 °C for 12 hours and then transferred into a quartz boat within a tubular furnace. Under an argon atmosphere, the sample was heated to 500 °C at a rate of 5 °C per minute and maintained at this temperature for 1 hour. Upon cooling, V₂O₅/GDY powder was obtained.

Characterization

Scanning electron microscopy (SEM) measurements were performed on a FEI Apreo SEM. Transmission electron microscope (TEM) and Energy dispersive spectrometer (EDS) elemental mapping images were recorded on a Talos F200X TEM at 200 kV. IR spectra were recorded with a Bruker Invenio S spectrometer with a resolution of 4 cm⁻¹, and each spectrum is an average of 64 scans. Raman spectra was measured by using HORIBA Raman spectrometer at 473 nm laser excitation wavelength. The X-ray photoelectron spectra (XPS) were recorded on an ESCALab-250 X photoelectron spectrometer using an Al K α source (1486.6 eV). XRD measurements were acquired by a Bruker D8 Advance operated at 30 kV voltage and 15 mA current using a Cu K α radiation ($\lambda=0.15406$ nm) at a step width of 4° min⁻¹. Electron paramagnetic resonance measurements were performed at room temperature using a Bruker EMX-10/12 EPR spectrometer operated in the X-band frequency using the following parameters: microwave frequency of 9.8 GZ, microwave power of 20 mW, modulation frequency of 100 kHz, and a 10 dB attenuator. The X-ray absorption spectroscopy experiments at the V K edge were conducted on the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF). V foil were used as reference sample. All spectra were recorded in transmission mode at room temperature.

The sample intended for in situ infrared spectroscopy was placed in a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) cell (Harrick Scientific Products, Praying Mantis™). This cell was linked to a flow system that facilitates the recording of spectra as gases flow through and around the sample. Prior to measurements, the samples in the infrared cell underwent a pretreatment at 200 °C for 1 hour and were then cooled to 70 °C under a flow of argon (30 ml/min). The infrared spectrum obtained at this stage acted as the background reference. Afterward, methane CH₄ and H₂O₂ were added to the gas stream, during which time-resolved spectra were gathered.

Catalysis test

Typically, H₂O (8 mL), catalyst (5 mg), H₂O₂ (2 ml), and CH₄ (3 MPa) were added to a 40 mL Teflon-lined stainless steel reactor. The reactor was sealed and purged with CH₄ five times to remove air. Then, the stirrer was started when the reactor temperature reached 70 °C. This moment serves as the starting point for the reaction time. After the reaction, the reactor was placed in ice water to quench the reaction, and the catalyst was separated from the solution with a filter. Liquid-state NMR experiments were measured on a Bruker Avance III 600 MHz spectrometer equipped with pulsed field gradient and ultralow-temperature probes; this is a highly accurate approach with high detection sensitivity and high reproducibility. The gas produced after the catalytic reaction was analyzed using a FULI GC9790 II gas chromatograph. For isotopic studies, methane that was ≥99% enriched with ¹³C was utilized to trace the carbon source in the resulting products.

To assess the catalyst's reusability, the following procedure was applied. After the initial reaction cycle, the catalyst (5 mg) was rinsed with deionized water and centrifuged multiple times, then left to dry overnight at room temperature in a vacuum desiccator. This dried catalyst was later tested again under identical reaction conditions to evaluate its performance in the second cycle.

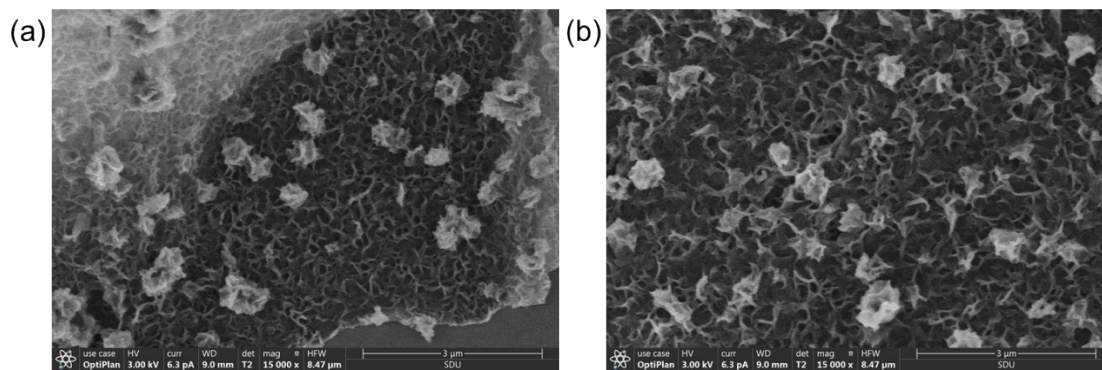


Fig. S1. SEM images of GDY (a) and V₂O₅/GDY (b).

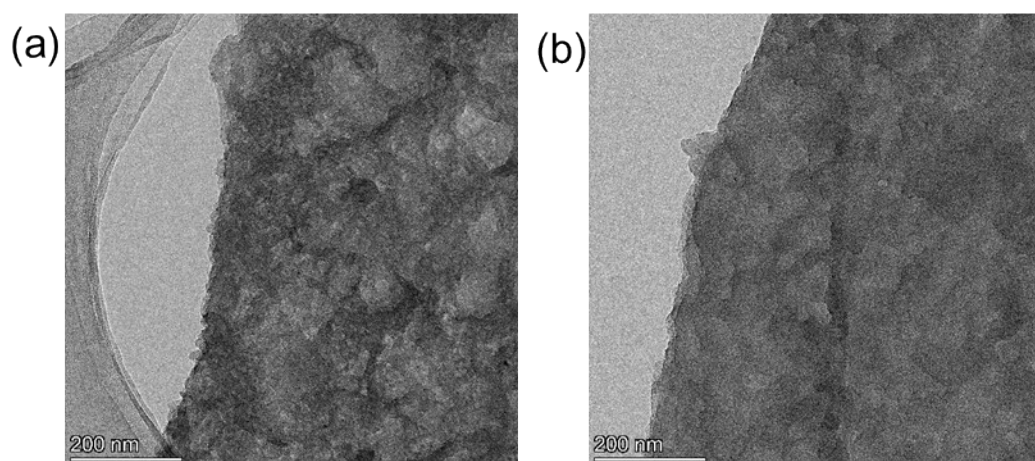


Fig. S2. TEM images of GDY (a) and V₂O₅/GDY (b).

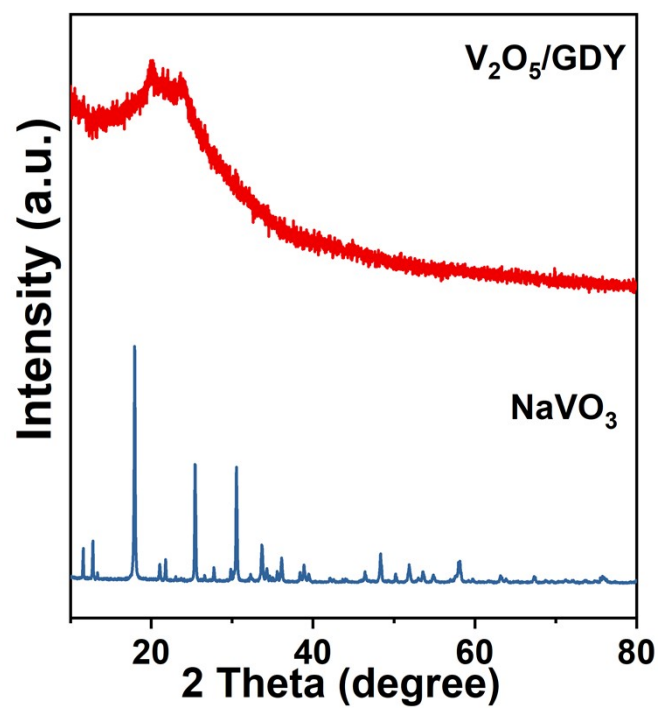


Fig. S3. X-ray diffraction patterns of $NaVO_3$ and V_2O_5/GDY .

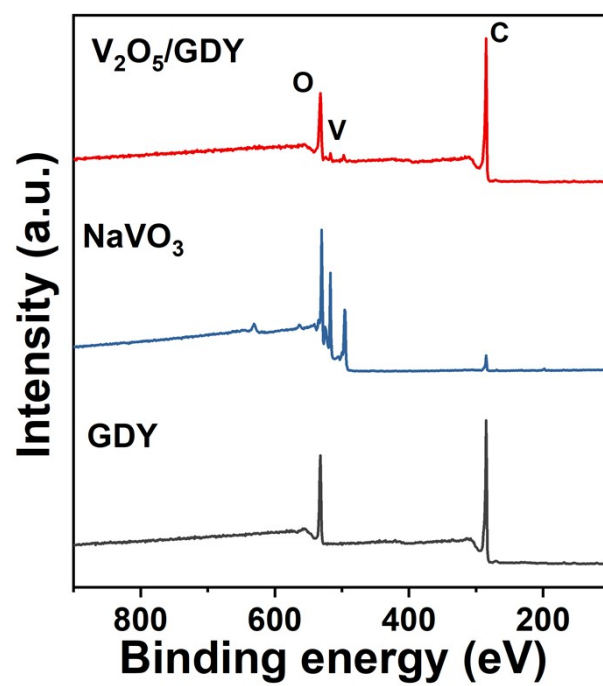


Fig. S4. XPS survey spectra of GDY, NaVO₃ and V₂O₅/GDY.

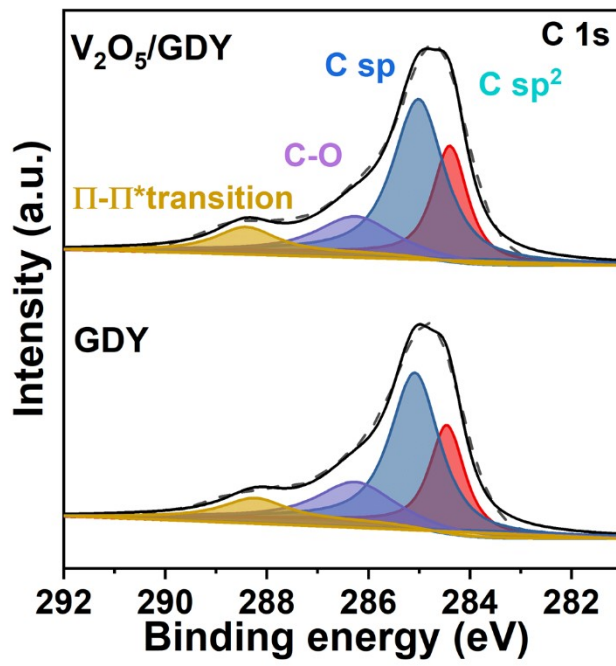


Fig. S5. C 1s XPS spectra of GDY and V_2O_5/GDY .

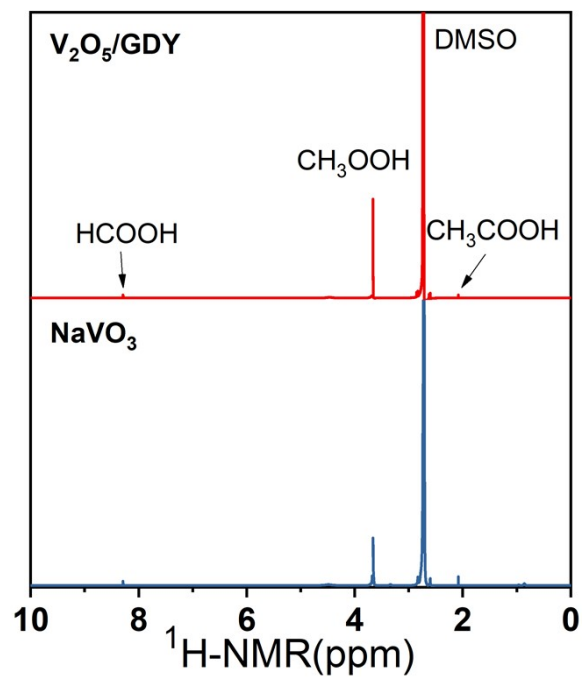


Fig. S6. ^1H NMR spectrum of liquid products over GDY, NaVO_3 and $\text{V}_2\text{O}_5/\text{GDY}$. Test conditions: Pressure (CH_4) = 3.0 MPa, Catalyst: 5 mg, 2 mL H_2O_2 , 8 mL H_2O , 70 $^\circ\text{C}$, reaction for 1 h.

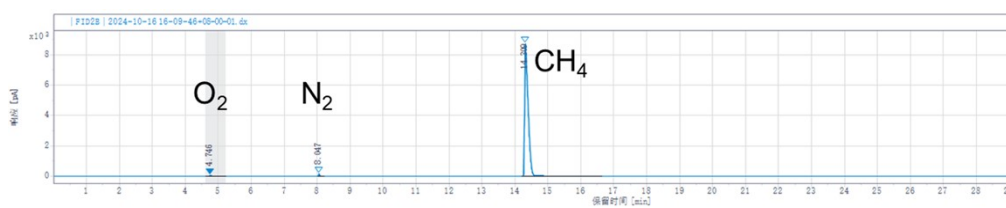


Fig. S7. The GC spectra of gaseous products over NaVO₃. Test conditions: Pressure (CH₄) = 3.0 MPa, Catalyst: 5 mg, 2 mL H₂O₂, 8 mL H₂O, 70 °C, reaction for 1 h. In the detection signal, O₂ (4.75 min) and CH₄ (14.3 min) were detected, while no signals of CO (4.9 min) and CO₂ (5.5 min) were observed.

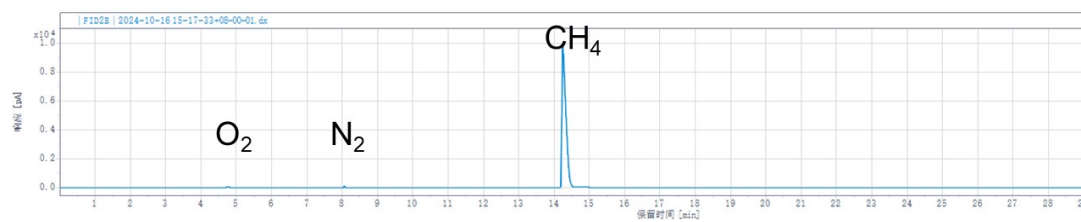


Fig. S8. The GC spectra of gaseous products over V_2O_5/GDY . Test conditions: Pressure (CH_4) = 3.0 MPa, Catalyst: 5 mg, 2 mL H_2O_2 , 8 mL H_2O , 70 °C, reaction for 1 h. In the detection signal, O_2 (4.75 min) and CH_4 (14.3 min) were detected, while no signals of CO (4.9 min) and CO_2 (5.5 min) were observed.

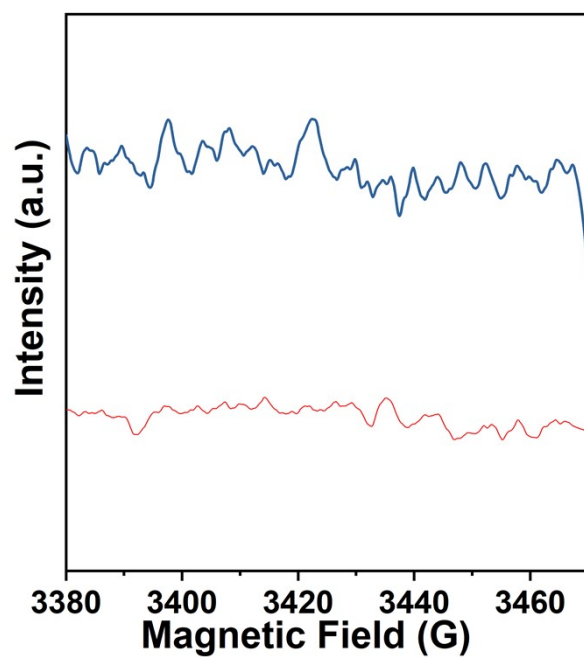


Fig.S9. EPR of NaVO₃, the blue and red line represents the EPR signal for *OOH and *OH, respectively. Reaction conditions: 5 mg catalyst, 8 mL H₂O or CH₃OH, 1 mL H₂O₂, 3.0 MPa CH₄ at 70°C for 5 min. Add a 100 ul DMPO as trapping agent under the same conditions to complete the free radical trapping experiment.

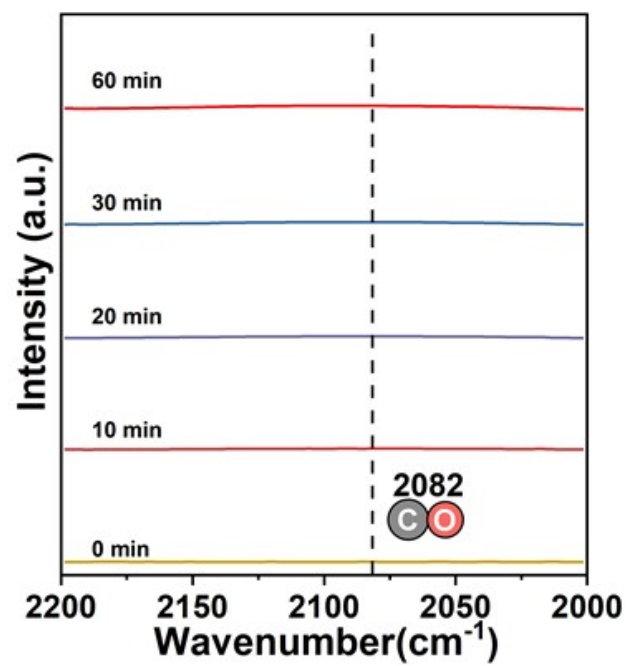


Fig.S10. In situ DRIFTS Spectra on V₂O₅/GDY under 1 atm of CH₄ at 70°C.

Table S1. The best-fit parameters of V K-Edge EXAFS Data for V₂O₅/GDY.

| Sample | Shell | CN | R(Å) | $\sigma^2 \times 10^{-3}(\text{Å}^2)$ | R-factor (%) | ΔE_0 (eV) |
|------------------------------------|------------------|-----|-----------|---------------------------------------|--------------|-------------------|
| V ₂ O ₅ /GDY | V-O ₁ | 0.9 | 1.80±0.01 | 5.2±3.8 | 0.7 | 8.11±3.73 |
| | V-O ₂ | 1.5 | 2.05±0.02 | 3.6±1.8 | | |
| | V-O-V | 1.1 | 2.71±0.01 | 8.2±2.4 | | |

Table S2. Oxidation properties of CH₄ on different catalysts.

| Sample Product | GDY | | NaVO ₃ | | V ₂ O ₅ /GDY | |
|----------------------|------|------|-------------------|------|------------------------------------|------|
| | P | S | P | S | P | S |
| HCOOH | 0.00 | 0.00 | 3.36 | 31.9 | 2.37 | 11.0 |
| CH ₃ OOH | 0.00 | 0.00 | 6.17 | 58.5 | 18.41 | 85.2 |
| CH ₃ COOH | 0.00 | 0.00 | 1.01 | 9.6 | 0.83 | 3.8 |

P represent productivity (mmol/g_{cat}/h), S represent Selectivity (%). Reaction conditions: 5 mg catalyst, 8 mL H₂O, 2 mL H₂O₂, 3.0 MPa CH₄, reaction at 70 °C for 1 h.