

Electronic Supplementary Information (ESI)

VOPO₄•2H₂O Encapsulated in Graphene Oxide as a Heterogeneous Catalyst for Selective Hydroxylation of Benzene to Phenol

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1. Experimental

1.1. Material synthesis

1.1.1. Synthesis of VOPO₄•2H₂O

VOPO₄•2H₂O was synthesized according to reported procedure with slight modifications.¹ V₂O₅ powder (0.50g) was dissolved in distilled water (12mL). Subsequently, H₃PO₄ (4.81g, 85%) was added into the dissolved mixture in a round bottom flask. The mixture was stirred and heated at 130 °C for 16 h, and then cooled down to room temperature and filtered. Distilled water and acetone were used to wash the obtained sample. Further drying was carried out by leaving the sample in an air oven at 120 °C overnight. The resultant yellow colored material was denoted as VPO for further studies.

1.1.2. Exfoliation of VOPO₄•2H₂O

A suspension of powdered VOPO₄•2H₂O (0.1 g) in isopropyl alcohol (50 mL) was placed in a round bottom flask (100 mL) equipped with a condenser, which was heated stepwise at 70°C, 80°C and 90°C with intervals of 30 min under vigorous stirring to obtain a yellow homogeneous solution of exfoliated VOPO₄.

1.1.3. Preparation of Graphene Oxide (GO)

GO was prepared by a modified Hammer's method.² Graphite (0.5 g) was suspended in concentrated H₂SO₄ (15 mL) under ice bath. KMnO₄ (1.5g) was added gradually with stirring. The mixture was stirred at 50°C for 3h, followed by the addition of distilled water (35mL). After stirring for 15min, distilled water (150 mL) was added to terminate the reaction. Then, H₂O₂ (10mL, 30%) was added and the solution color changed into bright yellow. The mixture was then washed with HCl solution (250mL, 10%) and distilled water. In order to exfoliate the oxidized graphite, the product was treated with an ultrasonic probe at 250W for 1h and centrifuged at 8000rpm for 30min. and the supernatant liquid was collected. The process was repeated three times and the supernatant (600mL) was collected as GO stock suspension. GO stock suspension (100mL) was mixed with NaOH (5g) and sodium monochloro acetate (5g), and the mixture was sonicated for 2h to convert the OH groups into COOH groups. The mixture was then washed with distilled water repeatedly until well-dispersed GO suspension was obtained.

1.1.4. Preparation of VPO@GO

Exfoliated VOPO₄•2H₂O (12.5 mL) in isopropyl alcohol (4mg/mL) was taken in a round bottom flask. GO in water (10 mL, 1mg/mL) was added dropwise with constant stirring at 90°C. After the completion of the GO addition, the resultant mixture was stirred at 90°C for another 6 h followed by aging the mixture at 70°C for 1h. Finally, the dark colored precipitate was collected by centrifugation while the mixture was hot. The product was washed with isopropyl alcohol several times and dried at 100°C.

1.1.5. Preparation of VPO@GO_mix

Powdered $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (10 mg) was suspended in GO aqueous solution (10 mL, 1mg/mL) in a round bottom flask (100 mL), and the suspension was sonicated at room temperature for 15 min. After that, H_2O was removed in vacuo, leaving a dark green colored solid. The solid was dried in vacuum oven.

1.2. Catalytic Evaluation

The catalytic tests were carried out in a two-necked round bottom flask. In a typical experiment, benzene (0.36 mL, 4 mmol) was added to an acetonitrile solution (10 mL) containing VPO@GO with benzene:V = 400:1. In order to avoid immediate decomposition of H_2O_2 and strong effervescence, H_2O_2 (1.36 mL, 30%) was added slowly to the mixture solution over a period of 1 h. The resulting mixture was stirred under 250 rpm at 60 °C for 8 h. The reaction mixture was first analyzed by Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela LC for identification of the reactants and products. The products were then quantified using an Agilent 6890 GC system equipped with a flame ionization detector.

1.3. Catalyst Characterization

The powder X-ray diffraction (PXRD) measurements were taken on a Bruker D8 diffractometer using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. FTIR spectra were recorded on a Perkin-Elmer 1760X FT-IR spectrometer with the sample powder diluted in KBr (1%). Typically 16 scans with a resolution of 4 cm^{-1} were collected for each sample. Scanning electron microscopy (SEM) images were collected on a field emission JSM-6700F (JEOL) machine. XPS analysis was carried out by a SPECS HSA3500 plus spectrometer using Mg X-ray source. N_2 adsorption/desorption measurements were conducted using an autosorp-IQ instrument from Quantachrome Instruments Corporation to calculate the specific surface areas of the materials. Thermo Fischer iCAP 6000 series ICP-OES was used for performing trace metal analysis. Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela LC and Agilent 6890 GC system equipped with a flame ionization detector were used for analysis of the reaction products.

2. Characterization of GO

2.1. FTIR of GO

The FTIR spectrum of GO prepared by Hummers method indicates the presence of various oxygen functionalities. The peaks at 3404 cm^{-1} , 1718 cm^{-1} , 1618 cm^{-1} , 1254 cm^{-1} and 1085 cm^{-1} correspond to O-H stretching, C=O stretching, C=C stretching, C-O-C stretching and C-OH stretching, respectively. These characteristic peaks demonstrate the presence of carboxyl, carbonyl, sp^2 -hybridized C=C, epoxide and hydroxyl functional groups in GO.

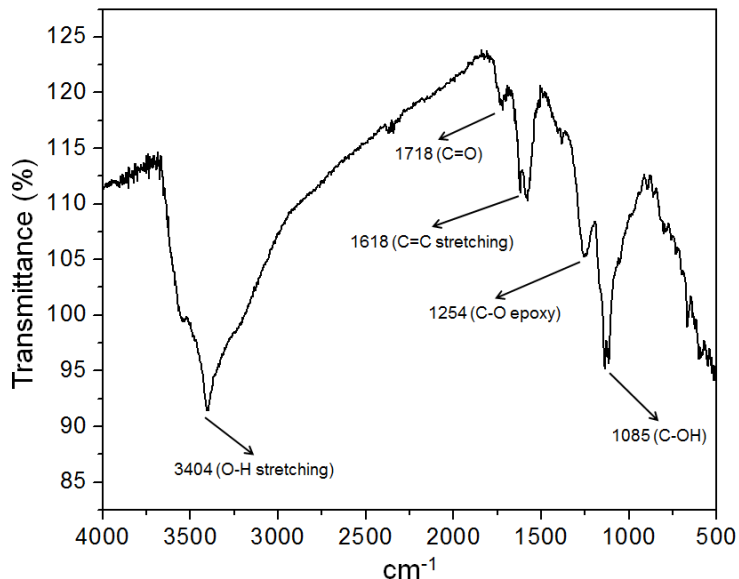


Figure S1: FTIR spectrum of GO.

2.2. Raman Spectroscopy

The Raman spectrum of GO (Figure S2) shows a broad G band at 1595 cm⁻¹, which is related to the C-C vibrations of the sp²-hybridized carbon atoms in the hexagonal lattice. Compared to pristine graphite, there is a blue shift in the G band by 15 cm⁻¹ from 1580 cm⁻¹,³ due to the presence of defects and the isolation of double bonds. There is also a prominent D band at 1349 cm⁻¹, which is assigned to the disorder band. The D band has similar intensity to the G band, which implies that the graphite was oxidized to a large extent, resulting in the generation of sp³ domains and the consequent disruption of the sp²-hybridized carbon atoms to give rise to the resonance in the Raman spectrum. From these results, it can be concluded that GO prepared by Hummers method was successful.

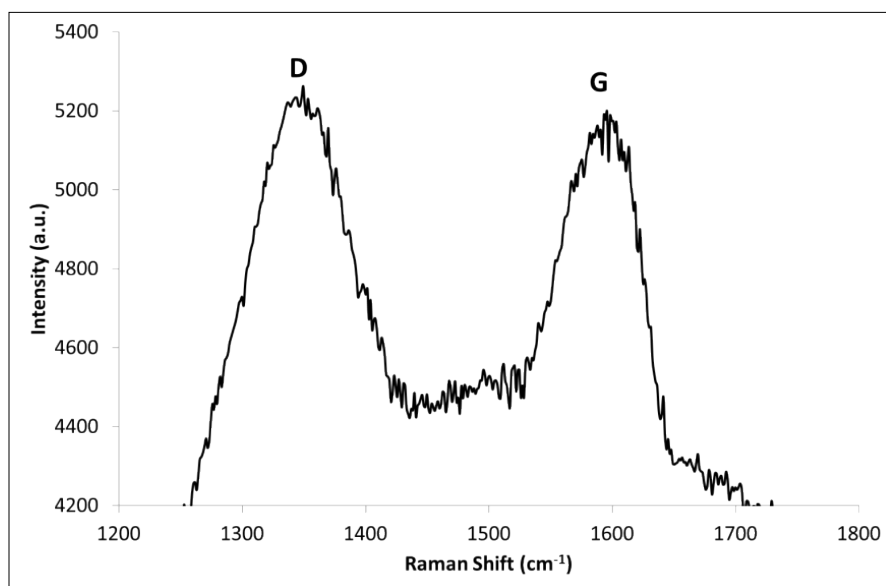


Figure S2: Raman spectrum of GO.

2.3. TEM Analysis of GO

The TEM image (Figure S3) reveals single layers of GO with sharp edges and flat surface.

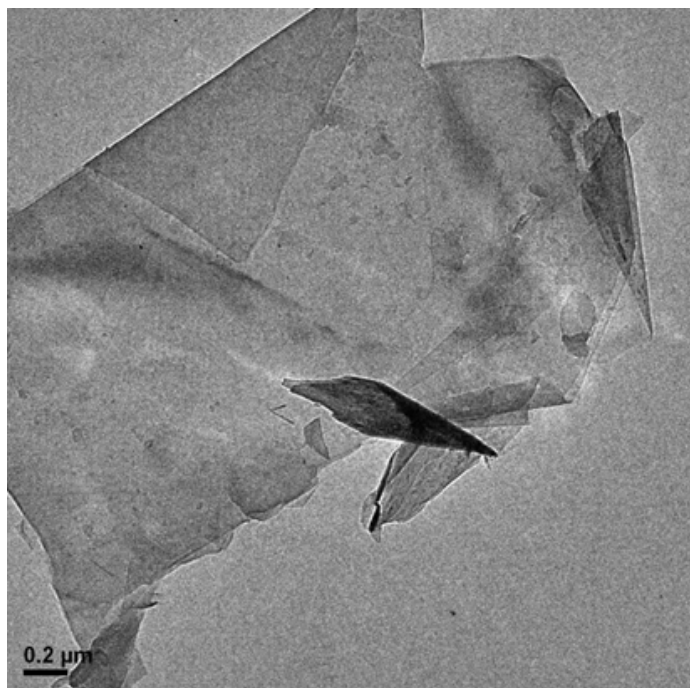


Figure S3: TEM image of GO.

3. Characterization of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{VPO}@GO$

3.1. Powder X-ray Diffraction (XRD)

The powder XRD pattern (Figure S4) of synthesized VPO shows all the characteristic diffraction peaks, which confirm the successful synthesis of the required $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ phase. The presence of the reflection at $2\theta = 11.86$ due to the 001 plane indicates the lamellar structure of VPO with an interlayer spacing of 7.4\AA .^{1,4} On the other hand, $\text{VPO}@GO$ also shows a similar powder XRD pattern to that of VPO, indicating the structural retention of the VPO phase even after incorporating with GO. However, broadened VPO peaks can be observed in the case of $\text{VPO}@GO$, demonstrating some losses of crystallinity in the VPO phase of the hybrid material. Moreover, there is an obvious decrease in the intensity of the [001] reflection whereas an increase in the intensity of the [200] reflection.

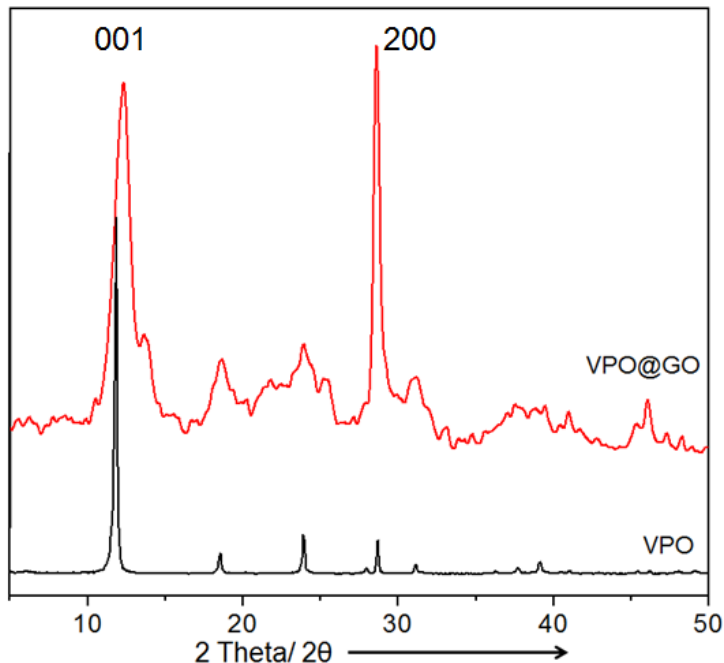


Figure S4: Powder XRD analysis of VPO and VPO@GO.

3.2 FTIR Spectra of VPO and VPO@GO

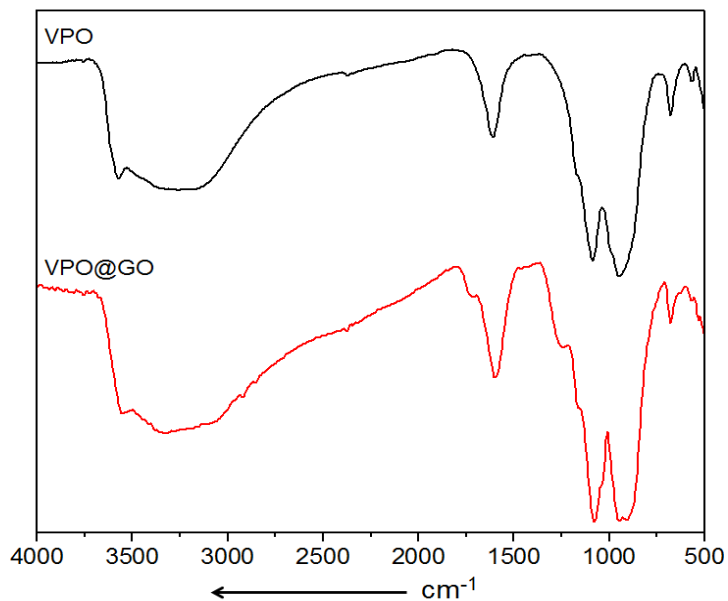


Figure S5: FTIR spectra of VPO and VPO@GO.

The FTIR spectra (Figure S5) show that both VPO and VPO@GO have similar signals at 947, 1038, 1088 and 1164 cm^{-1} , which can be attributed to various functionalities of VPO.^{1,4} In addition to these bands, VPO@GO shows additional peaks at 1725, 1296 and 896 cm^{-1} mainly due to the oxygenated species in the GO. In addition, there are several peaks in the region of 2800-3000 cm^{-1} on account of the C-H stretch from GO. This analysis indicates clearly that the

VPO@GO hybrid is a combination of GO and VPO without any distortion of individual components.

3.3 TEM Analysis of VPO@GO

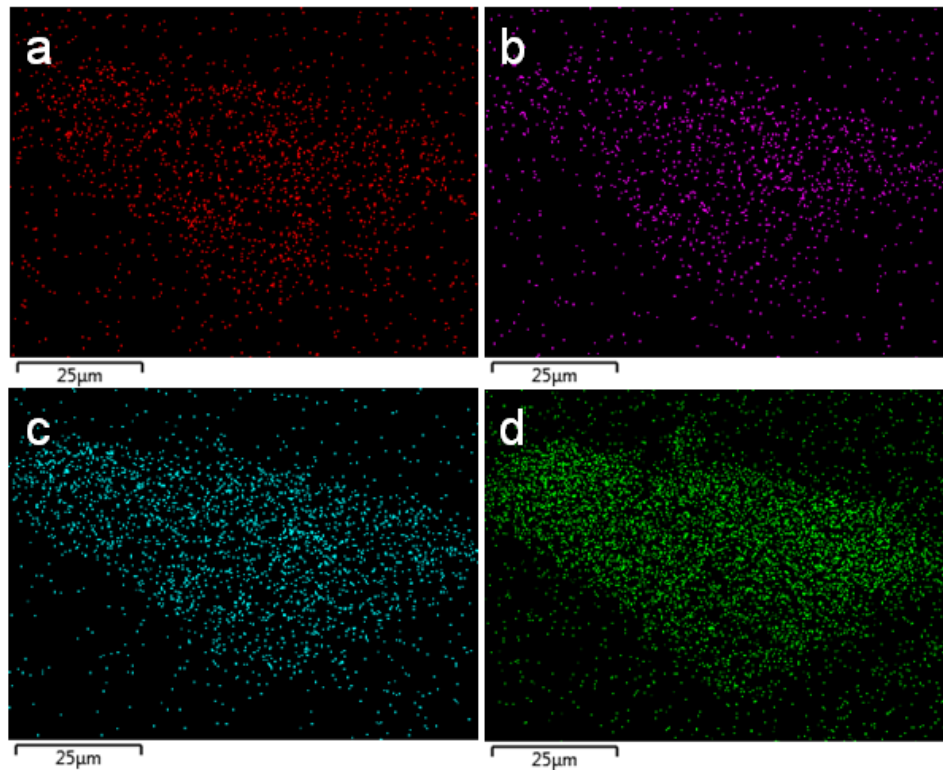


Figure S6: Energy-dispersive X-ray images of VPO@GO for four elements: (a) V, (b) P, (c) O, and (d) C.

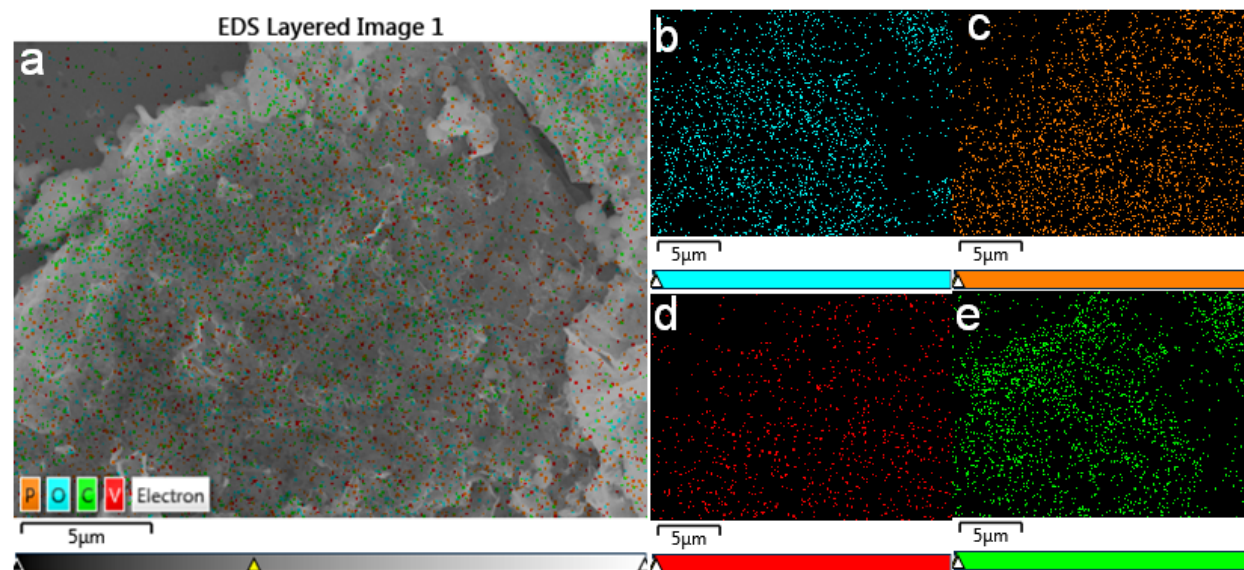


Figure S7: Energy-dispersive X-ray overlay image of (a) VPO@GO_U, and mapping images for four elements: (b) V, (c) P, (d) O, and (e) C.

3.4. Isothermal N₂ Adsorption/Desorption Measurements

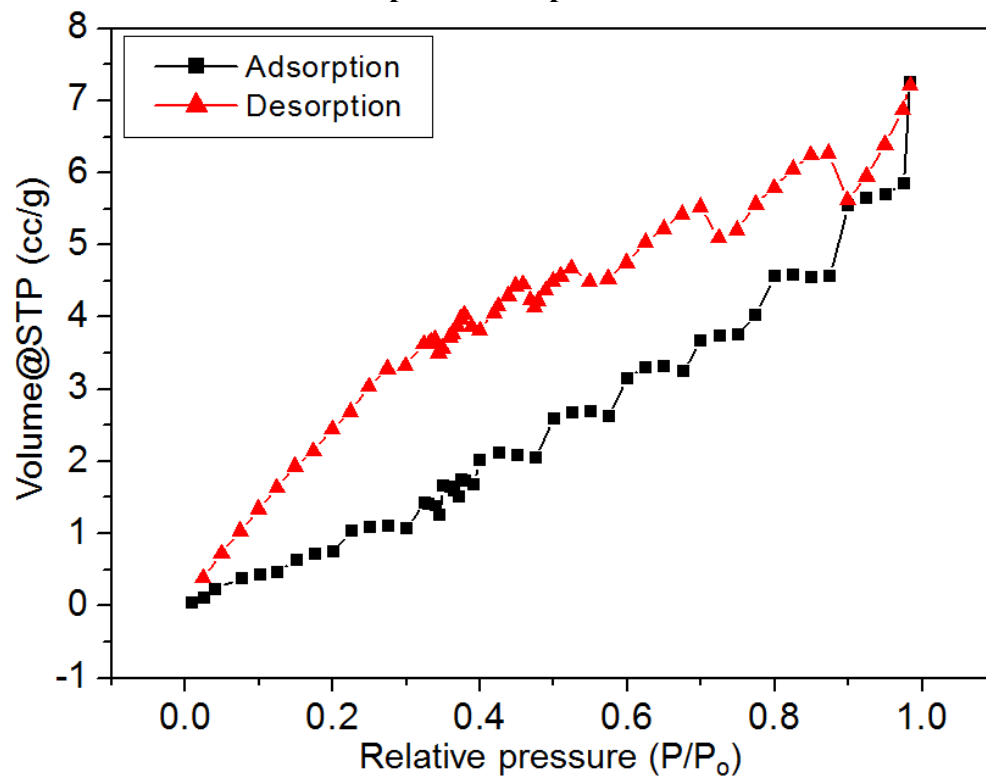


Figure S8: N₂ isotherm of VOPO₄•2H₂O.

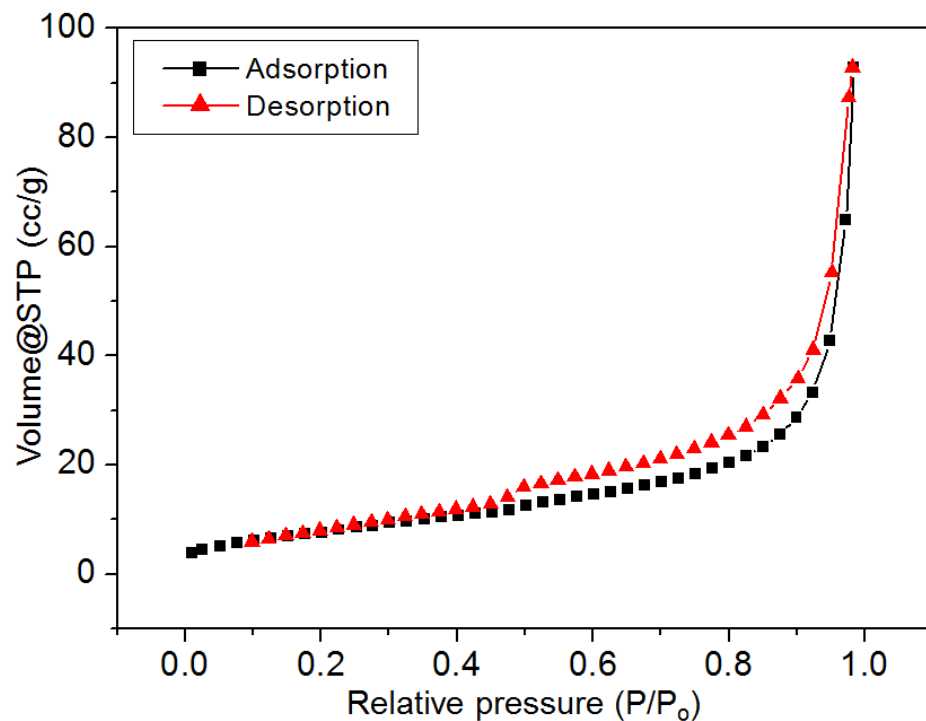


Figure S9: N₂ isotherm of VPO@GO.

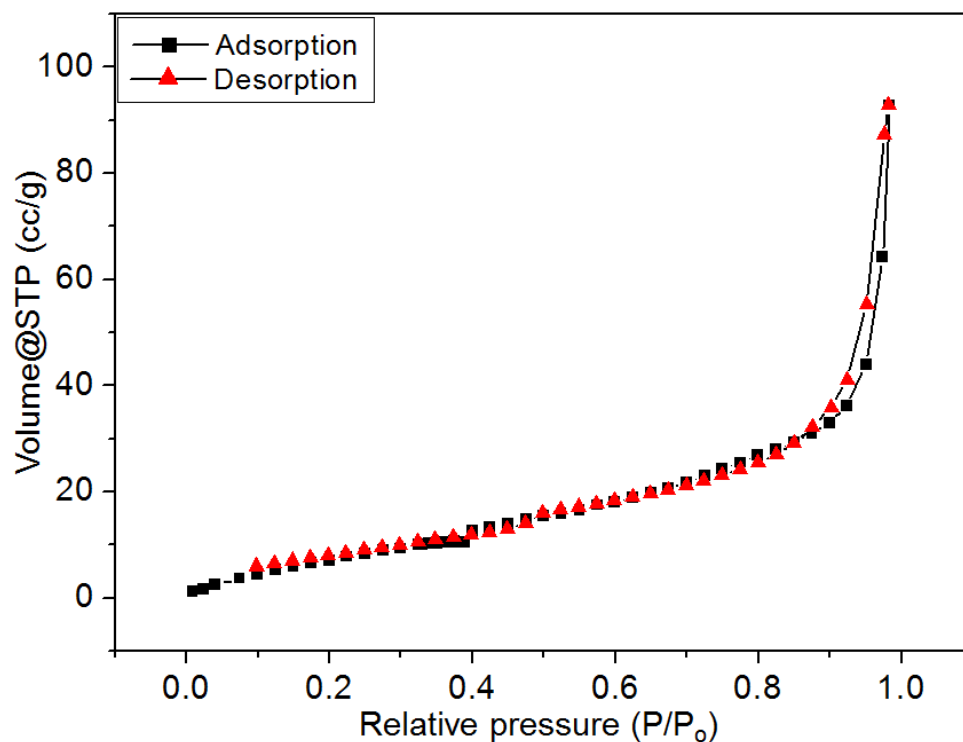


Figure S10: N_2 isotherm of VPO@GO_U.

3.5. XPS Analysis of $VOPO_4 \cdot 2H_2O$, VPO@GO and VPO@GO_U

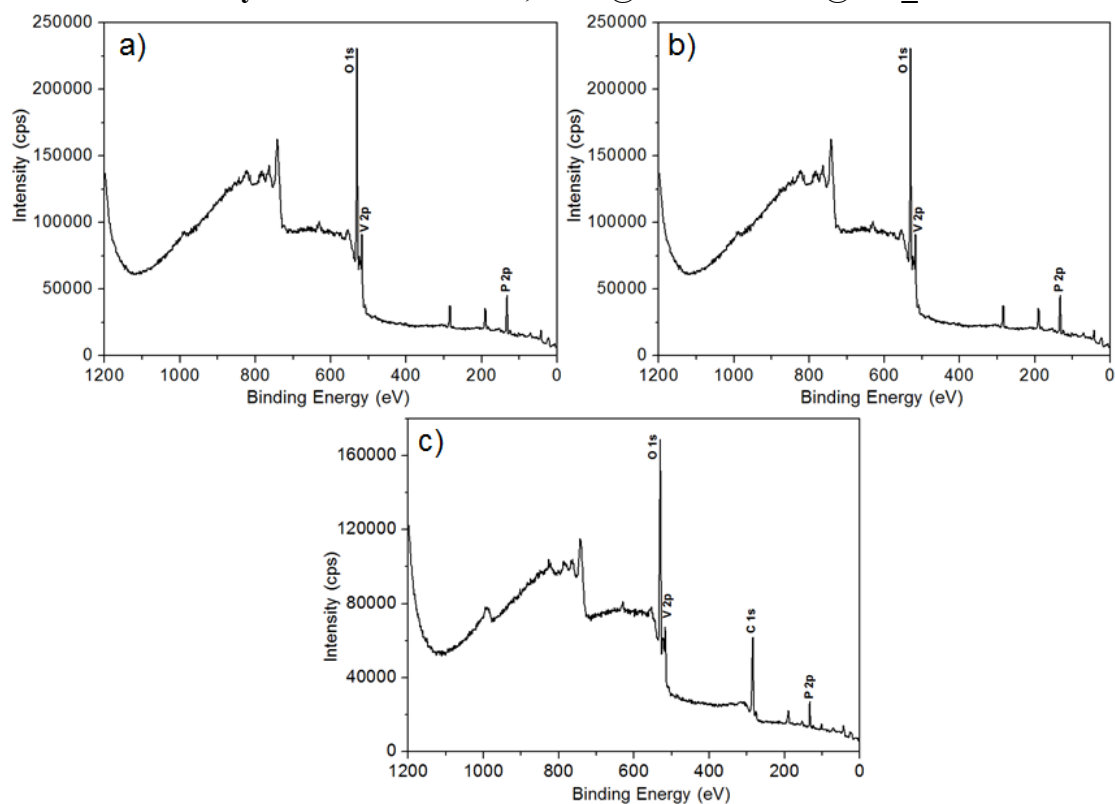


Figure S11: XPS survey spectra of (a) $VOPO_4 \cdot 2H_2O$, (b) VPO@GO, and (c) VPO@GO_U.

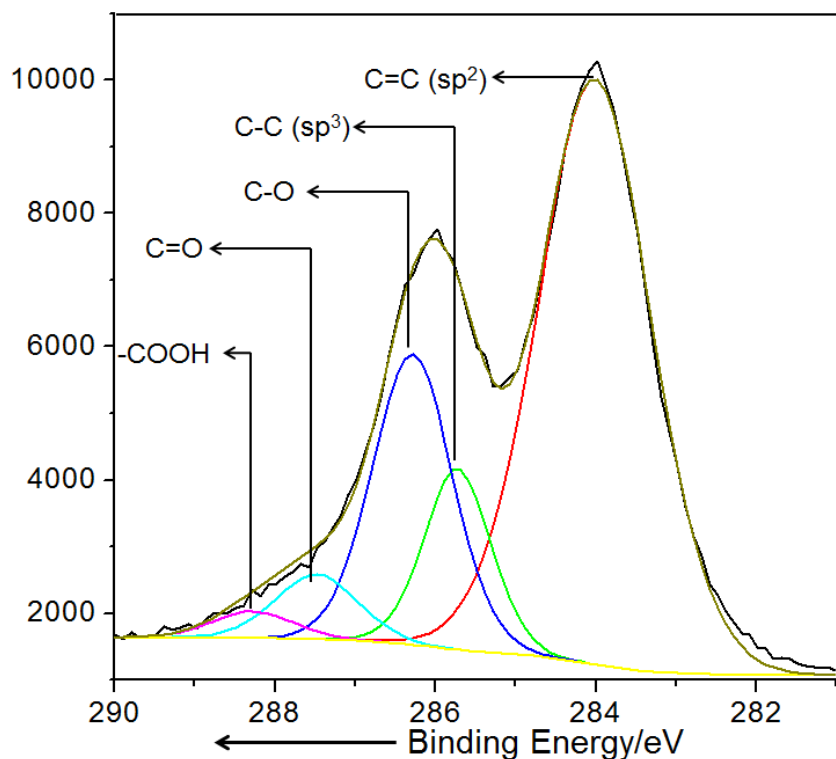


Figure S12: Resolved XPS spectrum of VPO@GO in C 1s region.

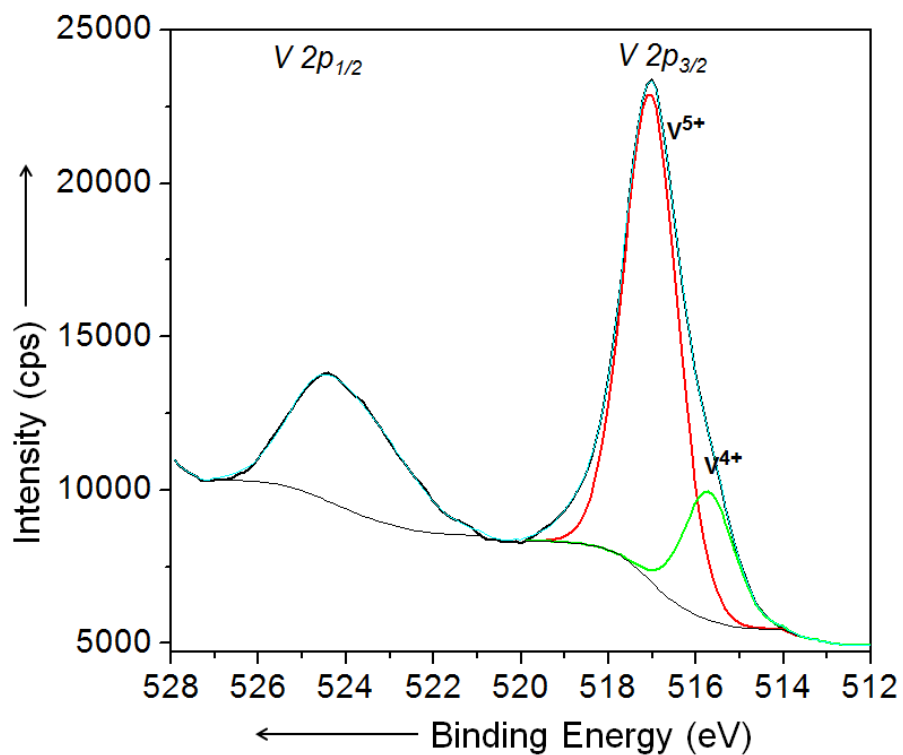


Figure S13: High resolution XPS spectrum of exfoliated VPO in V2p.

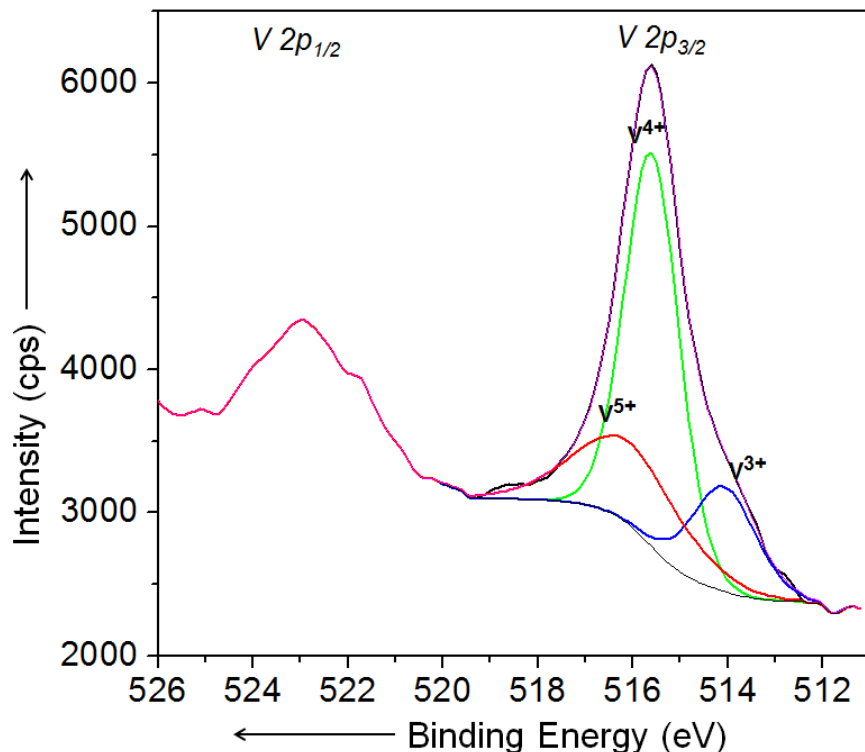


Figure S14: High resolution XPS spectrum of VPO@GO_U in V2p region.

4. Catalytic Evaluation

4.1. Catalytic Optimization

4.1.1. Optimization of Catalyst Loading

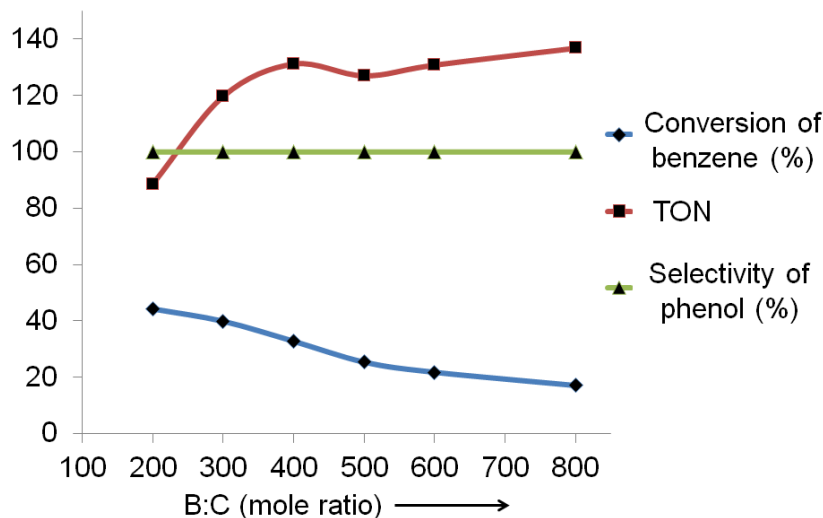


Figure S15: Catalytic activity of VPO@GO as a function of benzene/V (B:C) molar ratio. Reaction conditions: benzene:H₂O₂=1:3 (mole) at 60°C in acetonitrile for 8h. Selectivity = 100 X (total no. of moles of phenol formed / total moles of benzene converted). TON = turnover number calculated by moles of phenol formed / one mole of V in the catalyst.

Study on the variation of the catalytic activity with respect to the benzene : vanadium (B:C) mole ratio at 60°C using VPO@GO as the catalyst indicates a decrease in the benzene conversion upon decreasing catalyst amount. On the other hand, the TON changes slightly from B:C = 800 to 400, maximizes at 400 and then decreases gradually. This change can probably be ascribed to higher decomposition of H₂O₂ when larger amount of the catalyst was used. Considering higher TON and conversion in mind, a B:C value of 400 was regarded as the optimum for this reaction.

4.1.2. Optimization of H₂O₂

A variation of the benzene-to-phenol conversion as a function of the benzene/H₂O₂ molar ratio (B:H) was also examined. A selectivity of 100% for the phenol formation was observed when the benzene/H₂O₂ molar ratio was between 1:1 to 1:3. Although a significant increase of the benzene conversion was observed when B:H was above 1:3, other essential catalytic parameters such as selectivity and E_o decreased. Therefore, a B:H value of 1:3 that offers the highest E_o of 10.9 was considered as the optimum for further studies.

Table S1. Catalytic activity of VPO@GO as a function of benzene/H₂O₂ (B:H) molar ratio.

B:H	Conversion	TON	Selectivity	TOF	E _o
1:1	6.0	24.0	100	24.0	6.0
1:2	13.2	52.8	100	52.8	6.6
1:3	32.8	131.2	100	131.2	10.9
1:4	39.0	156.0	97	151.3	9.5
1:5	44.1	176.4	91	160.5	8.0
1:6	46.3	185.2	84	155.6	6.5

Reaction conditions: B:C = 400:1 (mole) at 60°C in acetonitrile for 8h. Selectivity = 100 X (total no. of moles of phenol formed / total moles of benzene converted). TON = turnover number calculated by moles of benzene converted / one mole of V in the catalyst. TOF = turnover number frequency calculated by moles of phenol formed / one mole of V in the catalyst. E_o = H₂O₂ efficiency calculated by 100 X (moles of phenol formed / total moles of H₂O₂ added).

4.1.3. Optimization of Reaction Temperature

Table S2. Catalytic activity of VPO@GO as function of reaction temperature.

Temperature (°C)	Conversion of Benzene (%)	TON	Selectivity for Phenol (%)	TOF
25	4.0	16.0	100	16.0
40	27.0	108.0	100	108.0
50	29.8	119.0	100	119.0
60	32.8	131.2	100	131.2
80/reflux	30.2	120.8	93	112.4

Reaction conditions: B:H=1:3 (mole), B:C=400:1 (mole) in acetonitrile for 8h. Selectivity= 100 X (total no. of moles of phenol formed/total moles of benzene converted). TON = turnover number calculated by moles of benzene converted/one mole of V in the catalyst. TOF = turnover number frequency calculated by moles of phenol formed/one mole of V in the catalyst.

Studies on the effect of temperature on the reaction indicate that when increasing temperature (up to 60°C), the conversion increased to 32.8% with TOF of 131.2. The conversion then decreased on further increase in temperature, probably due to uncontrolled decomposition of H₂O₂.

4.1.4. Optimization of Reaction Time

The evaluation of the catalyst activity as a function of reaction time showed that the maximum TOF and selectivity were observed at 8 h.

Table S3. Catalytic activity of VPO@GO as a function of reaction time.

Reaction Time (h)	Conversion of Benzene (%)	TON	Selectivity for Phenol (%)	TOF
4	22.2	88.8	100	88.8
6	28.9	115.6	100	115.6
8	32.8	131.2	100	131.2
12	34.1	136.4	95	129.6
24	38.8	155.2	78	121.0

Reaction conditions: B:H = 1:3 (mole), B:C = 400:1 (mole) at 60°C in acetonitrile. Selectivity = 100 X (total no. of moles of phenol formed / total moles of benzene converted). TON = turnover number calculated by moles of benzene converted / one mole of V in the catalyst. TOF = turnover number frequency calculated by moles of phenol formed / one mole of V in the catalyst.

4.1.5. Optimization of Solvent

Table S4. Catalytic activity of VPO@GO as a function of solvent.

No	Solvent	Results from GC (%)	
		Benzene conversion	Phenol selectivity
1	Acetonitrile	32.8	100
2	H ₂ O	Trace	-
3	No solvent	Trace	-
4	Methanol	25	100
5	Isopropanol	27	100
6	Dichloromethane	8	69
7	Chloroform	12	76

The catalyst activity was examined by using different solvents. From the results, it was evident that acetonitrile is the most suitable solvent for this catalytic reaction. No significant catalytic activities were observed in the case of H₂O and solvent free system. Alcohols were found to be favorable for the catalysis, although the benzene conversions were lower than that in the case of acetonitrile. Water immiscible solvents such as chloroform (CHCl₃) and dichloromethane

(DCM) were found to be less efficient. Severe aggregation of catalyst was also observed in entries 6 and 7 of Table S4. Preferential existence of catalyst with aqueous H₂O₂ could be the reason for low selectivity of phenol production in the case of DCM and CHCl₃.

4.2. Hot Filtration Test

The hot filtration test was conducted to investigate the heterogeneous nature of VPO@GO and to make sure that no leaching of V occurred during the catalysis. In this test, benzene (0.36 mL, 4 mmol) was added to an acetonitrile solution (10 mL) containing VPO@GO with Benzene:V = 400:1. In order to avoid immediate decomposition of H₂O₂ and strong effervescence, H₂O₂ (1.36 mL, 30%) was added slowly to the mixture solution over a period of 1 h. The resulting mixture was stirred under 250 rpm at 60 °C for 8h and then the catalyst was filtered off from the hot reaction mixture. Then, the benzene conversion was determined from the collected filtrate and it was found to be 32.8%. The reaction was continued in the filtrate at the same reaction temperature for another 5 h. But, no increase in the conversion was observed. After the completion of the reaction, no detectable leaching of vanadium was found by ICP-MS analysis.

4.3. Carbon Balance

Table S5. Calculation of carbon balance (CB) for the oxidation of benzene using various catalysts.

No	Catalyst	C before oxidation (mmol)	C after oxidation (mmol)							CB (%)	
			BZ	BZ	PH	HQ	BQ	CA	MA		Total
1	No catalyst	24	23.96	-	-	-	-	-	-	24.96	99.8
2	VPO@GO	24	16.12	7.81	-	-	-	-	-	23.93	99.7
3	GO	24	23.94	-	-	-	-	-	-	23.94	99.6
4	VPO@GO_mix	24	18.97	4.36	0.24	0.06	0.08	-	-	23.71	98.8
5	VOPO ₄ •2H ₂ O	24	19.67	3.70	0.25	-	0.09	0.07	-	23.78	99.1
6	V ₂ O ₅	24	19.69	3.57	0.21	-	0.12	0.07	-	23.66	98.6
7	VOHPO ₄ •0.5H ₂ O	24	15.37	8.68	-	-	-	-	-	24.05	100.2

Reaction conditions: benzene:V = 400:1 (mole), benzene:H₂O₂ = 1:3 (mole) at 60°C in acetonitrile for 8h. CB: carbon balance; BZ: benzene; PH: phenol; HQ: hydroquinone; BQ: benzoquinone; CA: catechol; MA: maleic anhydride. Carbon balance (CB) = [{(total no. of carbon (in mmol) present in the reaction mixture after catalysis) / (total no. of carbon (in mmol) present in the reaction mixture before catalysis)} X 100] %.

References:

- (1) P. Borah and A. Datta, *Appl. Catal. A*, 2010, **376**, 19.
- (2) W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- (3) S. Sreejith, X. Ma and Y. Zhao, *J. Am. Chem. Soc.*, 2012, **134**, 17346.
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