

Electronic Supplementary Information

Sustainable and efficient protocol for the synthesis of RGO-VPO composite with synergetic stability and reactivity

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Synthesis of VPO precursor:

The VPO precursor was prepared according to the procedure as follows: V₂O₅ (5.0 g, SBMC, 98.5%) and o-H₃PO₄ (30 ml, 85% Aldrich) was refluxed in deionised water (120 ml) for 24 h. The yellow solid was recovered by vacuum filtration, washed with cold water (100 ml) and acetone (100 ml) and dried in air (110 °C, 24 h). Powder X-ray diffraction studies confirmed that the solid was the dihydrate, VOPO₄.2H₂O¹.

The dihydrate (4 g) was refluxed with isobutanol (80 ml, 99%, Spectrochem) for 21 h, and the resulting hemi hydrate was recovered by filtration, dried in air (110 °C, 16 h), refluxed in deionised water (9 ml H₂O/solid(g)) for 2 h, filtered hot, and dried in air (110 °C, 16 h).

Synthesis of Graphene oxide (GO):

In a typical procedure, 1 g of graphite powder and 1 g of NaNO₃ were taken in a round bottom flask followed by the addition of 46 ml concentrated sulfuric acid in an ice bath. The mixture was then stirred for 15 mins followed by slow addition of 8 g of KMnO₄ powder. After complete addition of KMnO₄, the mixture was stirred at room temperature for

2 h. Then 80 ml of distilled water was added to the mixture and stirred for 1 h. At last, 200 ml of distilled water was added to it followed by the addition of excess of H₂O₂ (till the evolution of gas ceases). The GO formed was separated by centrifugation and dried at 70 °C for further use.

Synthesis of Reduced Graphene oxide-Vanadium phosphate (RGO-VPO) composite:

The RGO-VPO composite was prepared via two step route. In the first step, stoichiometric amount of GO in 5wt.% and VPO (0.25 g) was ultrasonicated for 1 h in two different beaker separately containing 40 ml of distilled water and 20 ml absolute ethanol, respectively. Then the VPO suspension was added drop wise to the GO suspension. The whole suspension was magnetically stirred for 2 h to get the mixture of VPO and GO. In the second step, the mixture was reduced using diethylene glycol under visible light irradiation in an irradiation chamber (BS 02, Germany) for 2 h.

Characterization techniques:

Raman spectra were recorded in Renishaw In-via Raman Microscope (Model H33197) system and excitation line was at 514 nm from an Ar-ion laser. Phase analysis of all materials was identified by XRD (PANalytical, X'pert PRO) using Cu K_α radiation of 1.543 Å. The Field Emission Scanning Electron Microscopy (FE-SEM) was performed with a ZEISS 55 microscope. Magnification in the range 15.83 - 44.90Kx has been done to get a better micrograph. Transmission electron microscopy (TEM) images were obtained on Philips TECNAI G2 operated at 200 kV, in which samples were prepared by dispersing the powdered samples in 2-propanol (except GO, dispersed in distilled water) by sonication for 3 mins and then drop-drying on a copper grid coated with carbon film. X-Ray photoelectron spectroscopy (XPS) measurements were performed on a VG Microtech Multilab ESCA 3000 spectrometer with a non-monochromatised Mg-K_α X-ray source. Energy resolution of the

spectrometer was set at 0.8 eV with Mg-K α radiation at pass energy of 50 eV. The binding energy correction was performed at 284.9 eV using C1s peak of carbon as reference. ^1H and ^{13}C NMR experiments were carried out on JEOL AL 400 FT NMR Spectrometer.

Raman Spectra studies:

Fig. S1 displays the Raman spectra of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. All the bands found in the spectra are well matched with the literature ². The first order Raman spectra of the GO (Fig.S2) shows two main peaks at 1349 cm^{-1} (D band) which is the characteristic feature of amorphous carbon material containing SP^2 graphitic islands and disorder samples of graphite and at 1574 cm^{-1} (G band) which shows the highly ordered crystalline graphite. In the second order Raman spectra two peaks are found at 2690 and 2923 cm^{-1} which is the characteristic peaks of G' and D+G band respectively.

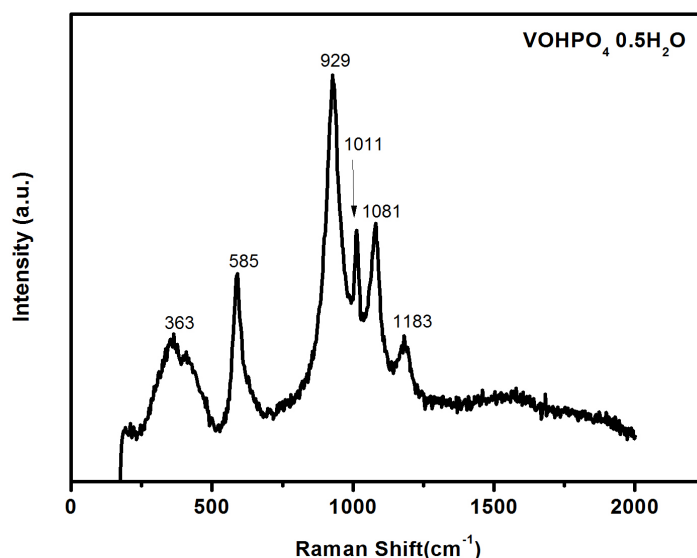


Fig. S1 Raman Spectra of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$

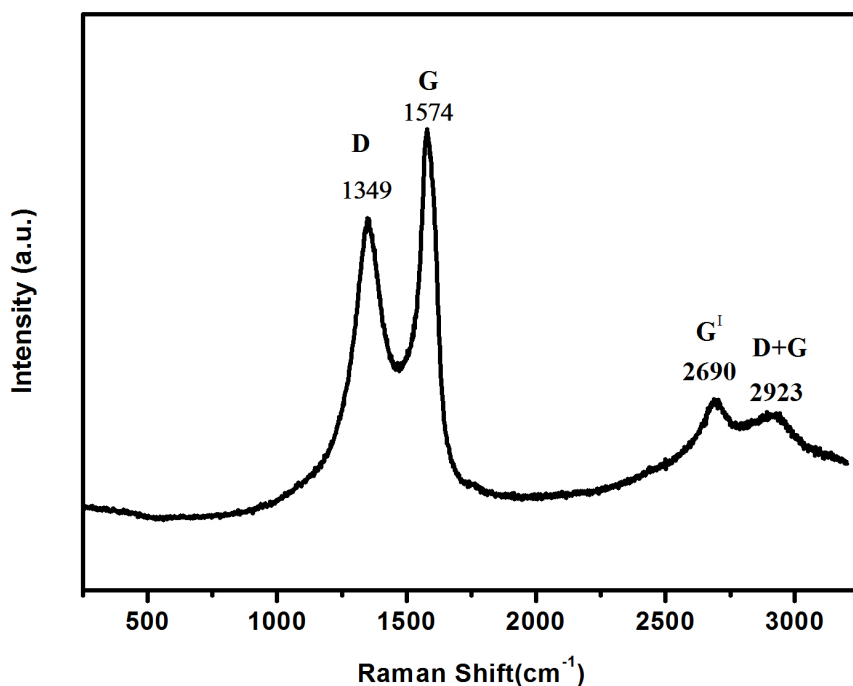


Fig.S2 Raman spectra of GO

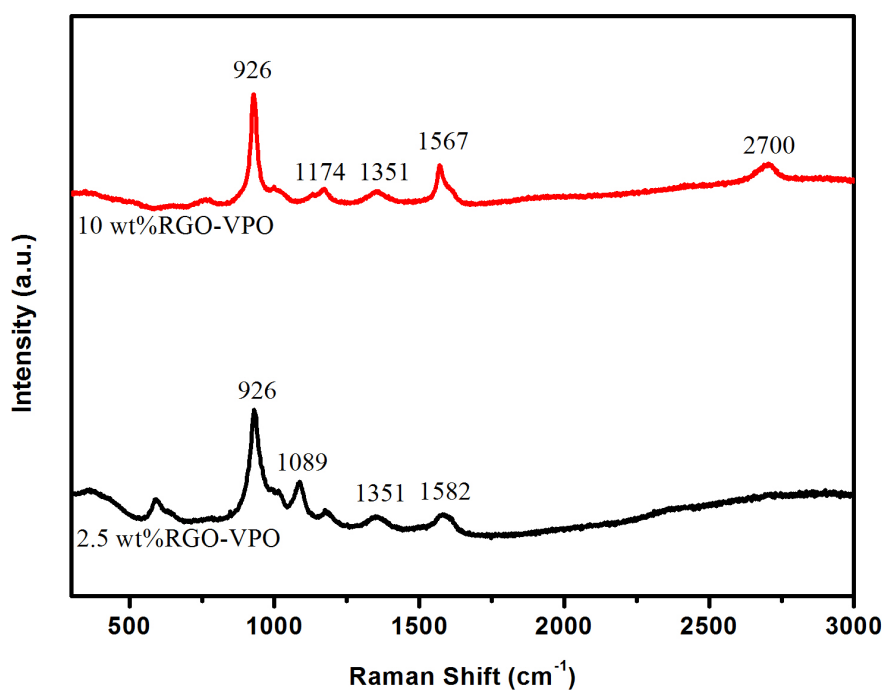


Fig.S3 Raman spectra of RGO-VPO

X-ray diffraction (XRD) Studies:

Fig. S3 displays the XRD patterns of VOHPO₄·0.5H₂O and RGO-VPO catalysts. All the major diffraction peaks can be ascribed to VOHPO₄·0.5 H₂O. At 2θ = 30.3° a highly intense (001) peak corresponds to the diffraction patterns of VOHPO₄·0.5 H₂O was obtained. The

XRD patterns reveal that the (001) peak for $\text{VOHPO}_4 \cdot 0.5 \text{H}_2\text{O}$ is reduced after interaction of the hemihydrates with GO in the RGO-VPO catalyst. A small peak at $2\theta = 12.8^\circ$ was found which corresponds to the reflectance pattern of VOPO_4 . This is due to the transformation of $\text{VOHPO}_4 \cdot 0.5 \text{H}_2\text{O}$ to VOPO_4 after interaction with the GO. This shows that the vanadium in the sole VPO catalyst sample is predominantly in the V^{4+} state with a small amount of V^{5+} species. The XRD pattern of the as synthesized GO shows a sharp peak at $2\theta = 10.3^\circ$, corresponding to the (001) reflection of graphite oxide²¹.

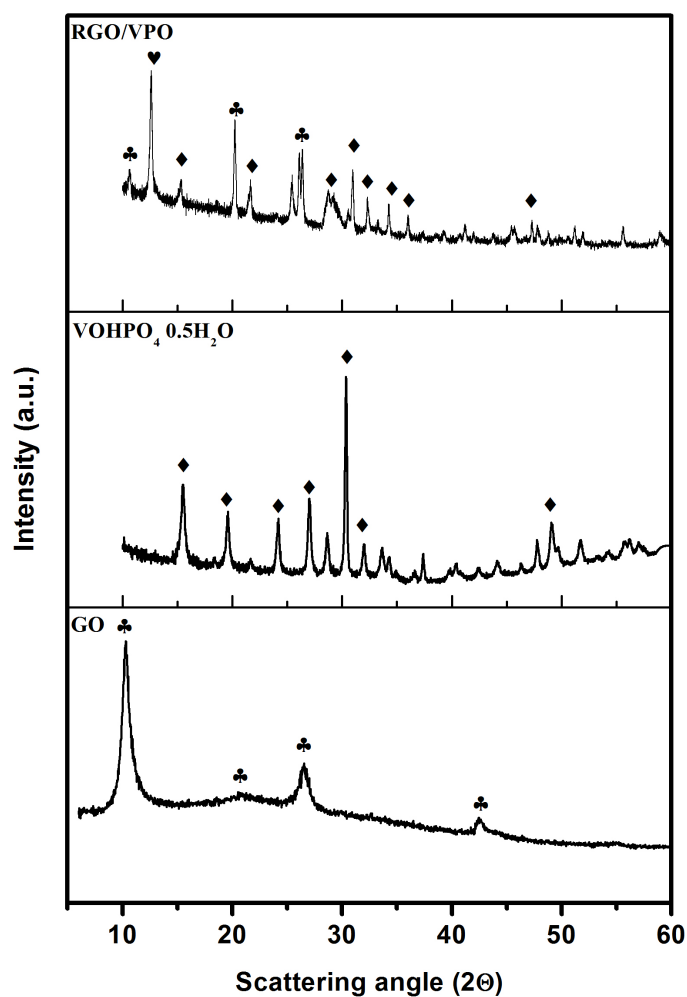


Fig.S4 XRD pattern of RGO-VPO composites

XPS Studies:

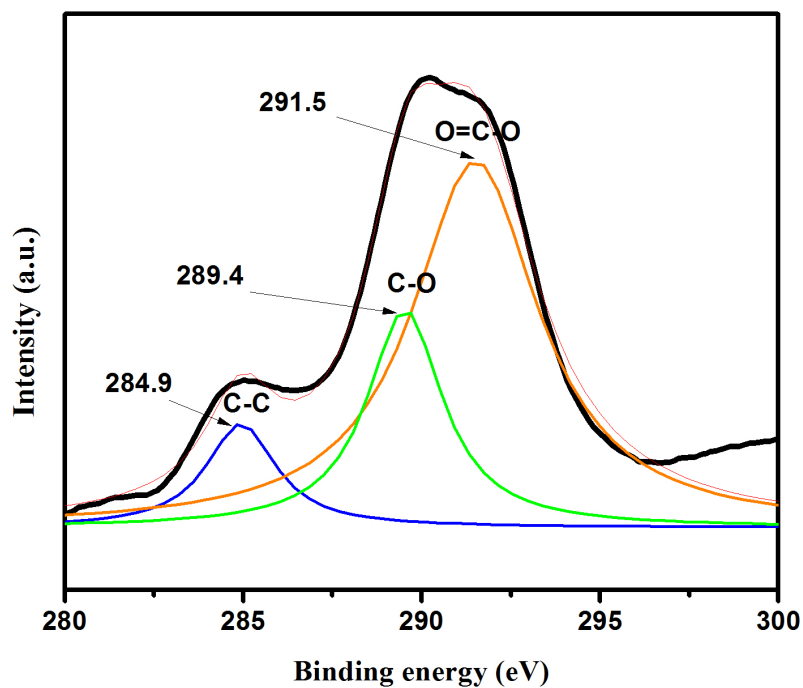


Fig. S5 (a) XPS spectra of GO

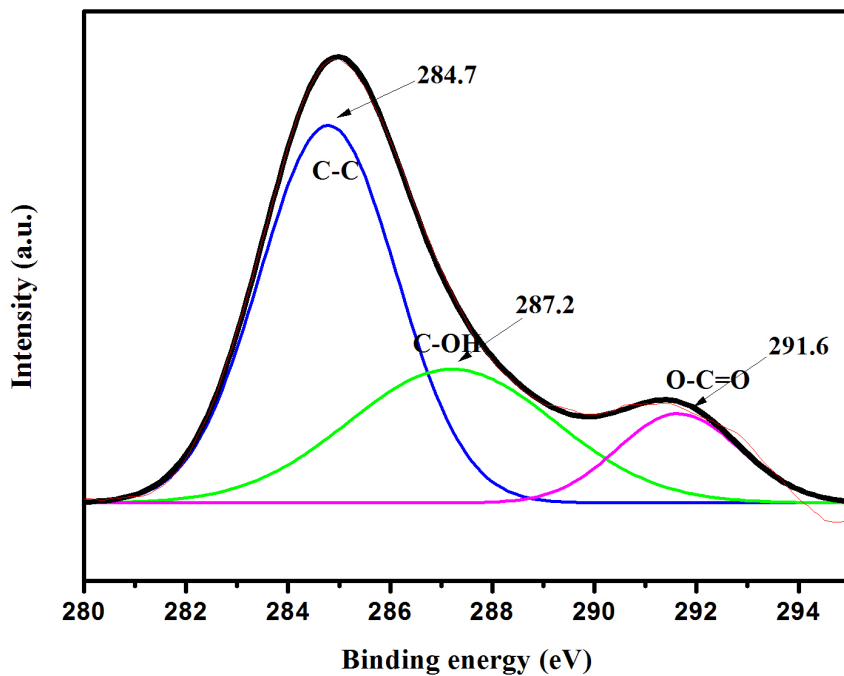


Fig. S5 (b) XPS spectra of C in RGO-VPO

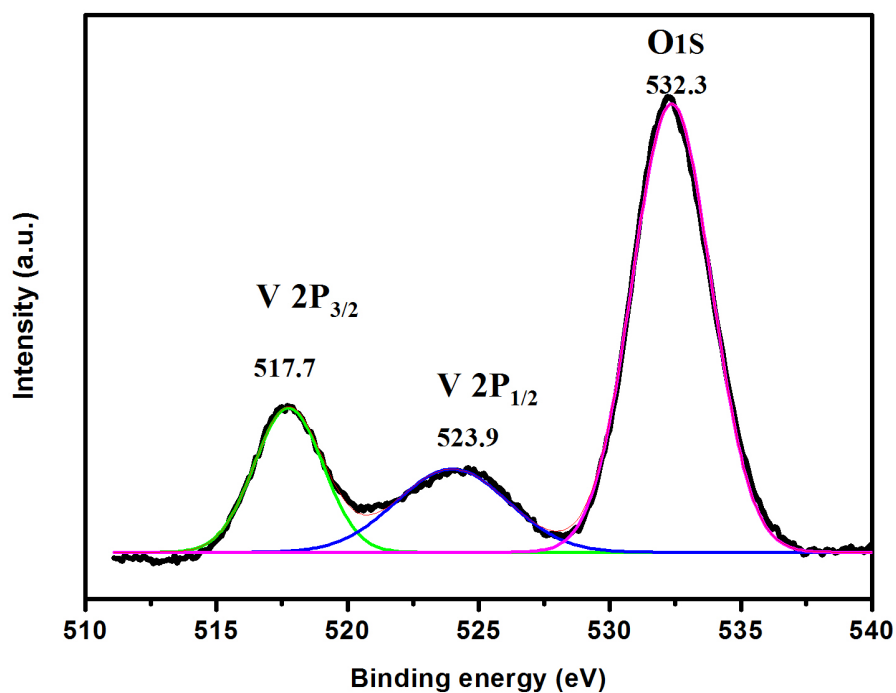


Fig. S5 (c) XPS spectra of V and O in RGO-VPO

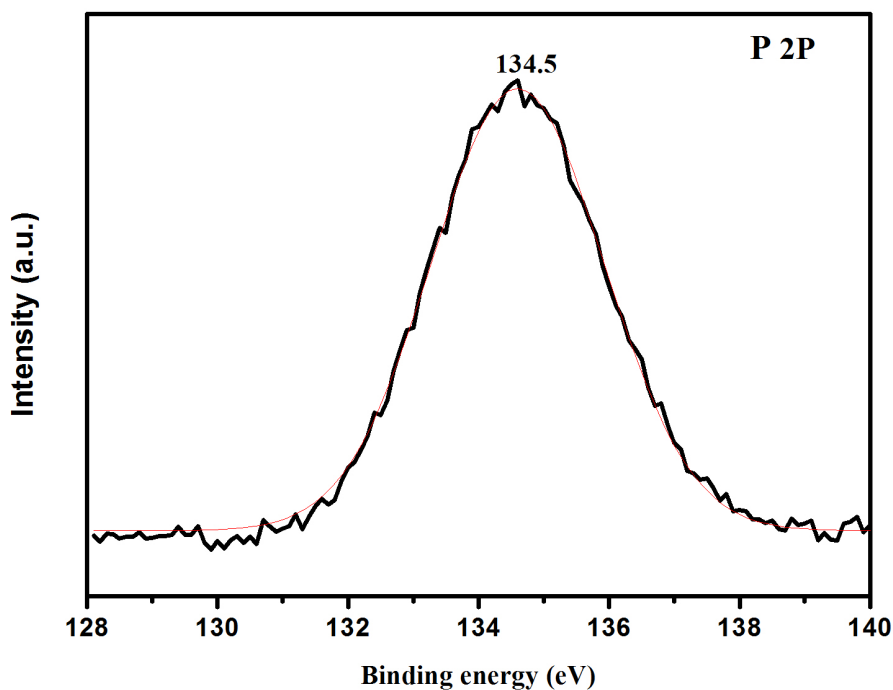


Fig. S5 (d) XPS spectra of P in RGO-VPO

Catalytic activity:

In a typical reaction procedure, a 100 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser was charged with 0.05g catalyst, 2.3 mL H₂O₂ (30%)

and 10.1 mL cyclohexene. In the first run the catalyst and H₂O₂ was run for 10 min at room temperature. Then cyclohexene was added. The mixture was stirred for 30 min interval from 60 °C to 80 °C and then at 90 °C for 6 h. After the completion of the reaction, the reaction mixture was altered and the products were analyzed by offline GC (Shimadzu, GC-17A) equipped with capillary column (ZB-1, 30 m length, 0.5 nm ID and 3.0 μ film thickness) using flame ionization detector (FID). The conversion, selectivity and yield were calculated by using equations (i), (ii) and (iii):

$$\text{Conversion}(\%) = \frac{\text{moles of cyclohexene reacted}}{\text{Total moles of cyclohexene}} \times 100 \quad (\text{i})$$

$$\text{Selectivity}(\%) = \frac{\text{moles of product formed}}{\text{moles of cyclohexene reacted}} \times 100 \quad (\text{ii})$$

$$\text{Yield}(\%) = \frac{\text{moles amount of product}}{\text{Initial moles amount of cyclohexene}} \times 100 \quad (\text{iii})$$

Table S1: Comparison of catalytic efficiency of RGO-VPO composites

Entry	Catalyst	Conversion (%)	Adipicacid Selectivity(%)
1	VPO	93.6	-
2	2.5wt% RGO-VPO	95	78.5
3	5 wt% RGO-VPO	97.5	90.7
4	10 wt% RGO-VPO	95.6	89.5

A comparison of our system with other systems has been illustrated in Table S1. The as synthesized RGO-VPO catalyst showed better results than the other systems.

Table S2: Comparison of catalytic efficiency of our systems with other systems*

Entry	Catalyst	Yield (%) Adipic acid	References
1	Bisquaternary ammonium & sodium tungstate	75	3
2	Ti-AlPO ₄	30.3	4
3	Na ₂ WO ₄ with CH ₃ (nC ₈ H ₁₇) ₃ N]HSO ₄	78	5
4	H ₂ WO ₄	61	6
5	WO _n Br _m . CoBr/NC	81.3	7
6	RGO-VPO	88.4	Our system

*Conditions are there in the references.

Heterogeneity Test:

A hot filtration test was performed in order to determine heterogeneity of the catalyst. In the course of the reaction, the solid catalyst was alienated from the reaction mixture by filtration after 3 h of the reaction. The filtrate thus obtained was continuously stirred for further 3 h under same reaction conditions. After completion of the reaction, the mixture was altered and the product was analyzed by offline GC (Shimadzu, GC-17A) equipped with capillary column (ZB-1, 30 m length, 0.5 mm ID and 3.0 μ film thickness) using flame ionization detector (FID). The conversion was found unaltered. This piece of evidence suggests that there is no loss of catalyst components during the course of reaction which confirmed the heterogeneity of the catalyst.

^1H and ^{13}C NMR Spectra of adipic acid:

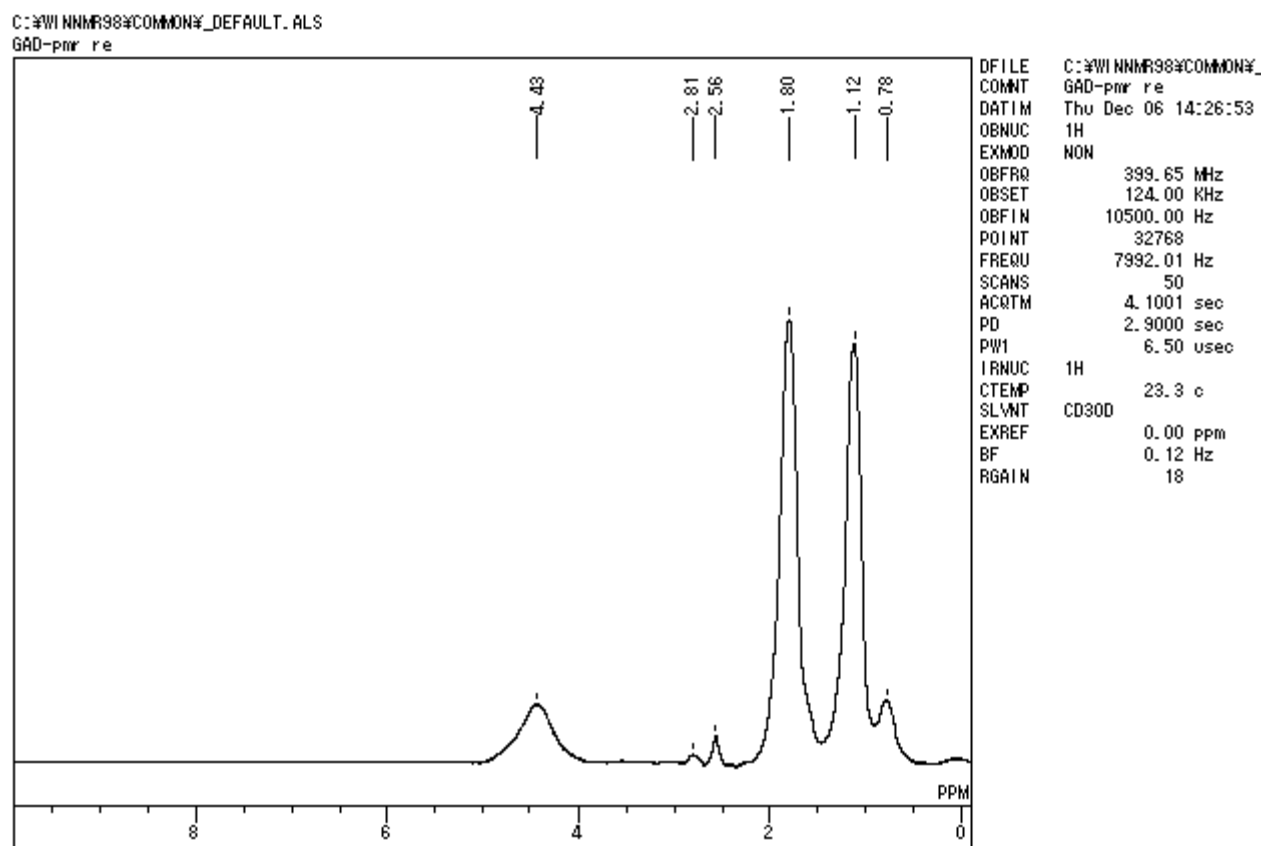


Fig. S6 ^1H NMR spectrum of adipic acid.

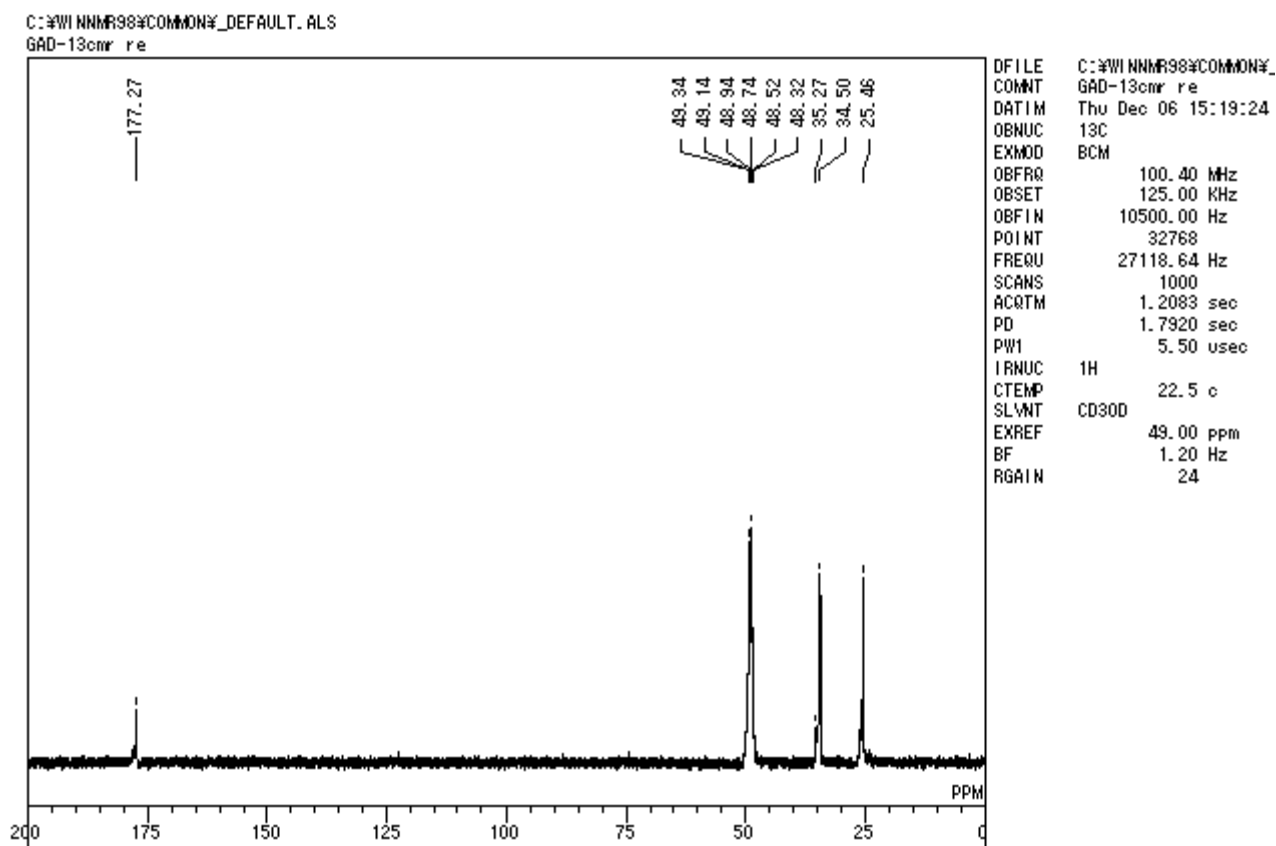


Fig.S7: ^{13}C NMR spectrum of adipic acid.

Recyclability Test:

For the evaluation of the recyclability of the RGO-VPO composite, the catalyst was recovered for further reaction by centrifugation, extensive washing with ethanol (until no trace of reaction solution was left from the previous reaction) and drying in vacuum. Fig. S5 shows the reusability performance of the RGO-VPO materials for 4 cycles. It was found that the VPO materials still retained a remarkably high proportion (%) of its original catalytic activity, even after 4 cycles. Thus the VPO catalyst had excellent operational stability.

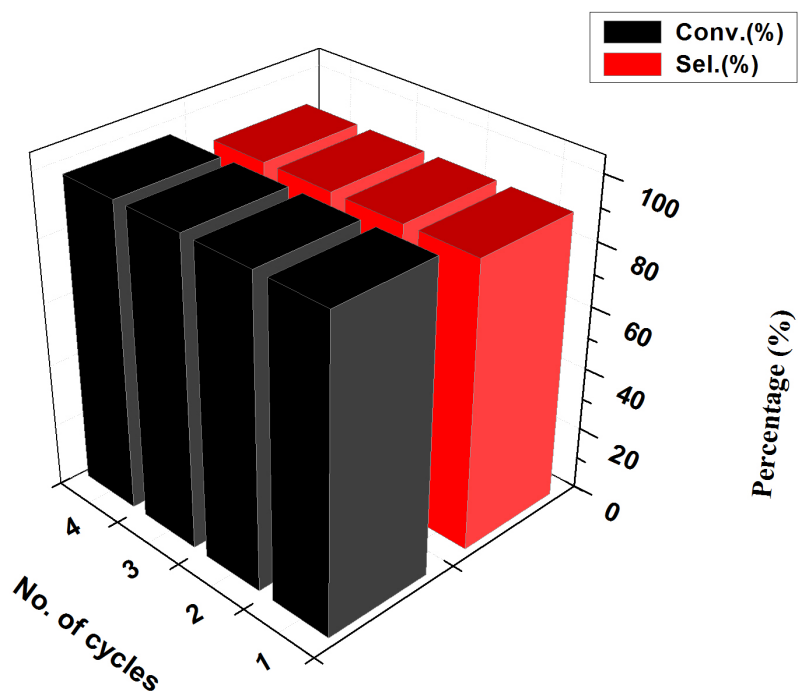
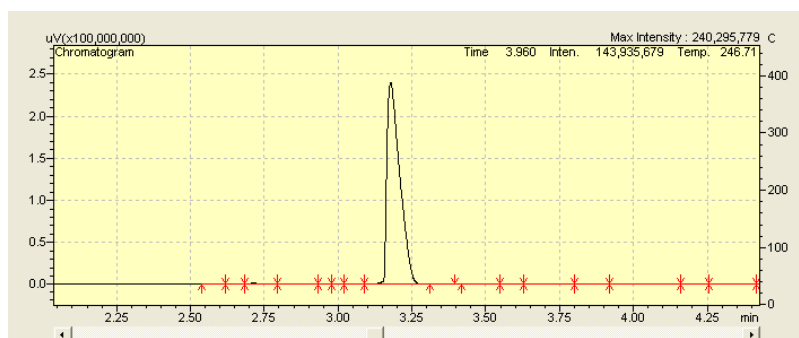
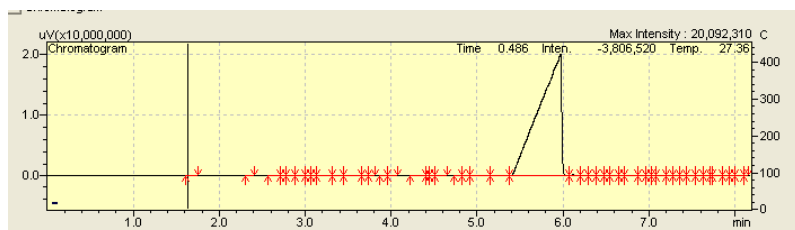


Fig. S8

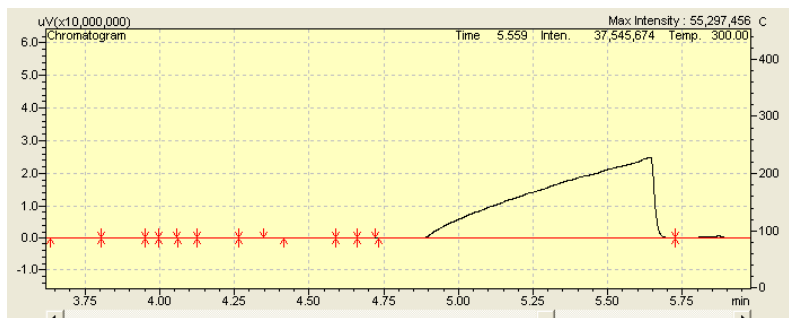
GasChromatogram of the reaction mixture



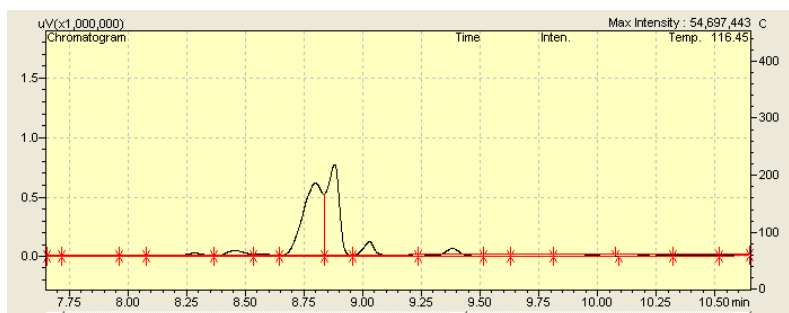
GC-1(Cyclohexene)



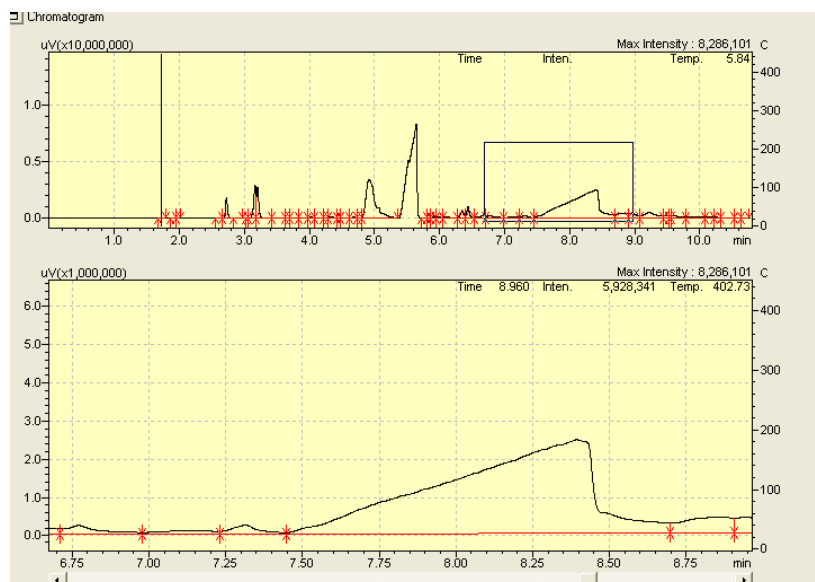
GC-2 (Cyclohexen-1-one)



GC-3 (Cyclohexen-1-diol)



GC-4 (Adipic acid std.)



GC-5 (Product by RGO-VPO)

References:

1 G. Busca , F. Cavani ,G. Centi ,F. Trifiro , *J. Catal.* 1986, **99**, 400.

- 2 L. Sartoni, J. K. Bartley, R. P. K. Wells, A. Delimitis, A. Burrows, C. J. Kiely, J. C. Volta, G. J. Hutchings, *J. Mater. Chem.*, 2005, **15**, 4295-4297.
- 3 X. Shi, S. Liu, F. Tong, Z. Wei, J. Shanxi Norm. Univ. *Natur. Sci. Ed.*, 2005, **33(1)** 7881.
- 4 S. O. Lee, R. Raja, K. D. M. Harris, et al., *Angew. Chem. Int. Ed.*, 2003, **42(13)**, 1520–1523.
- 5 K. Sato, M. Aoki, R. Noyori, *Science*, 1998, **281**,1646.
- 6 T. Fujitani, M. Nakazawa, *Japanese patent 63 93746*, 1988.
- 7 Kh. M. Alimardanov, O. A. Sadygov, N. I. Garibov, M. F. Abbasov, M. Ya. Abdullaeva, N. A. Dzhafarova, *Rus. J. Appl. Chem.*, 2011, **84(2)**, 236-242.