Electronic Supporting Information for

Visible light induced photo-hydroxylation of phenol to catechol over RGO-Ag$_3$VO$_4$ nanocomposites without the use of H$_2$O$_2$

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Preparation of graphene oxide (GO)

In a typical procedure, 1 g of graphite powder and 1 g of NaNO$_3$ 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 KMnO$_4$ powder. After complete addition of KMnO$_4$, 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 H$_2$O$_2$ (till the evolution of gas ceases). The GO formed was separated by centrifugation and dried at 70 ^{o}C for further use.

Preparation of graphene (GN)

A total of 25 mL of 0.5 mg/mL GO aqueous solution was transferred to a Teflon lined autoclave and heated at 180 ^{o}C for 6 h. The autoclave was then cooled to room temperature. The hydrothermally treated graphene was found to precipitate at the bottom of the autoclave as a black powder, possibly due to the low solubility in superfluidic water under hydrothermal conditions.[S1] The sample collected was designated as GN.

Preparation of xRGO-Ag$_3$VO$_4$

Stoichiometric amount of GO in wt.% was ultrasonicated in 100 ml of distilled water in a beaker for 1 h. 2.8028 g of AgNO$_3$ was added to the above GO dispersion followed by drop wise addition of 40 ml of an aqueous solution containing V$_2$O$_5$ (0.91 g)-NaOH (1.2 g). After complete addition, the mixture was aged for 24 h followed by irradiation under 125 W high pressure Hg visible lamp for 1 h in presence of ethanol. Ag$_3$VO$_4$ being a photocatalyst, by light illumination it produces e$^-$-h$^+$ pairs out of which h$^+$ is scavenged by ethanol leaving electrons to reduce GO to RGO making RGO-Ag$_3$VO$_4$ nanocomposites. The dark green colored material was centrifuged and dried at 70 ^{o}C. The materials are designated as xRGO-Ag$_3$VO$_4$ (x (C/Ag$_3$VO$_4$ ratio) = 0, 1, 2, 4, 8).

Preparation of graphene-Ag₃VO₄

For comparison purpose, GN (prepared by hydrothermal route) was dispersed in distilled water and sonicated for 1 h. 2.8028 g of $AgNO_3$ was added to the above GN dispersion followed by drop wise addition of 40 ml of an aqueous solution containing V_2O_5 (0.91 g)-NaOH (1.2 g). After complete addition, the mixture was aged for 24 h. The dark greenish solid was separated by centrifugation, subsequent washings and dried at 70 $^\circ$C. This sample is labeled as $xGN-Ag_3VO_4$ (x (C/Ag_3VO_4) = 4)

Characterization

All the samples were characterized by XRD, TEM/EDX, PL-studies, N_2 adsorption-desorption studies, XPS, photocurrent measurements, ICP-OES studies etc. X-ray diffraction patterns were recorded on a Rigaku Miniflex (set at 30 kV and 15 mA) powder diffractometer using Cu Kα radiation with 2θ ranging from 5 to 70 $^\circ$ at a rate of 5 $^\circ$/min. High resolution transmission electron microscopy (HRTEM) images were obtained on Philips TECNAI G^2 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. 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. Diffuse reflectance UV-vis (DRUV-vis) spectra of the catalyst samples were taken with a Varian Cary 100 spectrophotometer equipped with a diffuse reflectance accessory in the region 200-800 nm, with boric acid as reference. X-Ray photoelectron spectroscopy (XPS) measurements were performed on a VG Microtech Multilab ESCA 3000 spectrometer with a non-monochromatised Mg-Kα X-ray source. Energy resolution of the spectrometer was set at 0.8 eV with Mg-Kα radiation at pass energy of 50 eV. The binding energy correction was performed at 284.9 eV using C1s peak of carbon as reference. The filtrates of the reactions were analysed in ICP-OES (Optima 2100 DV, PerkinElmer) to know the amount of leached V^{+5} from the catalysts during reaction under light illumination. All the samples were analyzed thrice and the results presented here are the average values.

Catalytic activity test

Stoppered pyrex conical flask was charged with 0.02 g of the catalyst and 10 ml of 20 ppm phenol solution and exposed to visible light in an irradiation chamber (BS 02, Germany) for 2 h (Scheme S1). Experiments were performed with different parametric conditions and were compared with the blank experiments.

Scheme S1 Irradiation chamber for phenol hydroxylation.

The conversion (%) of phenol and selectivity (%) of CAT and HQ was calculated using the following formulae.

$$\text{Conversion (\%)}_{\text{reactant}} = \left(\frac{\text{Reactant converted (Conc}^n)}{\text{Reactant used (Conc}^n)} \right) \times 100$$

$$\text{Selectivity (\%)}_{\text{product}} = \left(\frac{\text{Product formed (Conc}^n)}{\text{Reactant converted (Conc}^n)} \right) \times 100$$

Where Conc^n = Concentration

Determination of •OH radical

Hydroxyl radicals (•OH) produced by the as-prepared photocatalysts under solar light irradiation were measured by fluorescence method using terephthalic acid (TA) as probe molecule. In brief, 10 mg of $RGO\text{-}Ag_3VO_4$ sample was dispersed in 40 mL of a 5×10^{-4} M TA aqueous solution with a concentration of 2×10^{-3} M NaOH. Then, the resulting suspension was exposed to visible light illumination for 2 h in chamber (Scheme S1). Then the suspension was centrifuged to measure the maximum fluorescence emission intensity with an excitation wavelength of 315 nm.
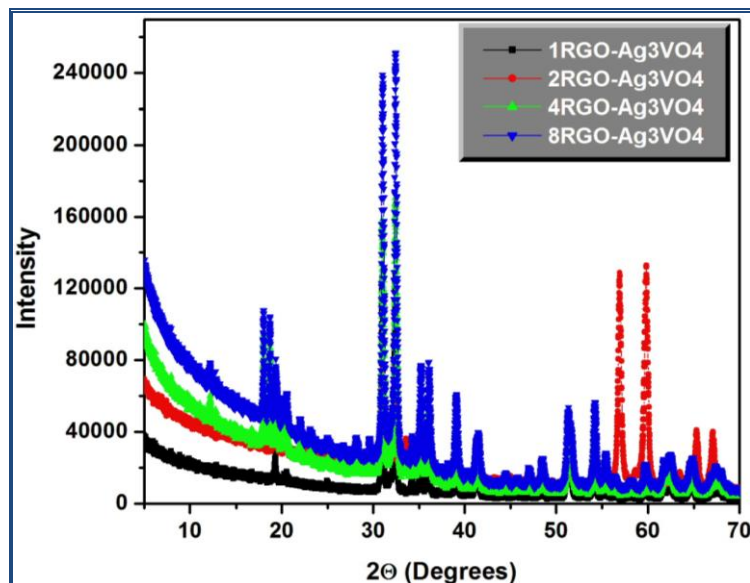
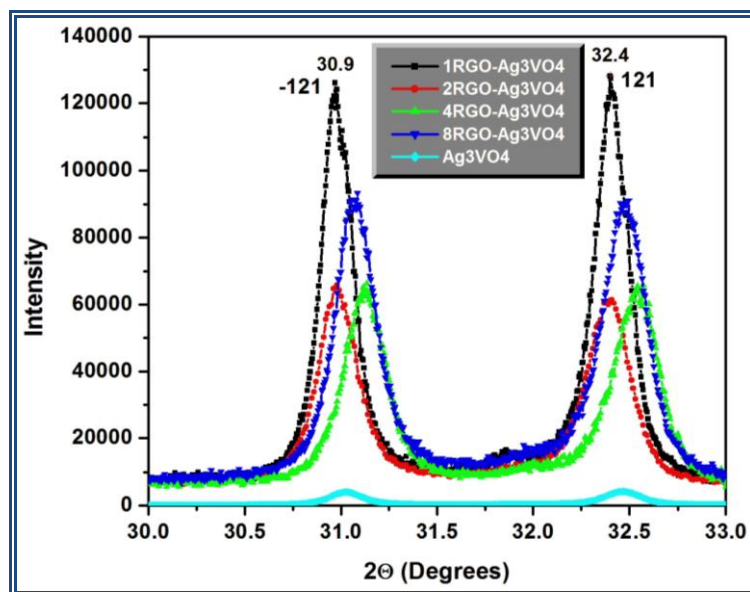**Results & discussion**

Fig. S1 XRD patterns of nanocomposites.

Fig. S2 XRD patterns of RGO-Ag$_3$VO$_4$ nanocomposites with 2θ =30-33 ^{o}.

The XRD patterns of graphene-Ag$_3$VO$_4$ nanocomposites are presented in Fig. S1. The peaks match with the monoclinic phase of Ag$_3$VO$_4$ (JCPDS no. 43-0542) except the peak at $2\theta = 34$ ^{o} which is assigned to Ag$_2$O which is having no effect on the photocatalytic activity of the nanocomposite.[S2] Fig. S2 depicts the XRD patterns of xgraphene-Ag$_3$VO$_4$ composites (x= 0-8 wt.%) within 2θ =30-33°. There is an indication of a change in Ag$_3$VO$_4$ lattice while comparing the XRD peaks of (-121) and (121) planes due to shifting of peak
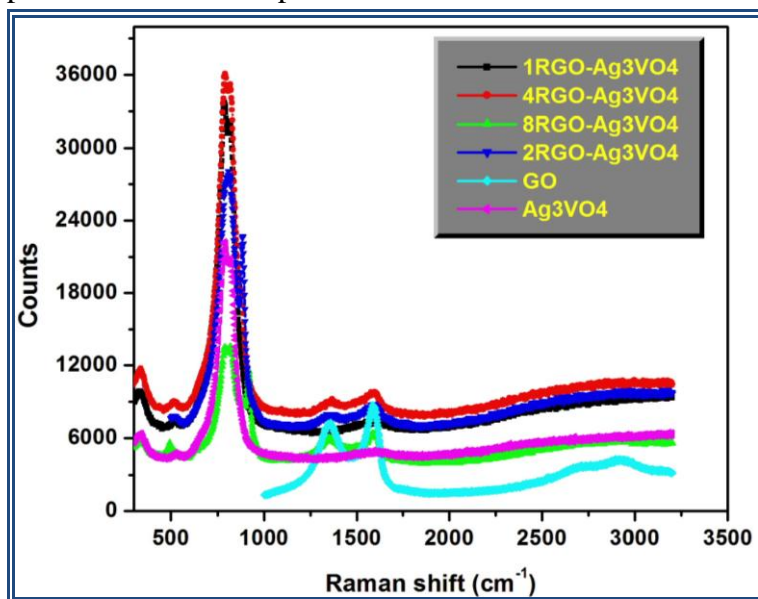
position in nanocomposites.

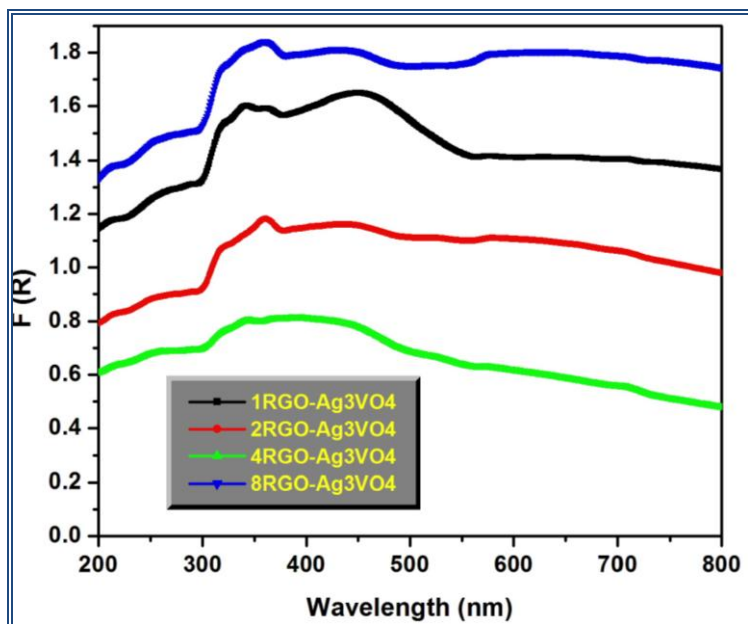**Fig. S3** Raman shift of neat and nanocomposites.
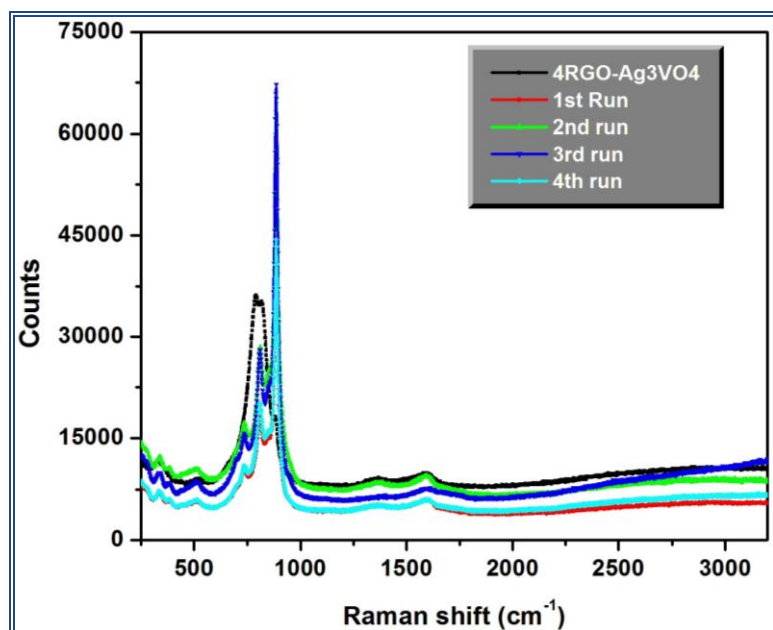

Fig. S4 DRUV-vis spectra of nanocmposites.

Fig. S5 Raman shift of reused catalysts.

Table S1 ICP-OES analysis of V^{+5} in the filtrate after reactions over the pristine and nanocomposites.

Catalyst	V^{+5} (%)
Ag_3VO_4	50.23
$1RGO-Ag_3VO_4$	0.10
$2RGO-Ag_3VO_4$	0.07
$4RGO-Ag_3VO_4$	0.00
$8RGO-Ag_3VO_4$	0.00
$4GN-Ag_3VO_4$	2.52

Reference

S1 Y. Zhou, Q. Bao, L. Ai Ling Tang, Y. Zhong, K.P. Loh, *Chem. Mater.*, 2009, **21**, 2950.

S2 H. Xu, H. Li, L. Xu, C. Wu, G. Sun, Y. Xu, J. Chu, *Ind. Eng. Chem. Res.*, 2009, **48**, 10771.