Electronic Supplementary Information (ESI)

Selective Photocatalytic Oxidation of Aromatic Alcohols into Aldehydes by Tungsten Blue Oxide (TBO) Anchored with Pt Nanoparticles

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Synthesis of Tungsten Blue Oxide. Tungsten oxide nanoparticles were synthesized by a hydrothermal process. A measured amount of sodium tungstate (1.4 g) was dissolved in 65 mL of water containing 3 mL of hydrochloric acid (pH ~1). After vigorous stirring, the suspension was transferred into Teflon-lined hydrothermal vessel and was heated at 200 °C for 24 h. After reaction, the product was collected and thoroughly washed with water and ethanol, and dried at 90°C overnight. After drying, a blue-colored WO_3 was obtained.

Synthesis of Pt/WO_3. The deposition of Pt nanoparticles onto the surface of WO_3 was performed using a photodeposition method in a similar immersion well photochemical reactor (Fig. S1). Briefly, 130 mL of water was added to the reaction vessel and the required amounts of metal salt (H_2PtCl_6) and photocatalyst were added. The suspension was stirred and purged with high purity nitrogen gas for at least 1 h to remove the dissolved oxygen. Methanol (10 vol %) was added as an electron donor. Irradiation was carried out using a 230 W tungsten−halogen lamp (OSRAM) for 4 h. After irradiation, the Pt loaded catalyst was washed with water and ethanol and separated through centrifugation and dried at 110 °C under vacuum overnight.

Synthesis of reduced graphene oxide (RGO). For the synthesis of RGO nanosheets, 5 g of Graphite and 2 g of sodium nitrate were added into 200 mL concentrated sulfuric acid (98%), and the resulting solution was transferred to an ice bath. Potassium dichromate (35 g) was added very slowly and the solution was kept under stirring for 6 days at room temperature. After reaction, the resulting graphite oxide was washed thoroughly and then exfoliated to graphene oxide through ultrasonication. Finally, graphene oxide was reduced into RGO by stirring graphene oxide solution with hydrazine for 24 h at 95 °C and the final products were washed and vacuum-dried.

Synthesis of RGO/WO_3. A homogeneous aqueous suspension consisting of WO_3 and RGO was prepared by ultrasonication. Then, the solution was transferred into a Teflon-lined hydrothermal vessel and heated at 200°C for 24 h. The product was separated by centrifugation, washed thoroughly with water and ethanol, and dried under vacuum.

Synthesis of Pt/RGO/WO_3. To prepare Pt/RGO/WO_3 nanocomposite, platinum nanoparticles were photoreduced onto the surface of synthesized RGO/WO_3 nanocomposite following similar deposition process as demonstrated above.

Evaluation of photocatalytic activity. The photocatalytic activity for oxidation of alcohols was evaluated using immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, a water circulating jacket and with openings for supply of gases. For irradiation experiment, 130 mL solution was taken into the photoreactor and required amount of photocatalyst was added, and the solution was stirred for at least 15 min in the dark. The zero time reading was obtained from the solution withdrawn before the light was turned on. Irradiations were carried out using a 230 W tungsten-halogen lamp (OSRAM), which emits <2% UV light. The temperature was controlled and kept at room temperature by circulating cold water through the outer jacket of the reactor. Samples (3 mL) were collected before and at regular intervals during the irradiation, and the catalyst was removed by filtration.

GC-MS analysis. All the irradiated solutions were extracted with 3 ml of chloroform in three portions, 1 ml each, for maximum extraction. Analysis of the extracted samples was carried out by gas chromatography mass spectrometer (Agilent Technologies) using capillary column (5% phenyl methyl siloxan, 30 m × 320 μm × 0.25 μm). Selected ion monitoring mode (SIM) was used for routine analysis. Programing of the GC oven temperature was as follows: it was set to reach 40 ^{0}C in 1 min, then 10 ^{0}C/min to reach 200 ^{0}C. Injection volume was 100 nl with split ratio 2:1. The calibration curves were obtained by injecting standards solutions of reactants and products, such as benzyl alcohol, benzaldehyde, 4-methoxy benzyl alcohol, and 4-methoxy benzaldehyde and so on. The concentrations of alcohols and aldehydes were determined from the peak areas. Percent (%) conversion, selectivity and yield were calculated using below formulae;

$$\text{Selectivity} = \frac{Cp}{(C\text{r}_0 - Cr)} \times 100$$

$$\%\,\text{Conversion} = \frac{(Cr_0 - Cr)}{C\text{r}_0} \times 100$$

$$\%\,\text{Yield} = \frac{Cp}{C\text{r}_0} \times 100$$

Cr_0 = the initial concentration of the reactant, Cr = the concentration of the reactant during the reaction, Cp = the concentration of the product during the reaction

Evaluation of photoelectrochemical (PEC) activity. The photoelectrochemical activity of the photocatalysts prepared in this work was studied using a 3-electrode quartz photoelectrochemical cell connected to a potentiostat (273A PAR). Saturated calomel electrode (mercury/mercury

chloride, SCE) and coiled platinum wires were used as the reference and counter electrodes, respectively. A homogeneous suspension consisting of 5% Nafion solution, photocatalyst, water and isopropanol was prepared by sonication and deposited on an indium tin oxide (ITO) substrate, dried, and used as the working electrode. A 0.1 M Na_2SO_4 solution was used as the electrolyte. The electrochemical cell was irradiated with a 300 W Xenon lamp with a cut-off filter kept 10 cm away from the cell to obtain the desired radiation (>420 nm). This illuminated ~1 cm^2 of the photocatalyst surface. The potential sweeps were performed at a rate of 5 mV s^{-1} in all the experiments.

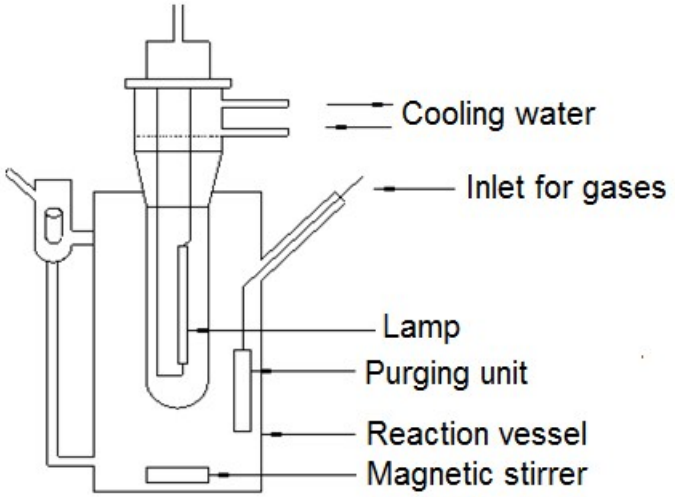

Fig. S1 Schematic of the photoreactor.

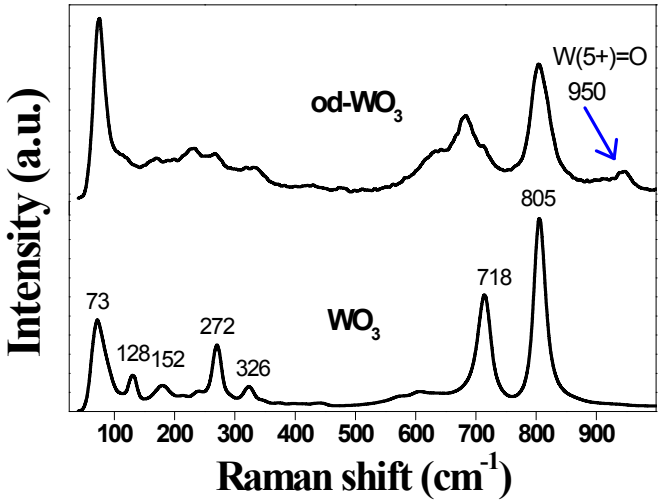

Fig. S2 Comparative Raman spectra of WO_3.

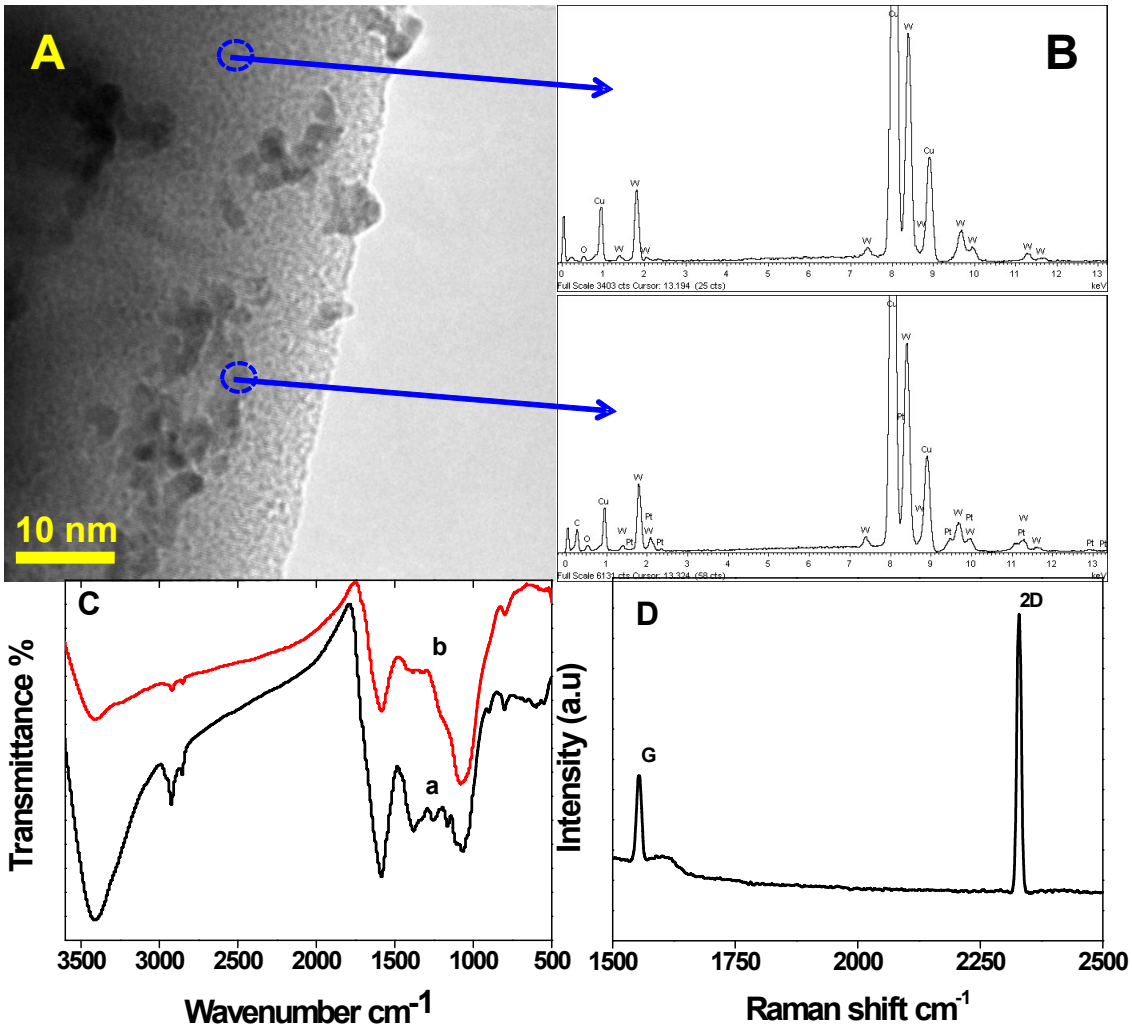

Fig. S3 (A) TEM showing Pt nanoparticles (small black dots) on surface of WO_3, (B) localized EDS spectra confirming the elemental composition and presence of platinum nanoparticles, (C) FTIR spectra of graphene oxide (a) and RGO (b), (D) Raman spectrum of RGO.

Table S1. A comparative oxidation of selected aromatic alcohols by heterogeneous photocatalytic process.

Catalyst	Substrate	Product	Conversion (%)	Selectivity (%)	Yield (%)	Conditions	Reference
TiO_2	BA	Benzaldehyde	50	38	(*)	H_2O, UV light	(1,2)
	4-MBA	p-Anisaldehyde	50	60	(*)		
TiO_2	BA	Benzaldehyde	42	95	(*)	Trifluorotoluene, UV light	(3)
SiO_2/TiO_2	BA	Benzaldehyde	46	95	(*)		
SiO_2/TiO_2 (modified with H_2SO_4)	BA	Benzaldehyde	90	95	(*)		
TiO_2	4-MBA	p-Anisaldehyde	65	(*)	41.5	H_2O, UV light	(4)
CdS/graphene	BA	Benzaldehyde	45	90	45	Trifluorotoluene, visible light	(5)
CdS/graphene/TiO_2	BA	Benzaldehyde	>80	>90	<80	Trifluorotoluene, visible light	(6)
Au/CeO_2	BA	Benzaldehyde	>99	>99	>99	H_2O, visible light	(7,8)
TiO_2	4-MBA	p-Anisaldehyde	50	56	(*)	H_2O, UV light	(9)
Pt/TiO_2	BA	Benzaldehyde	87	68	(*)	H_2O, visible light	(10)
	4-MBA	p-Anisaldehyde	85	90	(*)		
	CA	Cinnamaldehyde	95	71	(*)		
Ir/TiO_2	BA	Benzaldehyde	~9	92	(*)	H_2O, UV light	(11)
WO_3/TiO_2	BA	Benzaldehyde	50	56	(*)	H_2O, light >350 nm	(12)
HNb_3O_8	BA	Benzaldehyde	20	>99	(*)	Benzotrifluoride, visible light	(13)
	4-MBA	p-Anisaldehyde	63	85	(*)		
Ag_3PO_4	BA	Benzaldehyde	>85	>99	~85	H_2O, simulated sunlight	(14)
	4-MBA	p-Anisaldehyde	>85	>99	~85		
	CA	Cinnamaldehyde	~90	>90	~81		
Pt/Bi_2WO_6	4-MBA	p-Anisaldehyde	>95	>99	~95	H_2O, simulated sunlight	(15)
	4-NBA	p-Nitrobenzaldehyde	>85	>99	~85		
Pt/WO_3	BA	Benzaldehyde	>80	>99	~80	H_2O, simulated sunlight	(in this study)
	4-MBA	p-Anisaldehyde	>80	>99	~80		
	CA	Cinnamaldehyde	>85	>99	~85		

(*) not mentioned, BA – benzyl alcohol, 4-MBA – 4-methoxy benzyl alcohol, CA – Cinnamyl alcohol.

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