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## Supplementary Information

### Electronic Supplementary Information for Using Sunlight and Surface Complex Grafted Nanoparticles to Selectively Oxidize Alkyl Aromatics

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#### LEGENDS

#### Experimental Section

**Figure S1.** Thermal gravimetric analysis of the Nb series photocatalysts.

**Table S1.** Turn over number of 5 successful runs of hydrocarbon oxidation over NbBA sample.

**Table S2.** Active centres of the grafted surface groups estimated from TGA.

**Figure S2.** UV-Visible absorption of transition metal-organic group complexes: a Niobium complexes; b Titanium complexes; c Zirconium complexes; (BA: benzyl alcohol; MBA: 4-methoxy benzyl alcohol; EG: ethyl glycol).

**Figure S3** FT-IR spectra and UV-Visible absorption of NbMBA catalyst

**Scheme S1** Proposed pathways of selective oxidation of aromatic alcohol. Ph-CH<sub>2</sub>-O- is presented as representative example of the surface complex, and Ph-CH<sub>2</sub>-OH as the reactant example

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### Experimental Section

**Catalyst preparation:** Nb surface complexes: 0.15 mol of niobium chloride ultrasonically dispersed into 80 ml of anhydrous benzyl alcohol (NbBA), or ethylene glycol (NbEG). The resultant suspension transferred into a 125 ml Teflon-lined autoclave and maintained at 130°C for 48 h. After the autoclave was cooled to room temperature, the precipitate was recovered, thoroughly washed with acetone and rinsed with hexane once prior to the drying at 80°C overnight. To avoid the polymerization of 4-methoxybenzyl alcohol and NbCl<sub>5</sub>, Nb(OH)<sub>5</sub> was first prepared by hydrolyzing NbCl<sub>5</sub> in water at 130°C. Then, 0.15 mol of obtained Nb(OH)<sub>5</sub> ultrasonically dispersed into 80 ml of anhydrous 4-methoxy benzyl alcohol (NbMBA), then transferred into a 125-ml Teflon-lined autoclave and maintained at 130°C for 48 h. The solid was recovered, washed and dried in the same procedures used in the synthesis of NbBA and NbEG.

Ti surface complexes: 0.5 g of hydrogen-titanate (H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>) ultrasonically dispersed into 80 ml of anhydrous benzyl alcohol (for TiBA synthesis), 4-methoxy benzyl alcohol (for TiMBA synthesis) or ethylene glycol (for TiEG synthesis). The resultant suspension transferred into a 125 ml Teflon-lined autoclave and maintained at 130°C for 48 h. After the autoclave was cooled to room temperature, the solid was recovered, washed and dried as described above.

Zr surface complexes: 0.15 mol of zirconium oxychloride ultrasonically dispersed into 80 ml of anhydrous benzyl alcohol (for ZrBA synthesis), or ethylene glycol (for ZrEG synthesis). The resultant suspension transferred into a 125 ml Teflon-lined autoclave and maintained at 130°C for 48 h. After the autoclave was cooled to room temperature, the precipitate was recovered, washed and dried in the same procedures used for the synthesis of above photocatalysts. To avoid the polymerization of 4-methoxybenzyl alcohol and ZrOCl<sub>2</sub>, Zr(OH)<sub>4</sub> was first prepared by hydrolyzing ZrOCl<sub>2</sub> in water at 130°C. 0.15 mol of obtained Zr(OH)<sub>5</sub> dispersed into 80 ml of anhydrous 4-methoxy benzyl alcohol (ZrMBA) under sonication, then the suspension was transferred into a 125 ml Teflon-lined autoclave and maintained at 130°C for 48 h. The precipitate was recovered, washed and dried in the same procedures used for the synthesis of above photocatalysts.

**Activity test:** The photocatalytic properties of the samples for selective oxidation of hydrocarbons and alcohols were examined at 45 °C for visible light reaction and 30 °C for UV light reaction in 1 atm O<sub>2</sub> atmosphere. 1 mmol substrates dissolved in 10 ml α,α,α-trifluorotoluene, and then 100 mg

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catalyst were added into the solution, which was stirred with a magnetic stirrer during reaction system is illuminated with incandescent light or UV light. A halogen lamp (from Nelson, wavelength in the range 400–750 nm) was used as the visible light source and the light intensity was measured to be 0.30 W/cm<sup>2</sup>. At given irradiation time intervals, 2 ml aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.45 µm) to remove the catalyst particulates. The filtrates were analyzed in a Gas Chromatography (HP6890 Prometheus) to measure concentrations of aldehydes, carboxylic acids, alcohols and products.

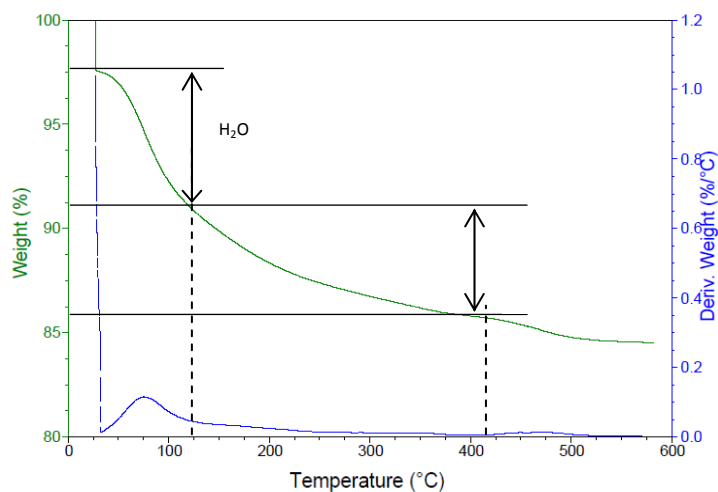
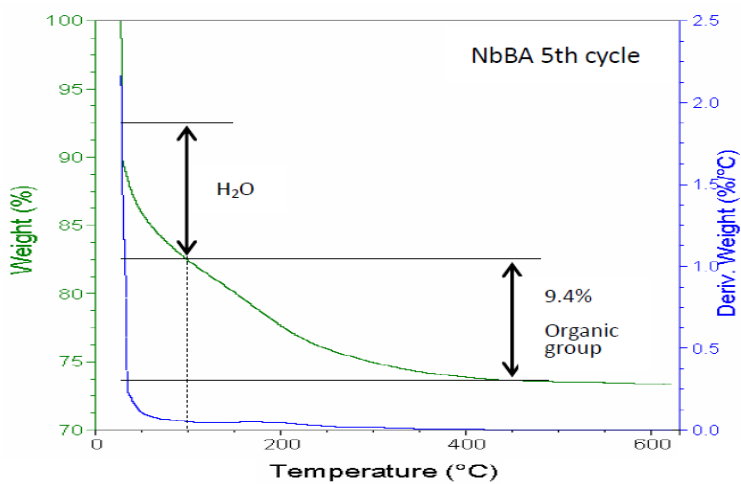
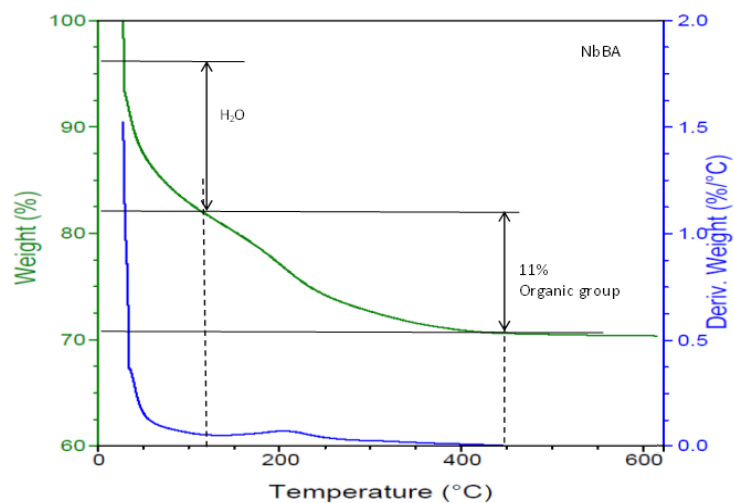
**Characterization:** Several techniques were used to characterize the catalysts. The microstructure and morphology of products was investigated using TEM and XRD techniques. TEM images were recorded on a Philips CM200 Transmission electron microscope employing an accelerating voltage of 200 kV. The specimens were sample powders deposited onto a copper micro grid coated with a holey carbon film. XRD analysis was performed on a PANalytical X'Pert PRO X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda=1.5418$  Å) and a fixed power source (40 kV and 40 mA) were used. The samples were scanned at a rate of 1° (2 $\theta$ )/min over a range of 2–80°, which covers the main characteristic diffraction peaks of the titanate, anatase, and rutile. Diffuse reflectance UV-visible reflectance spectra of the samples were recorded on a Cary 5000 spectrometer. Nitrogen adsorption/desorption isotherms of the samples were obtained on a Micrometrics ASAP 2010 at a liquid nitrogen temperature (77.3K). The samples were dried at 100°C overnight prior to measurement. The quantity of the surface grafted groups in a sample was estimated from TGA results obtained on a TA<sup>R</sup> instrument with a high-resolution thermo gravimetric analyzer (series Q500). The measurement was conducted in a nitrogen flow (60 cm<sup>3</sup>/min). Approximately 30 mg of a sample was heated in an air flow and the heating rate was 6°C/min. EPR spectra were recorded with a Bruker EPR ELEXSYS 500 spectrometer operating at a frequency of 9.5 GHz in the X-band mode. Measurements were performed with an ER 4131 VT variable temperature accessory at 130 K. The spectra were acquired when samples within the cavity were illuminated by UV light.

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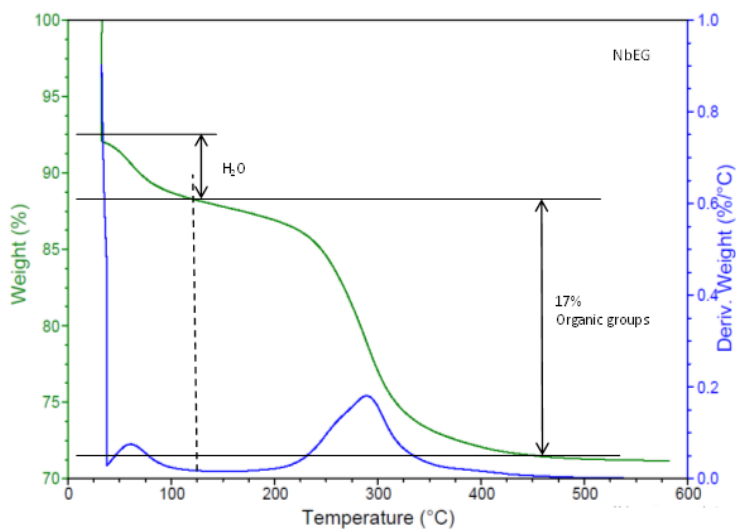
Figure S1 Thermal gravimetric analysis (TGA) of the Nb series photocatalysts.



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Table S1. Turn over number of 5 successful runs of hydrocarbon oxidation over NbBA sample.

Substrate	Light	TON After 5 runs
Toluene	UV	10.9
	Visible	5.56
Ethylbenzene	UV	13.3
	Visible	8.37
p-Xylene	UV	14.2
	Visible	7.09
m-Xylene	UV	14.6
	Visible	4.11
o-Xylene	UV	18.7
	Visible	5.18

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Table S1 Active centres of the grafted surface groups in 100mg of catalysts estimated from TGA

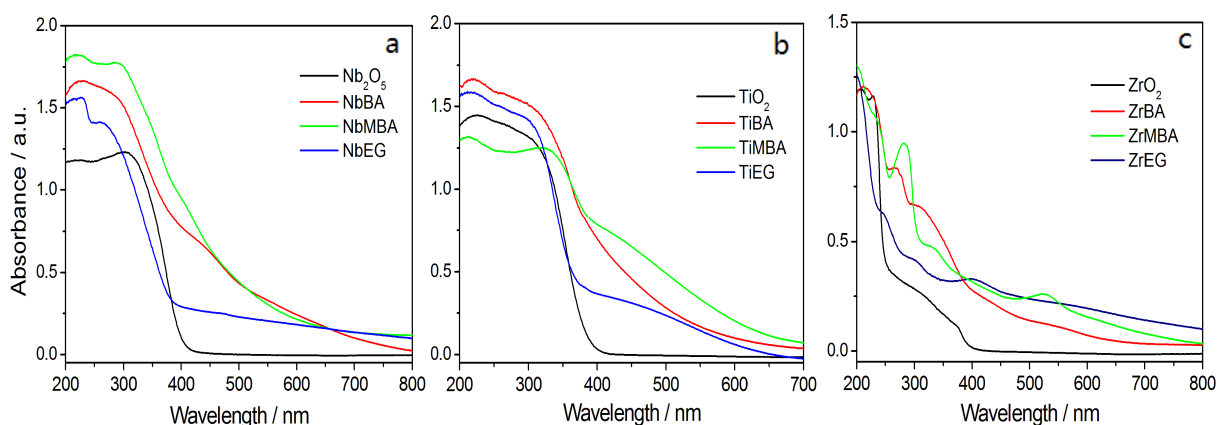
Sample	Active centres / mmol
NbBA	0.11
NbMBA	0.0376
NbEG	0.28
TiBA	0.06
TiMBA	0.064
TiEG	0.27
ZrBA	0.16
ZrMBA	0.041
ZrEG	0.28

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Figure S2 UV-Visible absorption of transition metal-organic group complexes: a Niobium complexes; b Titanium complexes; c Zirconium complexes; (BA: benzyl alcohol; MBA: 4-methoxy benzyl alcohol; EG: ethyl glycol)



The UV-visible diffuse reflectance (UV-vis DR) spectra of the sample show that the surface complex is responsible for the visible light absorption. For example, the NbBA sample has a considerable visible light absorption while benzyl alcohol does not absorb in visible light in the region of 400~800 nm, neither do Nb(OH)<sub>5</sub>. Similarly, the visible light absorption by TiBA, TiMBA, ZrEG and NbEG sample is due to the grafted surface complexes.

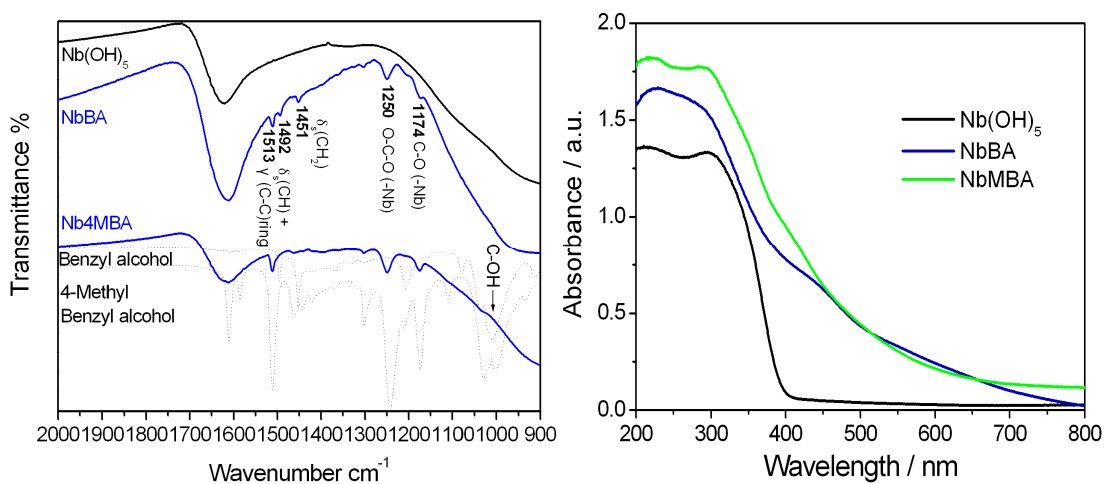


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Figure S3 FT-IR spectra and UV-Visible absorption of NbMBA catalyst



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