Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Surface Modification of Graphene Oxide *via* Noncovalent Functionalization with Porphyrins for Selective Photocatalytic Oxidation of Alcohols

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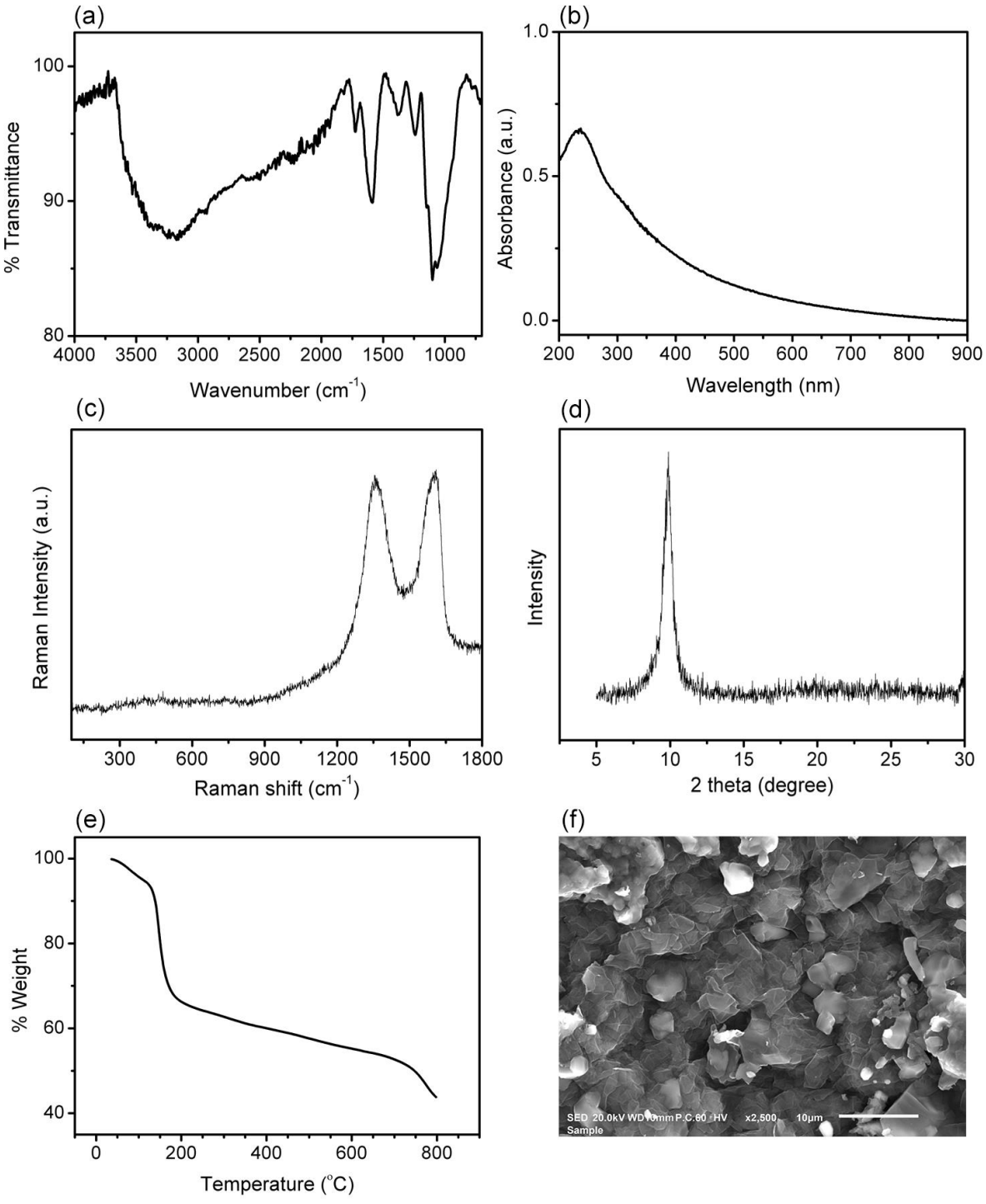


Figure S1 (a) FTIR spectrum; (b) UV-vis spectrum; (c) Raman spectrum; (d) XRD pattern; (e) thermogram; and (f) SEM image of synthesized graphene oxide (GO).

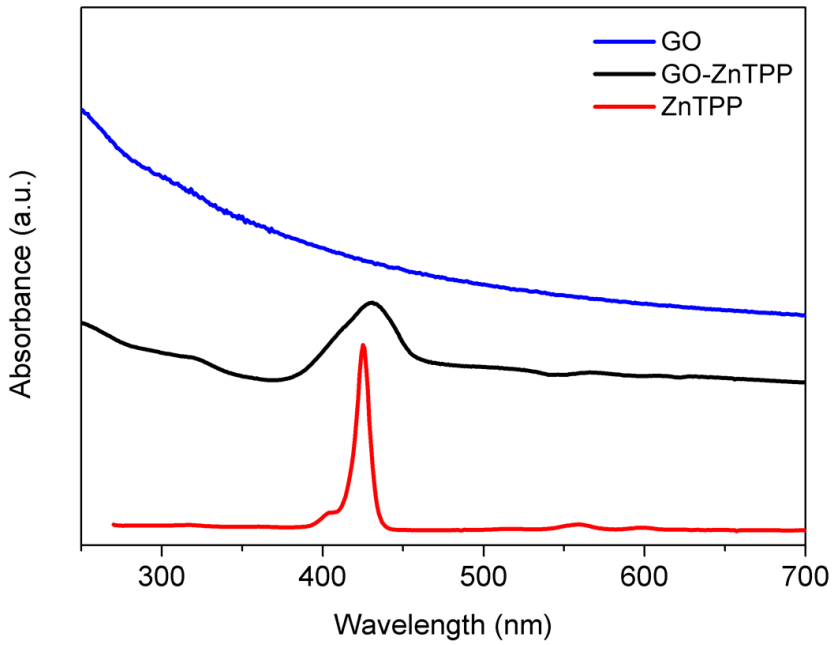


Figure S2 UV-vis absorption spectra of GO, ZnTPP, and GO-ZnTPP

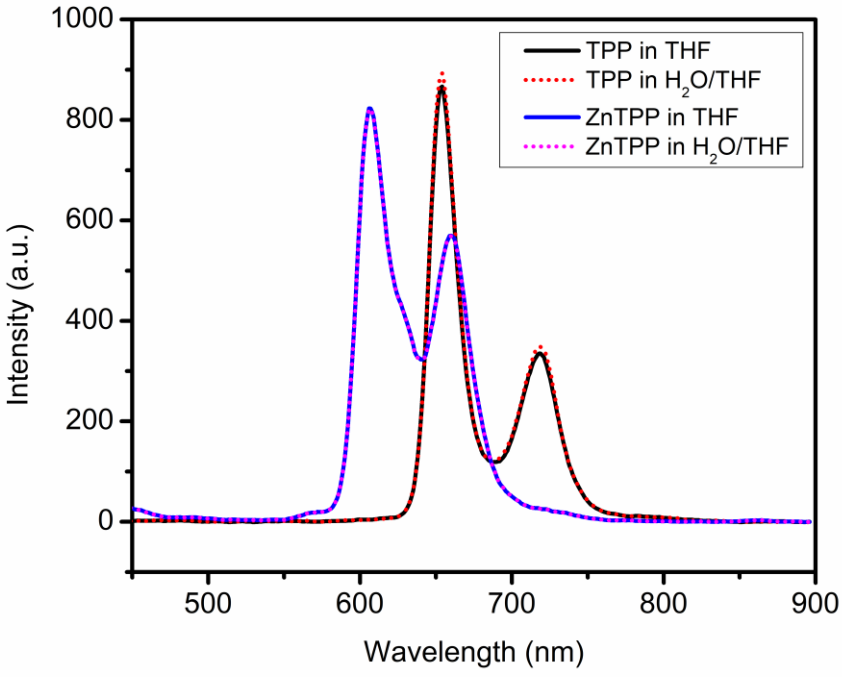


Figure S3 Fluorescence spectra of TPP in 2.00 mL THF (black), TPP in 2.00 mL H_2O/THF (1 : 15 v/v) (red dotted), ZnTPP in 2.00 mL THF (blue), ZnTPP in 2.00 mL H_2O/THF (1 : 15 v/v) (margenta dotted)

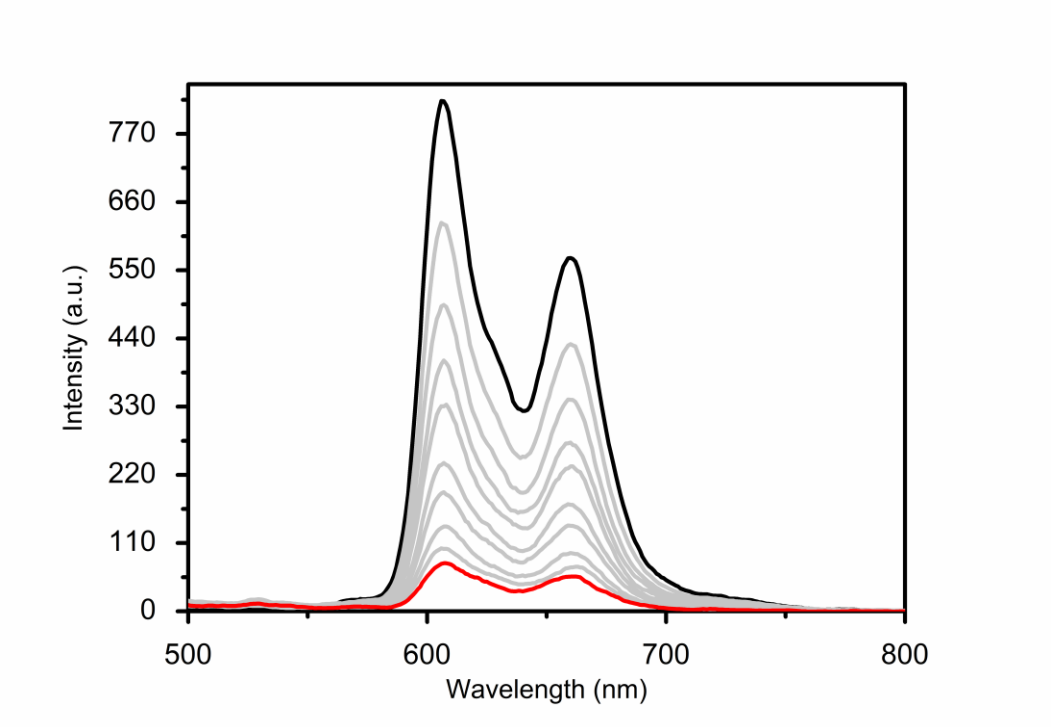


Figure S4 Fluorescence titration of ZnTPP upon the addition of 2 mg/mL GO (0-125 µL)

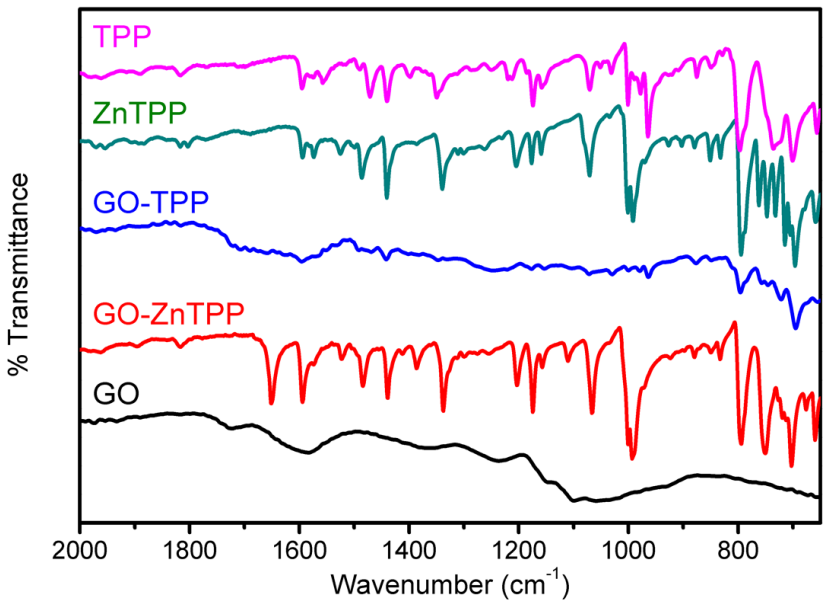


Figure S5 FTIR spectra of pristine graphene oxide, porphyrin derivatives (TPP and ZnTPP), and composites

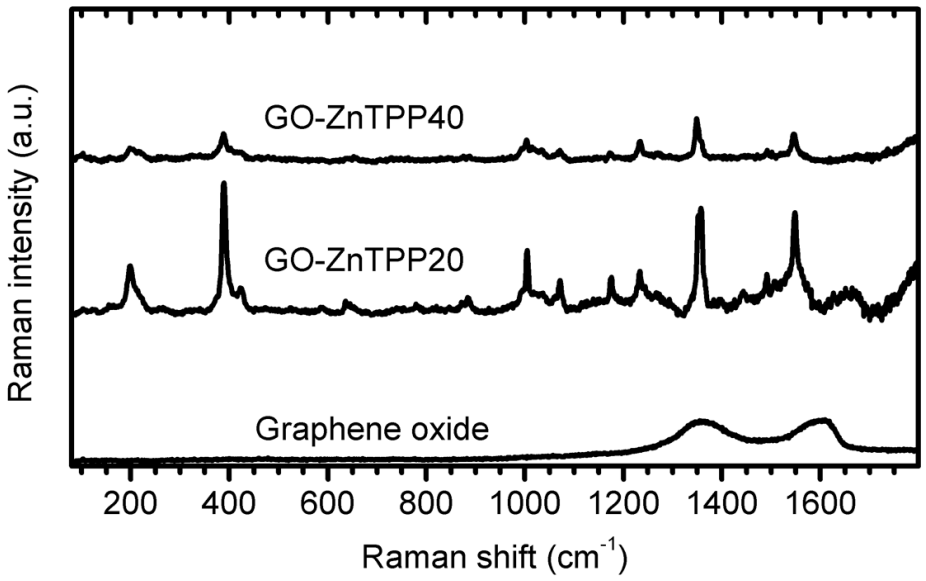


Figure S6 Raman spectra of graphene oxide flakes and GO-ZnTPP composites prepared in *two weight ratios*; GO-ZnTPP20 (GO:ZnTPP in a 1:2 weight ratio) and GO-ZnTPP40 (GO:ZnTPP in a 1:4 weight ratio). The spectra are stacked for clarity.

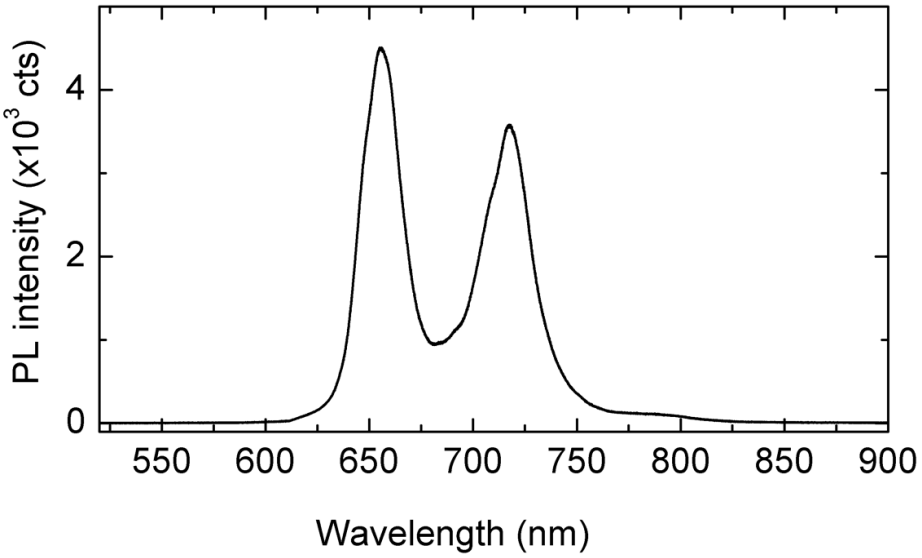


Figure S7 Photoluminescence spectrum of TPP dissolved in THF.

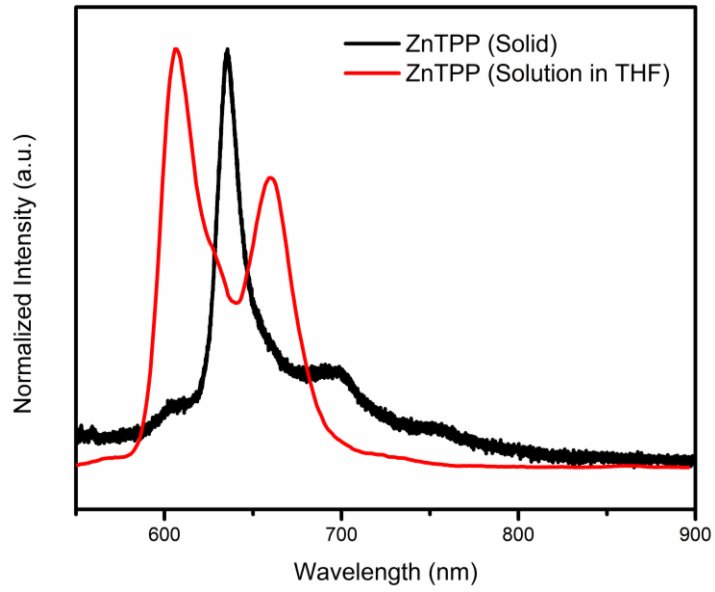


Figure S8 Photoluminescence spectra of ZnTPP (solid) and ZnTPP dissolved in THF.

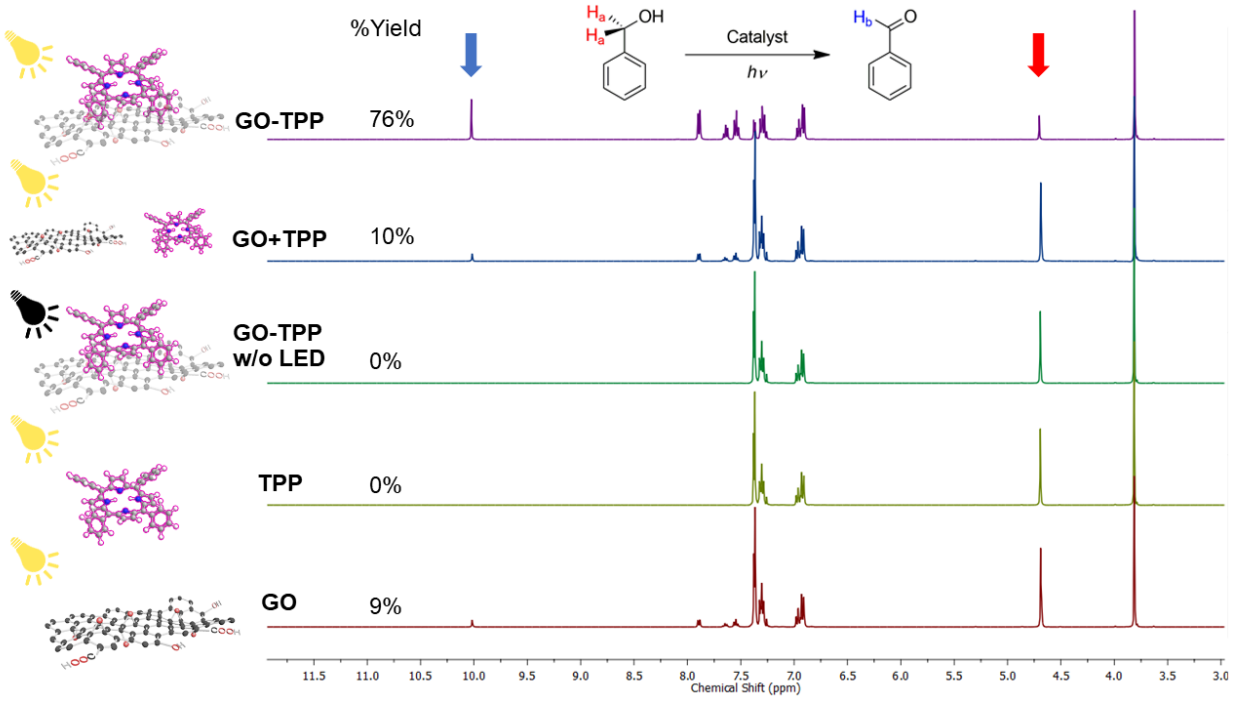


Figure S9 Comparison of photocatalytic activities of (a) GO, (b) TPP, (c) GO-TPP composite without LED irradiation, (d) non-sonicated GO and TPP mixture, and (e) GO-TPP composite. %yields were analyzed by ^{1}H NMR using anisole as an internal standard.

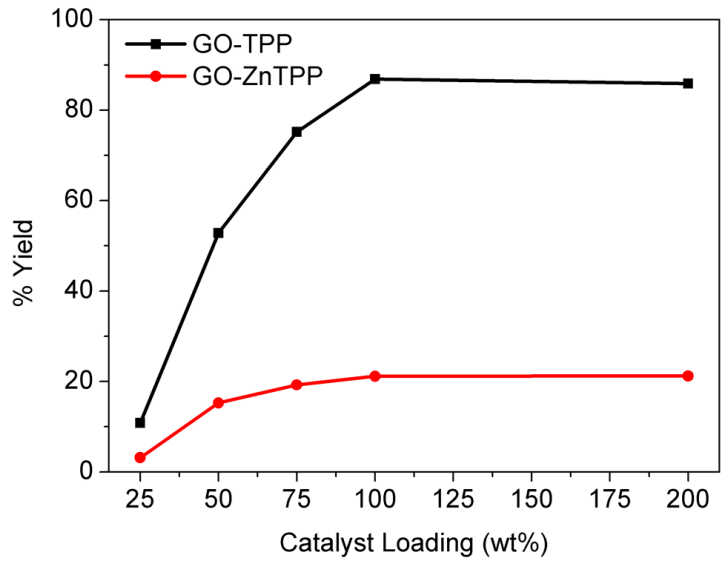


Figure S10 Photocatalytic reactivities toward oxidation of benzyl alcohol using a variety of catalyst loadings.

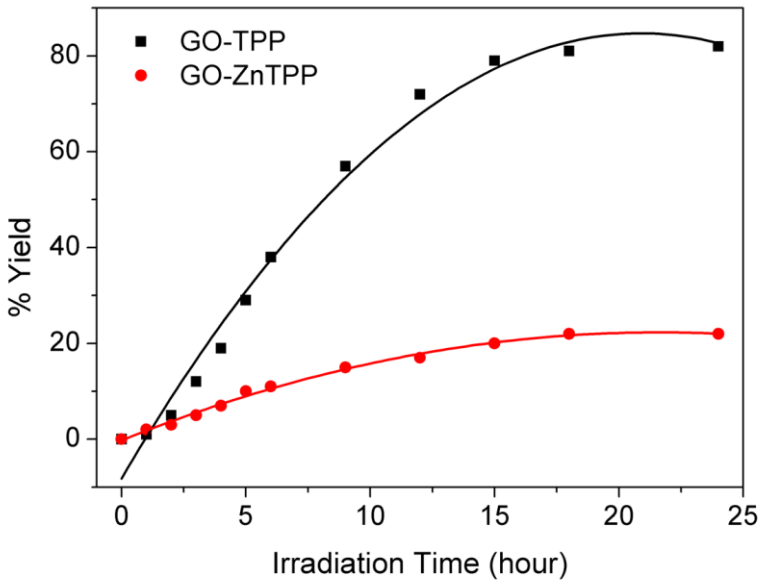


Figure S11 Monitoring photocatalytic activity of GO-TPP and GO-ZnTPP for oxidation of benzyl alcohol over time.

Parameters for GC analysis

Instrumentation: Gas chromatography (GC) was performed on a Varian CP-3800 gas chromatograph fitted with HP-5 capillary column (30m x 0.320 ID x 0.25 μm) and equipped with a flame-ionization detector. The gas chromatograph parameters are described as follow:

Determination of benzyl alcohol and benzaldehyde

Internal standard: nitrobenzene, injection temperature: 250 ˚C, FID detector: 250 ˚C, carrier gas: nitrogen, carrier gas flow rate: 1.0 mL min^{-1}, column temperature: 80 ˚C for 5 min, ramping up to 250 ˚C at 10 ˚C min^{-1}, holding at 250 ˚C for 8 min.

Determination of phenyl ethanol and acetophenone

Internal standard: nitrobenzene, injection temperature: 230 ˚C, FID detector: 270 ˚C, carrier gas: nitrogen, carrier gas flow rate: 1.0 mL min^{-1}, column temperature: 80 ˚C for 3 min, ramping up to 120 ˚C at 1 ˚C min^{-1}, holding at 120 ˚C for 2 min. ramping up to 250 ˚C at 10 ˚C min^{-1}, holding at 250 ˚C for 8 min.

Determination of cyclohexanol and cyclohexanone

Internal standard: 1-octanol, injection temperature: 240 ˚C, FID detector: 270 ˚C, carrier gas: nitrogen, carrier gas flow rate: 5.0 mL min^{-1}, column temperature: 60 ˚C for 4 min, ramping up to 150 ˚C at 10 ˚C min^{-1}, holding at 150 ˚C for 2 min

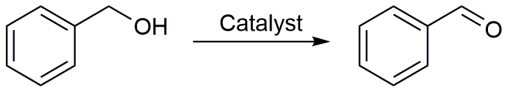
Determination of 2-thienylmethanol and thiophene-2-carbaldehyde

Internal standard: nitrobenzene, injection temperature: 270 ˚C, FID detector: 270 ˚C, carrier gas: nitrogen, carrier gas flow rate: 1.0 mL min^{-1}, column temperature: 70 ˚C, ramping up to 200 ˚C at 20 ˚C min^{-1}, holding at 200 ˚C for 3.5 min.

Investigation of photocatalytic activity by ^{1}H NMR

Unless otherwise noted, all reactions were carried out in ambient condition. The reaction mixture of benzyl alcohol (5.0 mg) and a catalyst (5.0 mg of GO, TPP or GO-TPP) was prepared in ultrapure water (2.00 mL) prior to irradiation. After irradiated with white cold LED for 24 h, the reaction mixture was filtered by a 0.22 μm Nylon syringe filter. Then, the filtrate was extracted by CH_2Cl_2 without pH adjustment. The organic phase was collected, dried over $NaSO_4$ and the solvent was removed in vacuo. After that, the crude product was added anisole (5.0 mg) as an internal standard and re-dissolved in deuterated solvent prior to ^{1}H NMR measurements.

Table S1. Comparison of catalytic activities toward benzyl alcohol oxidation



Catalyst	Solvent	Condition	Temperature (°C)	Catalyst Amount[a]	Reaction Time (h)	Conversion (%)[b]	Ref
GO-TPP	water	LED (visible light)	RT	100%w	24	80 (>99)	This work
GO	-	Teflon-lined autoclave	100	200%w	12	99 (92)	S1
Fe_3O_4@S/rGO	-	LED (visible light)	80	20 mg cat / 1 mmol BH	1.5	99 (>99)	S2
g-C_3N_4	acetonitrile	250W- W-filament bulb (>420 nm)	25	0.1 mg cat / 1 mmol BH	28	85 (82)	S3
CdS-MIL100(Fe)	toluene	500W Xe lamp (>420 nm)	RT	80 mg cat / 1 mmol BH	5	54 (>99)	S4
Au/rGO	Na_2O_3-$NaHCO_3$ in water	Teflon-lined autoclave	100	15.6 mg cat / 1 mmol BH	8	65 (93)	S5
Zr-MOF	toluene	26W helical light bulb (visible light)	80	0.04 molZr / 1 mmol BH	24	53 (>99)	S6
CeO_2@Pt@TiO_2	-	300W Xe lamp (>420 nm)	RT	0.08 mg cat / 1 mmol BH	5	39 (35)	S7
(Pd-Zn)/TiO_2	-	10%H_2/Ar, 1 bar	120	1%w	1	55 (81)	S8

[a] BH and cat refers to Benzyl alcohol as a substrate for alcohol oxidation and catalyst, respectively. [b] The percentages of selectivity shown in parentheses.

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