Electronic Supporting Information

Macro-mesoporous resorcinol-formaldehyde polymer resins as amorphous metal-free visible light photocatalysts

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Experimental:

Materials: Resorcinol (ACS, >99%, Alfa Aesar) (R), formaldehyde (Aldrich, 37 wt.% in water, stabilized by 10–15 wt.% methanol) (F), sodium carbonate (anhydrous, ACS, Fisher), and urea (98%, Aldrich) (U) were used as received. The synthesis procedure was developed by fixing the following parameters: Resorcinol 4.5 g and H_2O dilution volume = 9 mL. (i) RF12: molar ratio R/F = 1:2; and (ii) RF14: molar ratio R/F = 1:4; (iii)RFU: molar ratio R/F/U=1:2:0.5. Sodium carbonate (Na_2CO_3) were used as catalyst with amount of 0.5% of R.

Preparation of resins: Predetermined amounts of resorcinol was dissolved in distilled water at room temperature, and a certain amount of sodium carbonate was added as the catalyst. The solution was heated to ca. 313 K under stirring until all resorcinol was dissolved and the solution became transparent yellow. Then formaldehyde was added dropwise while stirring. Gelation of the sample was performed at 358 K for 72 h, when the gel appearance changed from opaque and light pink to translucent dark red. The aqueous gels obtained were then dried in a vacuum oven at 373 K for 1 day. The resorcinol–formaldehyde resin RF12 and RF14 were prepared in the same way without using urea. The resin samples were crushed into powder in a mortar and then suspended into acetone solvent with ball-milling for 1.5 h to get fine powder (10 mm zirconia ball, 6500 rpm). Then the fine powder samples were collected by filtration with DI water washing to remove some impurities.

Preparation of resin/reduced graphene oxide(RF/RGO) composite: Firstly, few layered graphene oxide was synthesized by the modified Hummers method from the natural flake graphite.[1] Concentrated H_2SO_4 and $KMnO_4$ were used to oxidize the graphite layer. The as-prepared oxidized graphite layers were exfoliated by the aid of ultrasonication. Then certain amount of 30% H_2O_2 was added in the suspension to eliminate the excess MnO_4^-. The solid products were washed many times with deionized water by high speed centrifugation and ultrasonication until the upper aqueous solution was neutral. Then the desired products were dried in a vacuum tank at room temperature. Detailed information on the synthesis and characterization of few-layered graphene oxide was shown in our published paper.[2]

The aqueous suspension of reduced graphene oxide was prepared by chemical-reduction of graphene oxide using hydrazine according to the literature.[3] Briefly, 2.5 mg graphene oxide was suspended into 10 ml water under sonication for 30 min. Then, 5 μL hydrazine solution and 28 μL 35% ammonia solution were added into the brown graphene oxide suspension in a glass vial. The vial was put in a water bath and kept at 95 ^oC for 1h. The reduced graphene oxide (RGO) suspension was obtained after cooling down to the room temperature. Then 100 mg RF12 resin powder was put into the RGO suspension with sonication for 30 min. After further stirring for 2 h, the solid powder (RF/RGO) composite was collected by filtration, washing and dried at 85 ^oC overnight.

Characterization of catalyst:

The porosity of the materials was determined based on the N_2 adsorption isotherms at 77 K with a Coulter Omnisorp 100 CX apparatus. Pore size distributions were obtained from the desorption branch of the isotherms using the Barrett, Joyner and Halenda (BJH) method. The pore volumes were determined by the BJH-desorption cumulative pore volumes. The specific surface areas were determined according to the Brunauer–Emmett–Teller (BET) plot of nitrogen adsorption isotherm in the relative pressure range 0.05–0.30. The surface analysis of sample powders by X-ray photoelectron spectroscopy (XPS) was obtained using the Mg Kα line (1253.6 eV) as the excitation source. C*1s* peak at 284.6 eV was used as reference. Elemental analysis (CHN) was also performed for determination of compositions of bulk samples. X-ray diffraction analysis of powders was examined on a SToe STADI/P powder diffractometer. Incident radiation was generated using a Cu k_α source (λ=1.54056 Å). Diffuse reflectance spectra were collected on an ultraviolet-visible spectrophotometer (JASCO-V550). The absorbance was transformed by the Kubelka-Munk method to calculate band-gap energy. Microstructure of samples was observed on a JEOL JSM-6700F Scanning Electron Microscope (SEM). Scanning electron microscopy (SEM) at 5 kV The SEM sample was prepared by placing small amounts of sample powders onto a carbon plate attached to an Aluminum sample holder and gold powder was allowed to evaporate under vacuum at room temperature.

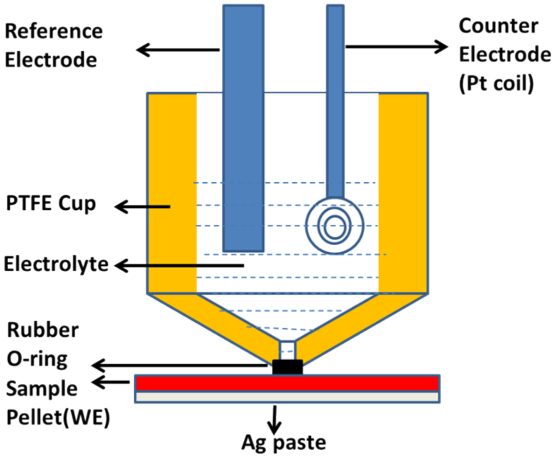
Photocatalytic reactions: Photocatalytic activities were evaluated by monitoring the degradation of 4-chlorophenol (4-CP) and the decolourization of methylene blue (MB) dye. Visible light irradiation was generated by a 250 W iron-doped metal halide Ultraviolet-Visible lamp with an Ultraviolet cut-off filter (≥ 420 nm; Borosilicate Coated Glass HM07, UQG (optic), Cambridge UK). For the degradation of 4-CP, 5 mg of sample powder (RF12, RF14 and RFU) was dispersed in distilled water. An aliquot of the 4-CP stock solution was subsequently added to the suspension to give a desired concentration of 100 μM (15 ml), and then the glass vial reactor was irradiated from the top with the visible light after stirring for 2 h in the dark. Sample aliquots were withdrawn from the reactor intermittently during the illumination and filtered through a 0.45 μm PTFE syringe filter. The degradation of 4-CP was monitored using a high performance liquid chromatograph (Agilent 1100 series). For methylene blue degradation, 2 mg of sample powders were suspended in 15 ml of methylene blue aqueous solution (100 μM). The suspension was first kept in a dark condition for 2 h to minimize adsorption effect before irradiation. The photoactivity of the samples was then evaluated by monitoring the intensity of the strongest absorption peak of methylene blue at 664 nm on a Perkin Elmer Lambda 35 ultraviolet/visible spectrometer along with irradiation time. 0.5 ml aliquots were sampled at various time intervals. The temperature during irradiation was controlled at about 35 ^{o}C by means of a water bath to remove infrared radiation and heat. For the recycling test, the RF14 powder after performing MB degradation was collected by filtration with DI water washing and dried at room temperature for the further use. The collected solid sample was re-dispersed into the MB solution with suitable sonication in order to minimize the decreased activity due to the reduced surface area.

Water oxidation experiments were performed with 10 mg sample powders suspended in100 ml silver nitrate solution (5 mM) under visible light irradiation. The suspension was sealed in a home-made photoreactor purged with pure Ar as a protective gas. Before photoirradiation, the sealed photoreactor was purged with Ar for 1 h to remove the O_2 and N_2 in air and dissolved in water. Both of the O_2 and N_2 in the head-space of photoreactor under irradiation were examined using an online gas chromatograph (Agilent 3000 Micro Gas chromatograph). During 4 h irradiation, the temperature of photoreactor increased from ~ 25 ^{o}C to ~ 40 ^{o}C. The O_2 content coming from the dissolved O_2 in water due to the reduced solubility at elevated temperature was calibrated with the N_2 content. At least three tests were repeated for each sample.

Photocurrent measurements: Current was collected on an inert electrode (Pt) immersed in a 50 mL aqueous solution with 25 mg resin powder (0.5 g/L) on the bottom of the photoelectrochemical cell. There was no direct contact between the catalysts and electrode. The Fe^{3+} (0.1 mM) was used as an electron acceptor and shuttle that carries the electron from the catalyst particles to the Pt electrode upon the redox reaction of Fe^{3+}/Fe^{2+}. 0.1 M Na_2SO_4 was used as electrolyte. A Pt mesh (1×2 cm), an Ag/AgCl electrode, and a steel foil (1×2 cm) were used as a working, a reference, and a counter electrode, respectively. A 50 W LED with monochromatic light (460 nm) was used as the light source.

Photocurrent was collected by applying a potential of +1.2 V to the reference electrode (~0.2 V bias) using a potentiostat connected to a computer.

Flat-band potential measurement experiment: The experiment was carried out with three electrodes system in a home-made cell as shown in Scheme S1. ~ 0.1 g resin power was pressed at a uni-axis static pressure of 200 MPa to give a pellet of 0.8 cm in diameter. The pellet was mounted in epoxy for better mechanical strength. One side of the pellet was painted with silver paint for current collection and the other side was covered with a rubber O-ring to control the active area to be 0.07 cm^2 for Mott-Schottky measurements. 1.0 M KCl aqueous solution was used as the electrolyte. The impedance under bias between -0.6 V and 1.0 V *vs*. Ag/AgCl reference was carried on an electrochemical workstation (Zahner-electrik GmbH & Co. KG) in the frequency range between 100 kHz and 0.1 Hz with a sine wave perturbation of 10 mV. The points at 13 Hz, 104 Hz and 1029 Hz were selected to estimate the flat-band potential of each sample.



Scheme S1. Schematic illustration of home-made electrochemical cell for flat-band potential measurement.

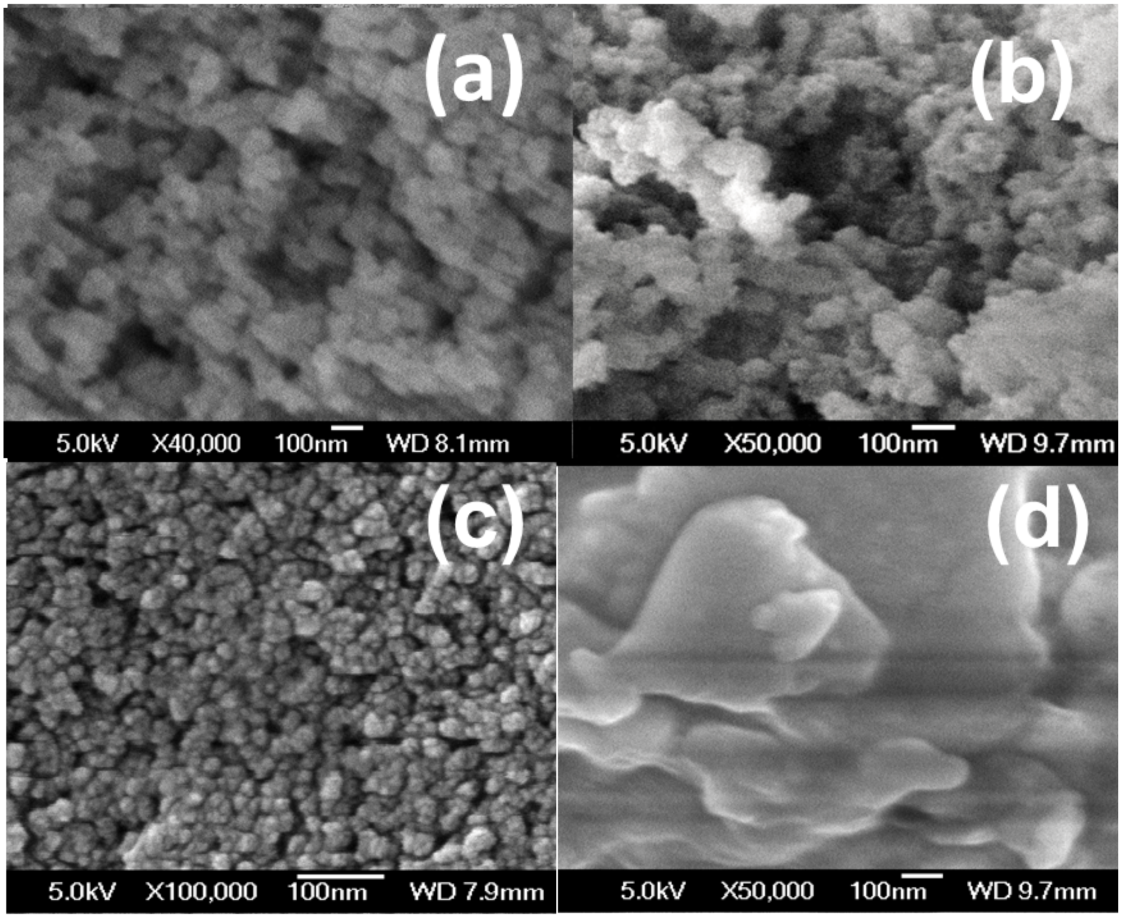


Fig. S1 SEM images of RF12 (a), RF14 (b, d), RFU (c) powder samples.

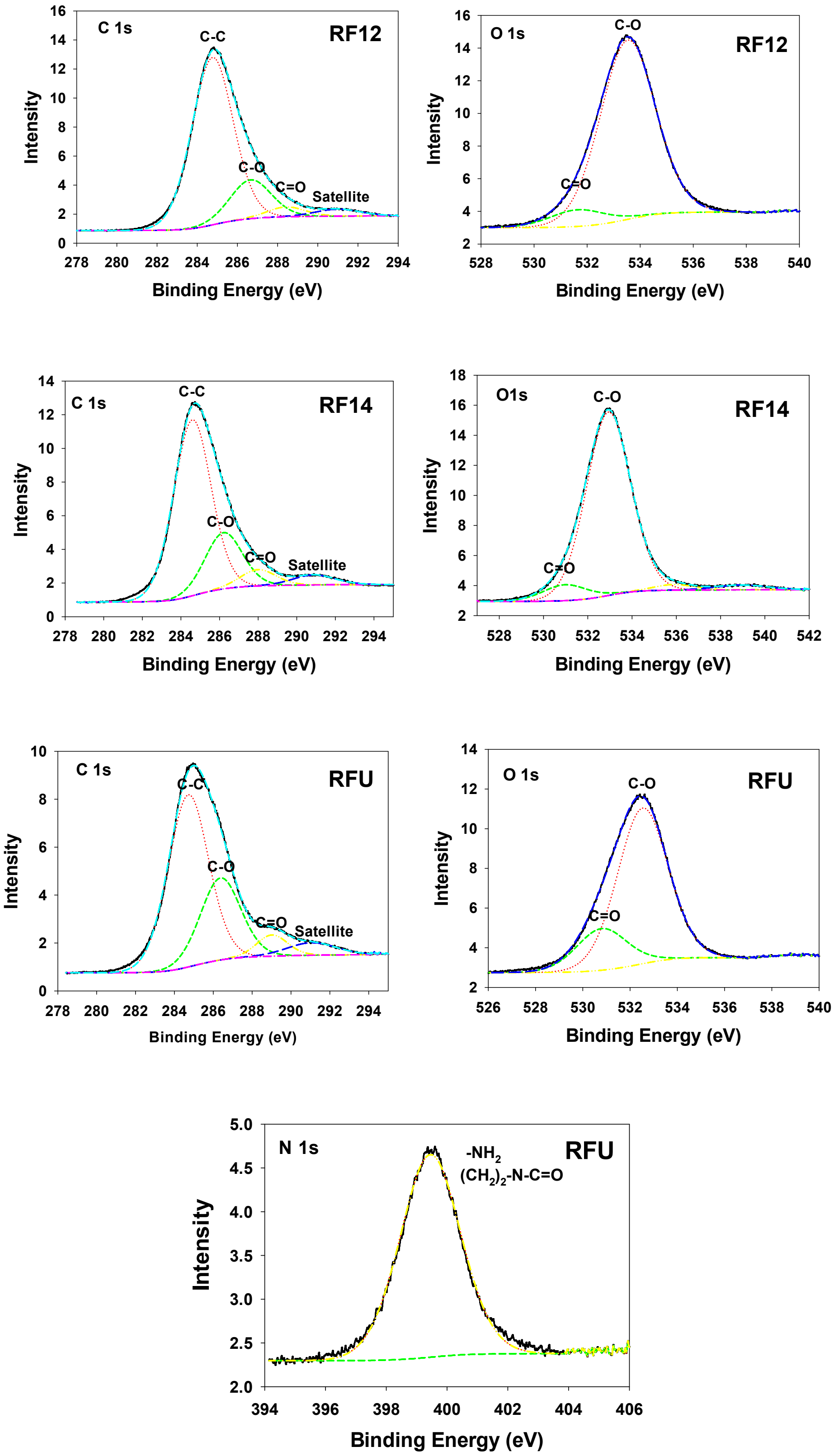


Fig. S2 Deconvolution of C*1s*, O1*s* and N*1s* XPS spectra of RF12, RF14 and RFU samples .

Table S1 Summary of XPS deconvolution results of RF12, RF14 and RFU samples

Sample	Regions BE(eV) and Area(at%)	Components assignment BE(eV) and Area(at%)	
RF12	C1s 285.0 (56)	C-C	284.90(75.11)
		C-O	286.65 (17.40)
		C=O	288.52 (4.06)
		π-π* satellite	291.08 (3.43)
	O 1s 533.5 (44%)	C-O	533.50(91.50)
		C=O	531.71(8.50)
RF14	C1s 284.81 (51.52)	C-C	284.59 (67.90)
		C-O	286.21(21.69)
		C=O	287.99 (6.04)
		π- π* satellite	290.88 (4.37)
	O 1s 533.01(48.48%)	C-O	532.93(87.32)
		C=O	530.97(7.57)
		H_2O	535.90 (2.43)
		CH_2O	538.96(2.69)
RFU	C 1s 284. 90(49.64)	C-C	284.8(60.23)
		C-O	286.45(28.7)
		C=O	289.1(5.73)
		π -π* satellite	291.14(5.34)
	O 1s 532.49(41.19)	C-O	532.9(78.91)
		C=O	531.17(21.09)
	N 1s 399.8(9.17)	$-NH_2$ $(CH_2)_2$-N-C=O	399.8

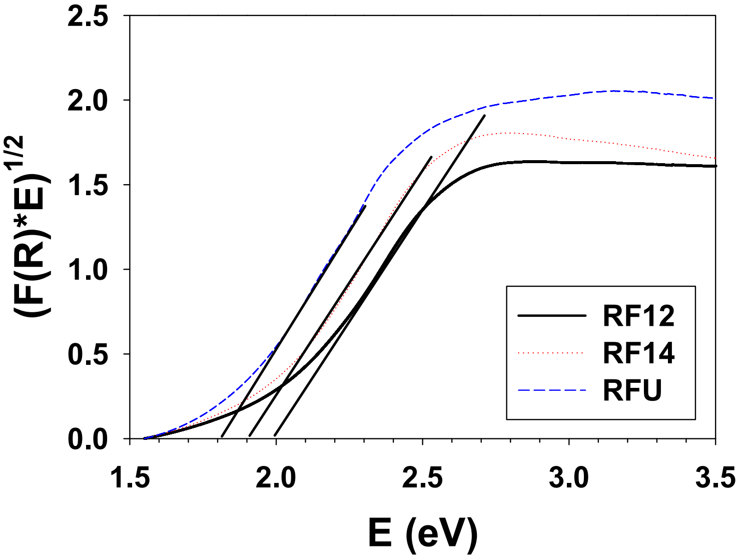


Fig. S3 Conversion of the UV-Vis absorbance spectra into the plot of Kubelka–Munk function versus photon energy ($[F(R)\times E]^{1/2}$ vs E).

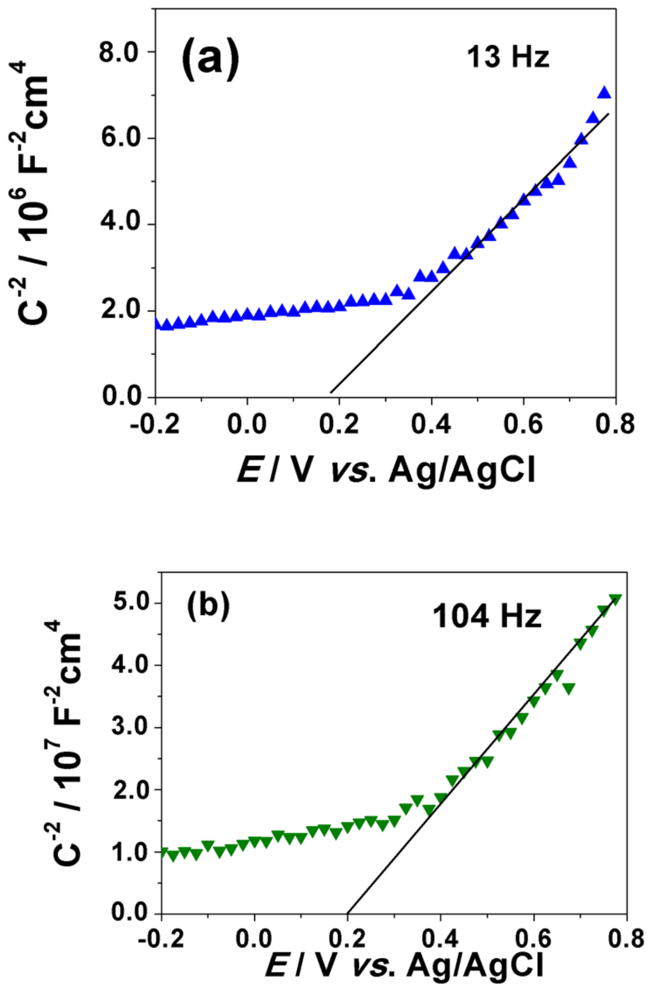


Fig. S4 Mott-Schottky plots of RF12 were measured at fixed frequencies of (a) 13 Hz and (b) 104 Hz in dark with potential amplitude of 10 mV.

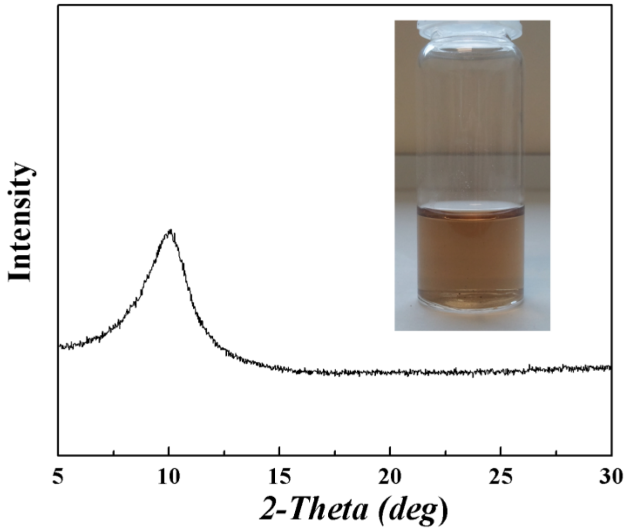


Fig. S5 XRD pattern of as-prepared few layered graphene oxide and photo image of graphene oxide aqueous suspension (1 mg/10 ml). Few layered graphene oxide was quite easily suspended in water with appropriate sonication to form a transparent solution.

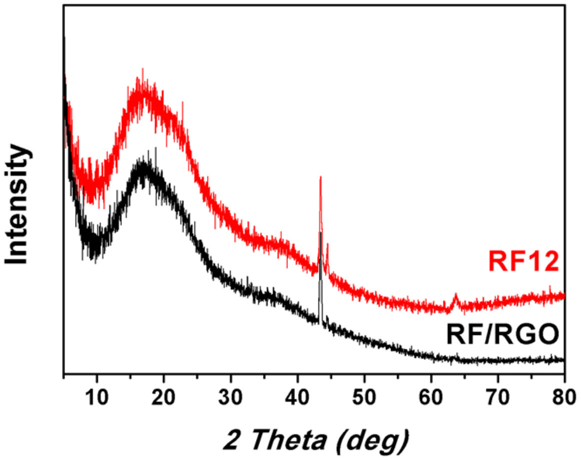


Fig. S6 XRD patterns of RF12 and RF/RGO (mass ratio of RF: GO = 40:1). There was no significant difference between two samples.

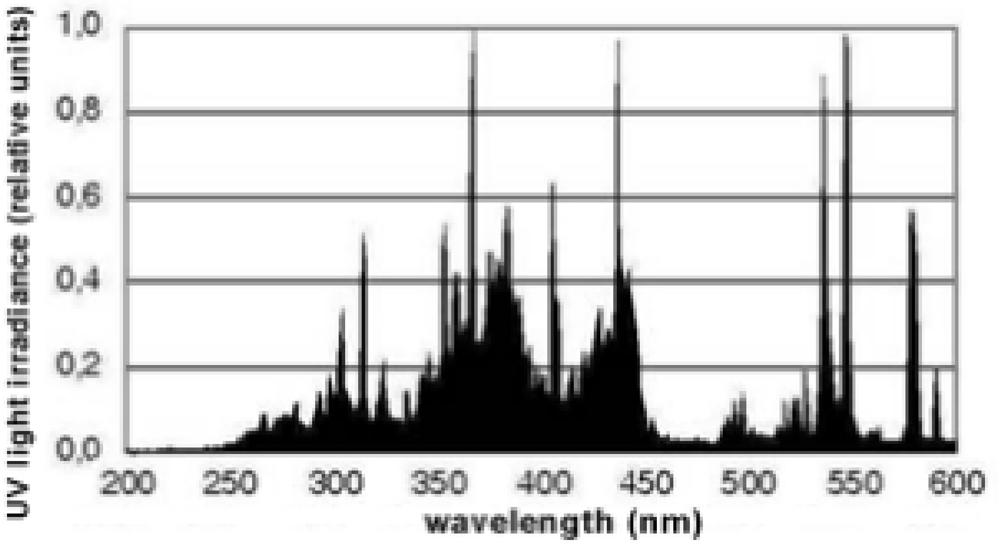


Fig. S7 Emission spectrum for Iron doped metal halide UV lamp (Source from google photos)

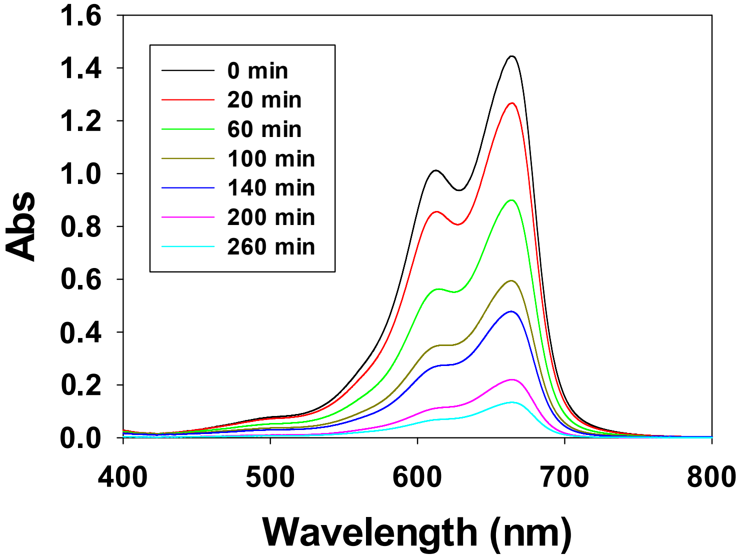


Fig. S8 UV-vis absorption spectra of MB dye during the photocatalytic decomposition.

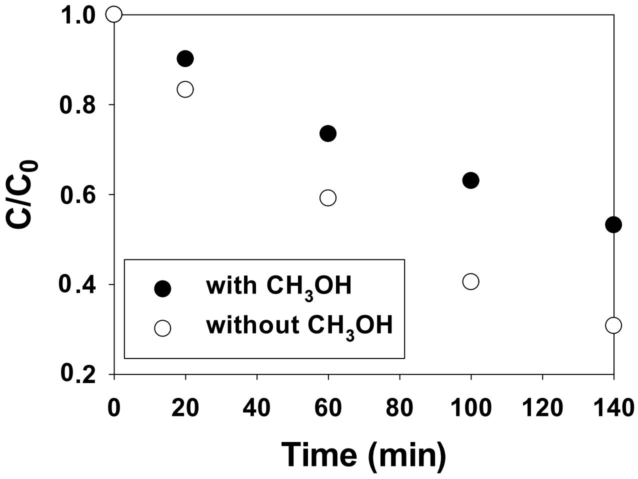


Fig. S9 Photocatalytic decomposition of MB dye with RF12 catalyst under visible light irradiation. [CH_3OH] = 10 vol.% [MB]$_i$= 100 µM, 2 mg catalyst, 15 ml aqueous solution.

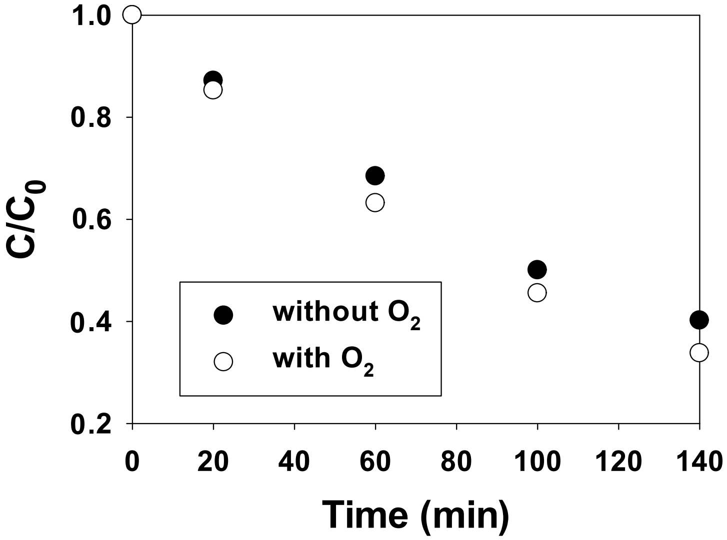


Fig. S10 Photocatalytic decomposition of MB dye with RF12 and RF/RGO samples under visible light irradiation. [MB]$_i$= 100 µM, 2 mg catalyst, 15 ml aqueous solution.

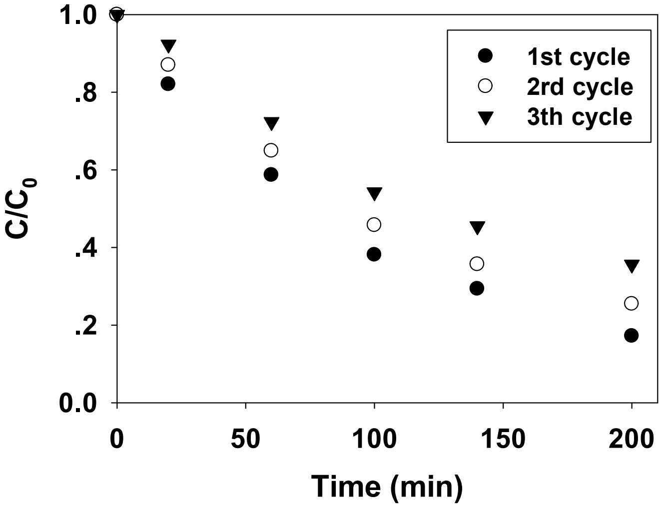


Fig. S11 Recycle test on the photocatalytic decomposition of MB dye with recovered RF14 catalyst under visible light irradiation.

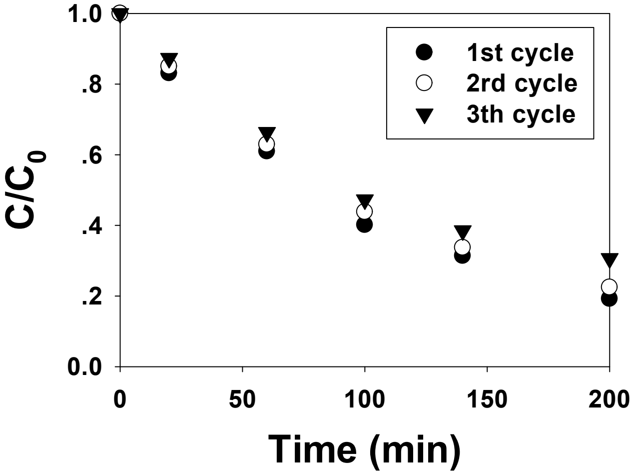


Fig. S12 Recycle test on the photocatalytic decomposition of MB dye with dispersing recovered RF14 catalyst by sonication under visible light irradiation.

Reference

1. M. Hirata, T. Gotou, S. Horiuchi, M. Fujiwara, M. Ohba, *Carbon*, 2004, ***42***, 2929-2937

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3. D. Li, M B. Muller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nature Nanotech*., 2008, ***3***, 101-105