A flow-circulation system incorporating a PVP-BiOBr@rGO assembly for simultaneous degradation and detection oxytetracycline in fish farm wastewater

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Preparation of graphene oxide (GO) [1]

Graphite oxide was synthesized through a modified Hummers' method that oxidizes graphite with a strong acid and oxidizing agent. Briefly, 2.0 g of graphite powder (Sigma-Aldrich, USA) was first mixed with 6.0 g of $KMnO_4$ (Merck, Germany) in a beaker. The mixed powder was transferred into a 500 mL-round bottomed flask and cooled to 0 °C in an ice bath for 10 min. Second, 46.0 mL of H_2SO_4 (Merck, Germany) was gradually added under stirring and cooling, maintaining the temperature below 15 °C. Then, the mixture was stirred at 40 °C in a water bath for 30 min. Third, 90.0 mL of DI water was slowly added, followed by heating the mixture under stirring at 95 °C in an oil bath for another 60 min. Subsequently, the reaction was stopped by adding 250.0 mL of DI water and 10.0 mL of H_2O_2 (Sigma-Aldrich, USA). H_2O_2 was used as an oxidizing agent to remove metal and metal oxide residuals (Mn and MnOx). The resulting product was separated by centrifugation and washed with a 5% HCl solution (Merck, Germany) to remove sulfates. After that, the product was filtered and washed several times with DI water until the pH of the filtered solution was about 7. After that, the obtained solid paste was dried overnight in an oven at 65 °C, yielding a graphite oxide powder.

The synthesized graphite oxide (0.80 g) was re-dispersed in DI water (120.0 mL) under ultrasonication for 90 min, followed by centrifugation to prepare a GO suspension. Finally, a dark-brown GO supernatant was obtained.

Reference

[1] Chaiwat Phrompet, Keerati Maneesai, Wattana Tuichai, Attaphol Karaphun, Chaval Sriwong, Chesta Ruttanapun, Electrochemical properties of tricalcium aluminate hexahydrate-reduced graphene oxide nanocomposites for supercapacitor device, J. Energy Storage 30 (2020) 101474.

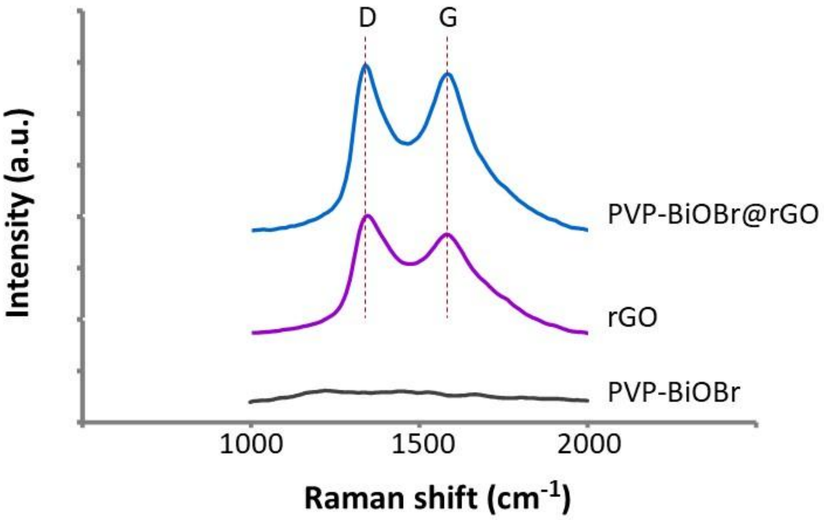
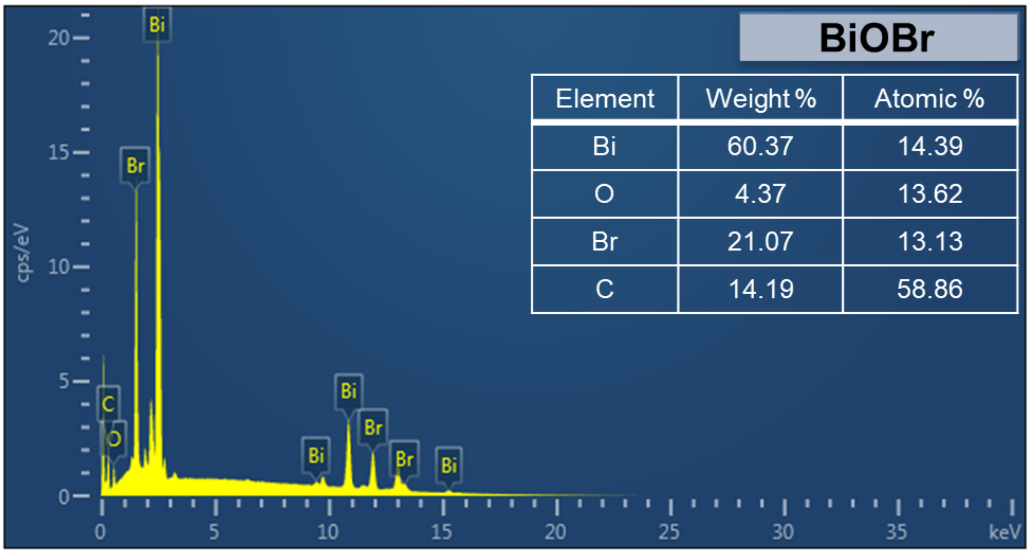


Fig. S1 Raman spectra of rGO, PVP-BiOBr and PVP-BiOBr@rGO composites.



Element	Weight %	Atomic %
Bi	60.37	14.39
O	4.37	13.62
Br	21.07	13.13
C	14.19	58.86

Fig. S2 EDX spectrum of bare BiOBr and the atomic percentages of Bi, Br, O and C.

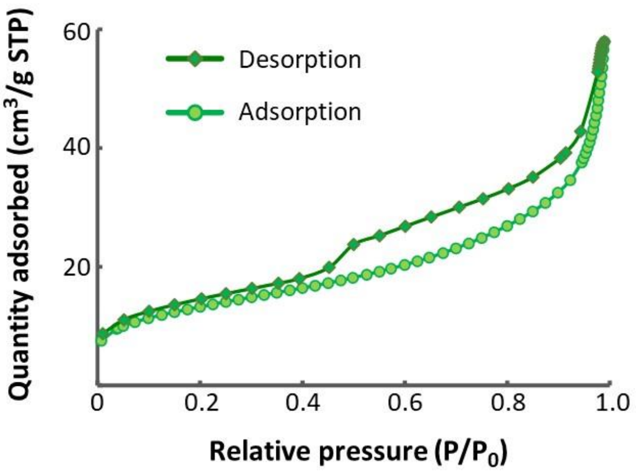


Fig. S3 Nitrogen adsorption-desorption isotherms of the PVP-BiOBr@rGO photocatalyst.

Trapping experiment

The mechanism of OTC removal was investigated through radical trapping experiments. Specific scavengers were introduced during the photodegradation process to quench different reactive species. Isopropyl alcohol (IPA), 1,4-benzoquinone (BQ), and disodium ethylenediaminetetraacetate (EDTA-2Na) were used as quenchers for hydroxyl radicals ($OH^{\bullet}$), superoxide anion radicals ($O_2^{\bullet-}$), and photogenerated holes (h^+), respectively.

Photodegradation experiments were conducted under a 125 W LED light source. The photocatalyst (25 mg) was dispersed in 100 mL of 10 ppm OTC solution. To achieve adsorption-desorption equilibrium, the suspension was stirred in the dark for 60 minutes prior to illumination. During photo-irradiation, approximately 5 mL of the solution was withdrawn at regular intervals. The OTC concentration was determined by measuring the absorbance at 368 nm using a UV–Vis spectrophotometer.

Terephthalic acid experiment for hydroxyl radical measurement [2]

The hydroxyl radicals generated during the photocatalysis were evaluated using a terephthalic acid (TA) photoluminescence probe. Briefly, 50 mg of the photocatalyst was dispersed into a 0.5 mM TA solution under basic conditions (0.002 M NaOH). The suspension was agitated in the dark for 120 min to obtain the adsorption-desorption equilibrium before light irradiation. Three mL of the TA solution was withdrawn at different times and then centrifuged to separate the catalyst from the suspension. Photoluminescence spectra of the supernatant were recorded using a spectrofluorometer (RF-5301PC Shimadzu), at an excitation (λ_{ex}) and emission (λ_{em}) wavelengths of 315 nm and 425 nm, respectively.

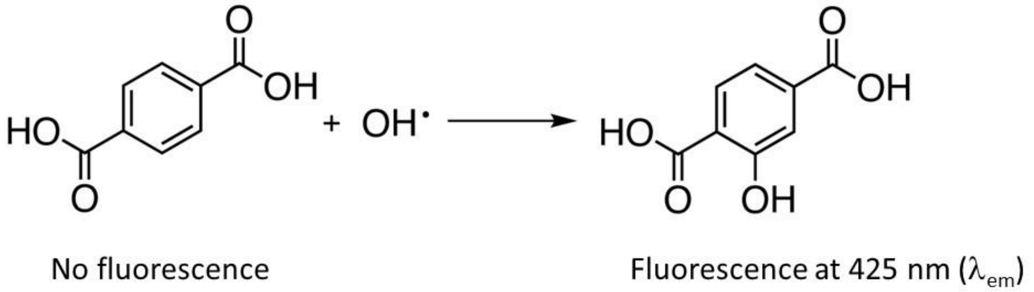


Fig. S4 Reaction of terephthalic acid (non-fluorescent) with a hydroxyl radical yielding fluorescent 2-hydroxyl terephthalic acid.

Reference

[2] Teeradech Senasu, Tammanoon Chankhanittha, Khuanjit Hemavibool, Suwat Nanan, Solvothermal synthesis of BiOBr photocatalyst with an assistant of PVP for visible-light-driven photocatalytic degradation of fluoroquinolone antibiotics, Catal. Today 384-386 (2022) 209-227.

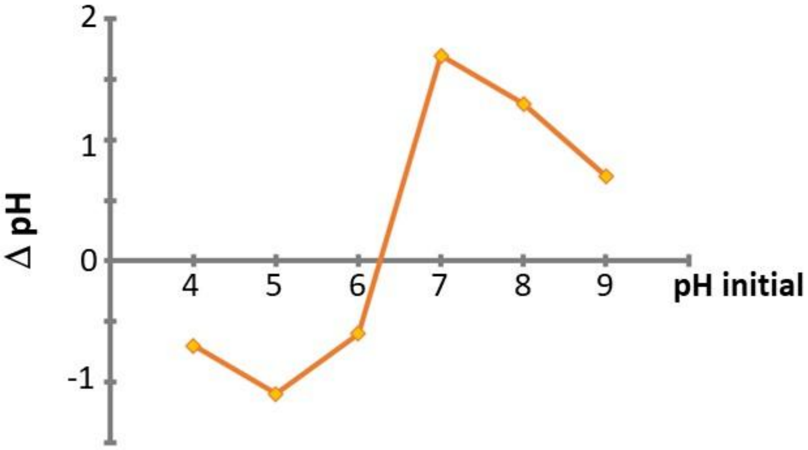


Fig. S5 The point of zero charge (pH_{pzc}) of the PVP-BiOBr@rGO, plotting the difference between final and initial pH values (ΔpH) against the initial pH values. The pH_{pzc} value was taken as the initial pH at which ΔpH is 0.

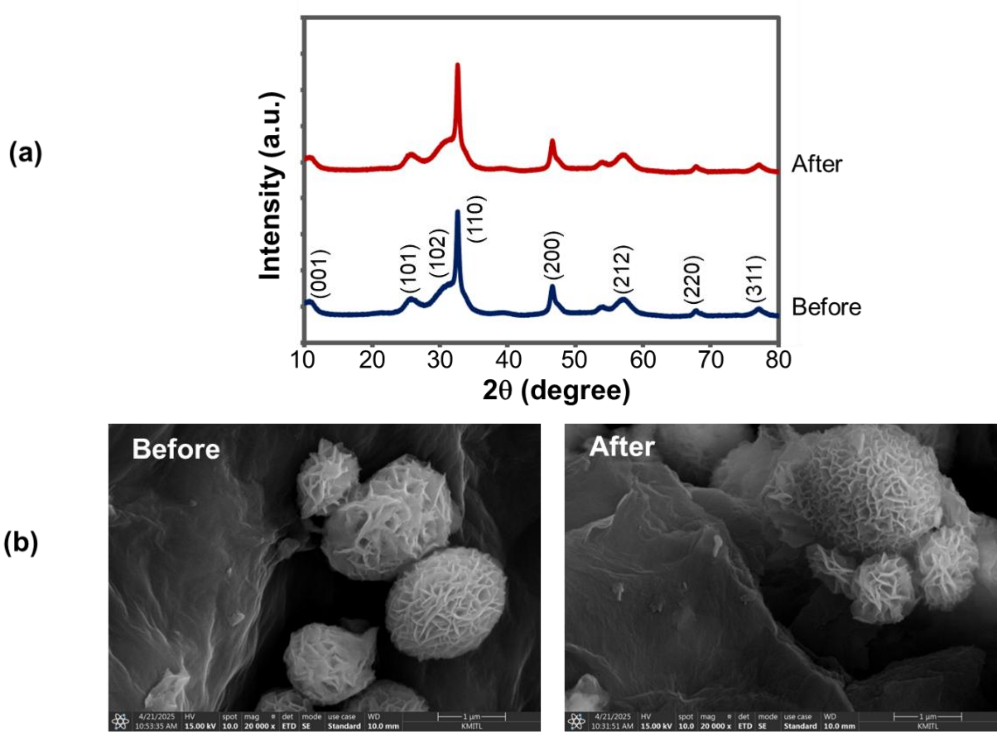


Fig. S6 (a) XRD patterns and (b) SEM micrographs of PVP-BiOBr@rGO photocatalyst before and after use for OTC degradation.