Supplementary Information (SI) for New Journal of Chemistry.

Engineering of Hybrid Nanostructured Boron-rGO-VO_2(B) Catalysts for Organic Pollutant Degradation

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4. Experimental section

4.1 Chemicals

The graphite flakes (99.9 %, metal basis) and ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$, 99%) were purchased from Alfa Aesar. Vanadium pentoxide (V_2O_5, Extra pure*),* Sulfuric acid (H_2SO_4, ~95%), potassium permanganate ($KMnO_4$, ~99.3%), hydrogen peroxide (H_2O_2, 30%), orthophosphoric acid (H_3PO_4, 98%), ethanol (EtOH, 94.5%), boric acid (H_3BO_3) powder and ethylene glycol were obtained from Duksan Chemicals and Metals, the Republic of Korea. Methyl Orange ($C_{14}H_{14}N_3NaO_3S$, Extra pure), 1, 4-Benzaquinone ($C_6H_4O_2$), isopropyl alcohol (C_3H_8O, above 99.5%), and ethanol (EtOH, 94.5%) were obtained from DaeJung Chemicals & Metals, the Republic of Korea.

4.2 Preparation of VO_2 (B), rGV and BrGV

Initially, 20 mL of deionized water was mixed with 500 mg of V_2O_5 and stirred for 15 min at room temperature. Next, 10 mL of ethylene glycol was added to this suspension and stirred for 30 min before being transferred to a 50-mL hydrothermal reactor. The mixture was subsequently maintained at a temperature of 180°C for a duration of 6 hours, followed by allowing the reactor to cool naturally to ambient temperature. The resulting products were transferred to a centrifuge tube and washed three times each with deionized water and absolute ethanol. Finally, the as-prepared VO_2(B) was placed in a vacuum-drying oven at 80°C for 12 h [S1]. A similar synthesis process was carried out to develop the rGO-VO_2(B) by adding GO (100 mg) before including V_2O_5 and sonicating for 20 min. Figure S1 shows that the rGO-VO_2(B) catalyst doped with boron was prepared by extending the rGO-VO_2(B) synthesis with the addition of 3.4 mg and 17.9 mg of boric acid (H_3BO_3) to the suspension and stirred for 30 min. Following, B-rGO-VO_2(B) catalysts were developed and obtained resulting an identical rGO-VO_2(B) procedure. The as-developed material of VO_2(B), rGO-VO_2(B), B-rGO-VO_2(B)-1 and B-rGO-VO_2(B)-2 are denoted as VO_2, rGV, BrGV-1 and BrGV-2, respectively.

4.3 Material Characterization.

X-ray diffraction (XRD) investigation with Cu Kα radiation using an Xpert Pro equipment verified the crystalline characteristics. Fourier-transform infrared (FT-IR) spectroscopy was used to perform functional group analysis using a Perkin Elmer Spectrum 100 device. Using an XploRA Plus device from HORIBA Jobin Yvon S.A.S., France, Raman spectroscopy made it easier to analyse the chemical composition of the substance. By using a Thermo Scientific K-α surface analysis equipment and X-ray photoelectron spectroscopy (XPS), the surface chemistry was further clarified. A HITACHI H-7600 device from Japan was used for transmission electron microscopy (TEM) analysis in order to do a thorough investigation of morphology and structure. Using a HITACHI S-4800 equipment, field emission-scanning electron microscopy (FE-SEM) in conjunction with an EDAX system was used to examine surface microstructures, particle size, elemental composition, and mapping.

4.4 Sonocatalytic Activity of BrGV Nanocomposites

The effects of sonodegradation were studied using a standard stock solution of 0.1 g/L of methyl orange dye in distilled water. A Power Sonic 620 ultrasonic system was used to evaluate dye degradation. The degradation reaction was carried out at room temperature in ultrasonic bath technique. The sonocatalytic degradation was performed at 700 W at 50/60 Hz. For measuring the sonocatalytic effect, the catalysts were added to the desired volume of methyl orange dye solution. Before ultrasonication, the system was allowed to 30 min reach equilibrium to ensure a balanced interaction between the catalyst and dye molecules. Once equilibrium was achieved, ultrasonic process was applied. We employed a micropipette to extract 4,000 µL of the reaction mixture, followed by centrifugation for 20 min to isolate the catalyst. After the removal of the settling catalyst, the absorbance of the solution was evaluated using a UV-Vis spectrophotometer. To find the optimal sonocatalytic degradation conditions, the performance was carried out with various ultrasonic irradiation periods (0-60 min), solution pH (4-8), catalyst dose (30-50mg), and scavengers such as benzoquinone (BQ), ethylenediaminetetraacetic acid (EDTA), and isopropyl alcohol (IPA).

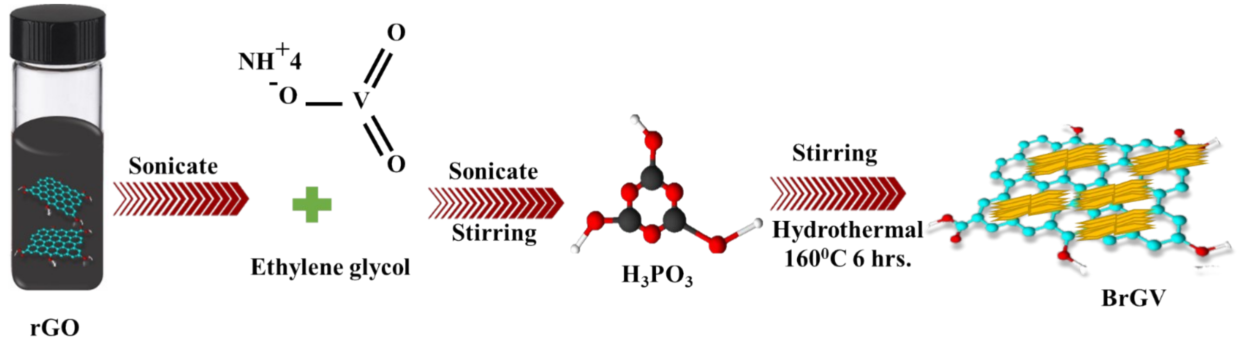

Figure S1: Schematic of BrGV catalyst synthesis process.

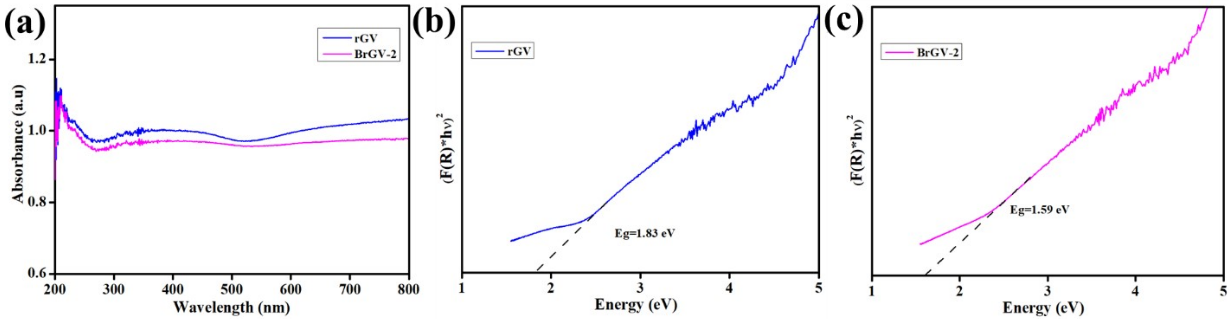

Figure S2: (a) UV DRS, and Tauc plot of (b) rGV and (c) BrGV-2.

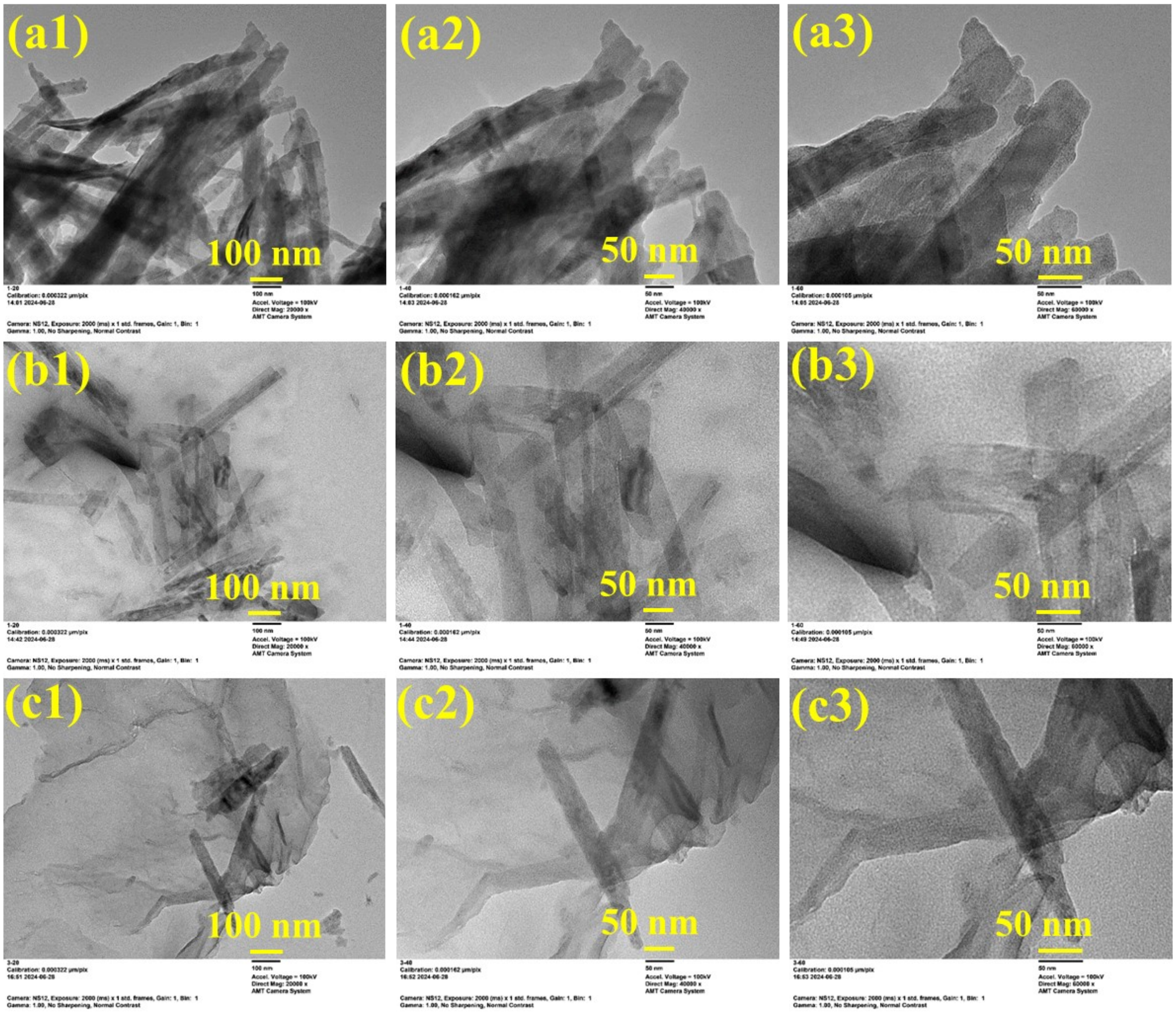

Figure S3: TEM images of (a1-a3) VO_2, (b1-b3) rGV and (c1-c3) BrGV-2.

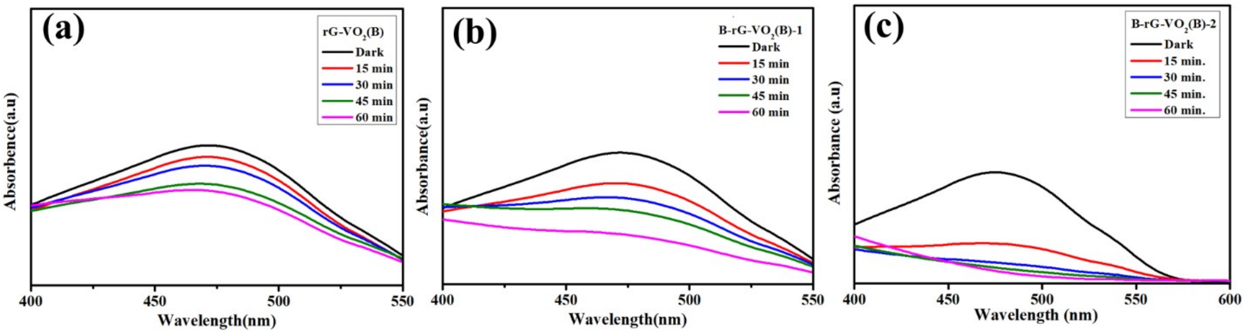

Figure S4.UV-Vis absorbance spectra for 10 ppm MO dye degradation in the presence of 40 mg catalyst loading: Effect of (a) rGV (b) BrGV-1 and (c) BrGV-2 catalyst on removal of MO.

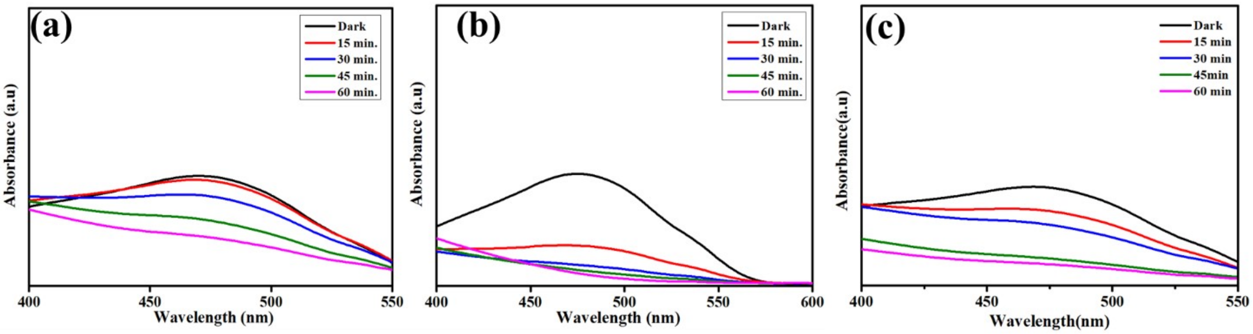

Figure S5. UV-Vis absorbance spectra of different dosages using BrGV-2 catalyst: (a) 30 mg, (b) 40 mg, and (c) 50 mg for MO dye degradation.

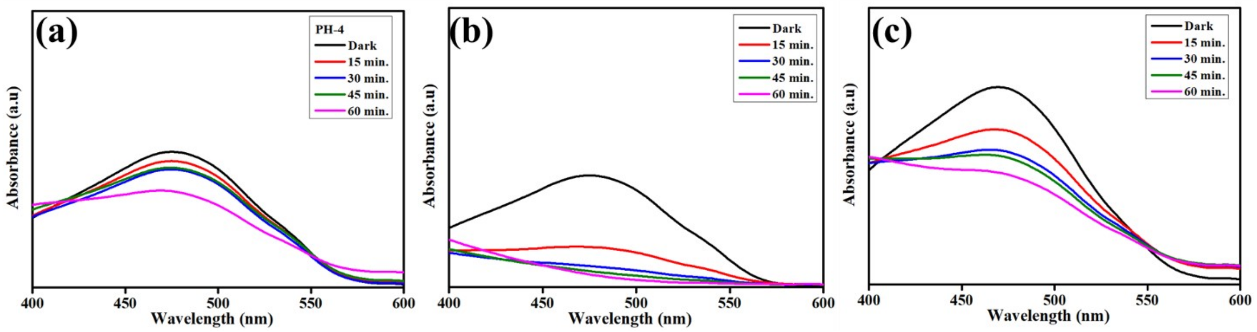

Figure S6. UV-Vis absorbance spectra of different pH using BrGV-2 catalyst: (a) pH 4, (b) pH 6, and (c) pH 8 for MO dye degradation.

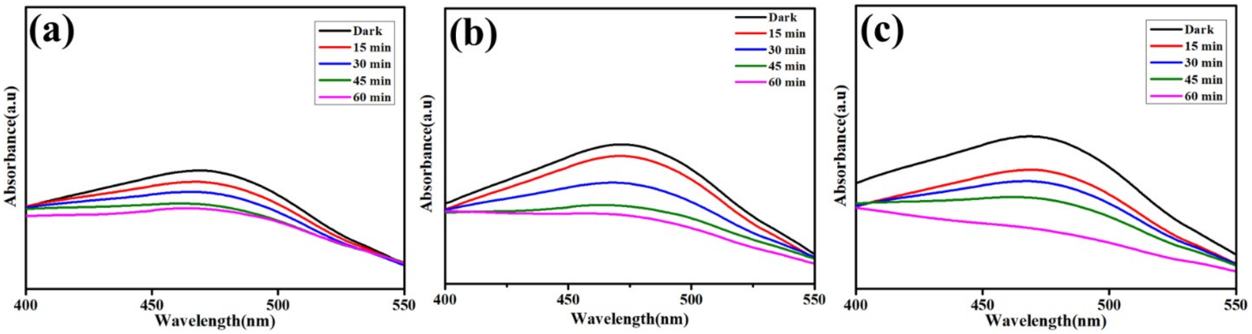

Figure S7. UV-Vis absorbance spectra of different scavengers using BrGV-2 catalyst: (a) BQ, (b) IPA, and (c) EDTA for MO dye degradation.

References

[S1] S. Wang, H. Zhang, K. Zhao, W. Liu, N. Luo, J. Zhao, S. Wu, J. Ding, S. Fang, F. Cheng, Designing interstitial boron-doped tunnel-type vanadium dioxide cathode for enhancing zinc ion storage capability, Carbon Energy, 5 (2023) e330