

Supporting Informations

Bi₃O₄Br Nanosheets Immobilized in Chitosan Microspheres as Efficient and Recyclable Hybrid Catalysts for Water Treatment

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Experimental details

- **Preparation of Bi₃O₄Br nanosheets**

Bi₃O₄Br nanosheets were prepared through a solvothermal synthesis in water/ethylene glycol mixture using Bi(NO₃)₃·5H₂O and NaBr as starting materials followed by thermal treatment at 500°C. To achieve this, 3 g of Bi(NO₃)₃·5H₂O (~6.18 mmol) were mixed with a mixture of water (40 mL) and ethylene glycol (40 mL) and sonicated for about 10 min. Then, 317.9 mg of NaBr (~3.09 mmol) was added to the above mixture under magnetic stirring. After about 15 min, the mixture was transferred into an Autoclave of 100 mL and heated at 180°C for 17.5h. Next, the precipitates were collected by centrifugation, washed several times with distilled water and methanol and oven-dried in air at ~75°C. Finally, the resulting product was calcined at 500°C for 2 hours with a heating rate of about 5°C/min. A schematic illustration of the synthetic process is described in Figure S1.

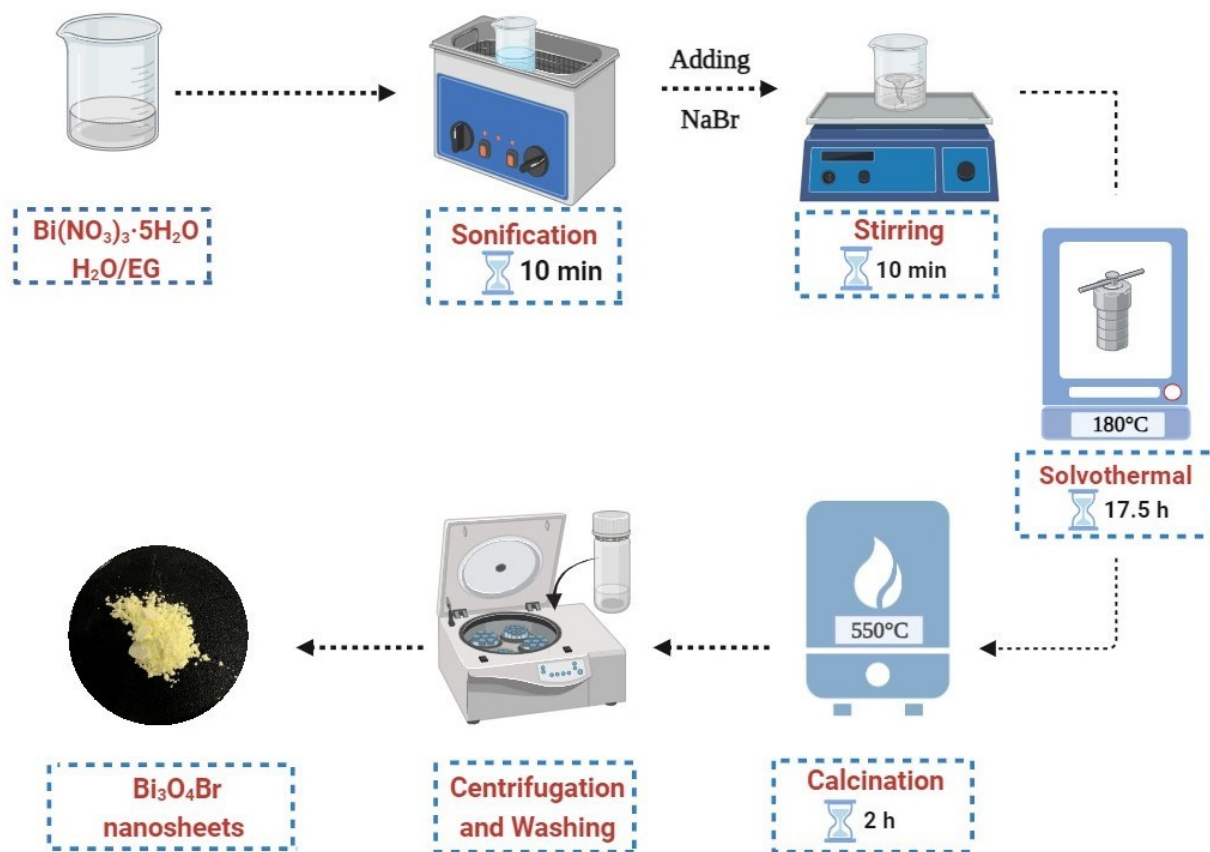


Figure S1 | Schematic illustration for the synthesis of $\text{Bi}_3\text{O}_4\text{Br}$ nanosheets.

- **Preparation of $\text{Bi}_3\text{O}_4\text{Br}$ @Chitosan Hybrid Materials**

$\text{Bi}_3\text{O}_4\text{Br}$ @Chitosan hybrid materials were obtained by physically imprinting $\text{Bi}_3\text{O}_4\text{Br}$ in chitosan beads through a co-precipitation method in a nonsolvent media. Briefly, 400 mg of chitosan and 150 mg of were sonically dispersed in 20 ml of H_2O for 1h. Then, 0,2 ml of acetic acid was added to the above solution under magnetic stirring to dissolve the chitosan. The formation of chitosan beads was achieved by dropping the obtained solution with a syringe in sodium hydroxide aqueous solution (200 mL, 2M), which causes the instantaneous precipitation of $\text{Bi}_3\text{O}_4\text{Br}$ @Chitosan beads in the basic medium. After 1 hour in the alkaline solution, the $\text{Bi}_3\text{O}_4\text{Br}$ @Chitosan beads were filtered and washed with distilled water several times until a neutral pH solution ($\text{pH} \approx 7$). A scheme of these synthetic steps is illustrated in Figure S2.

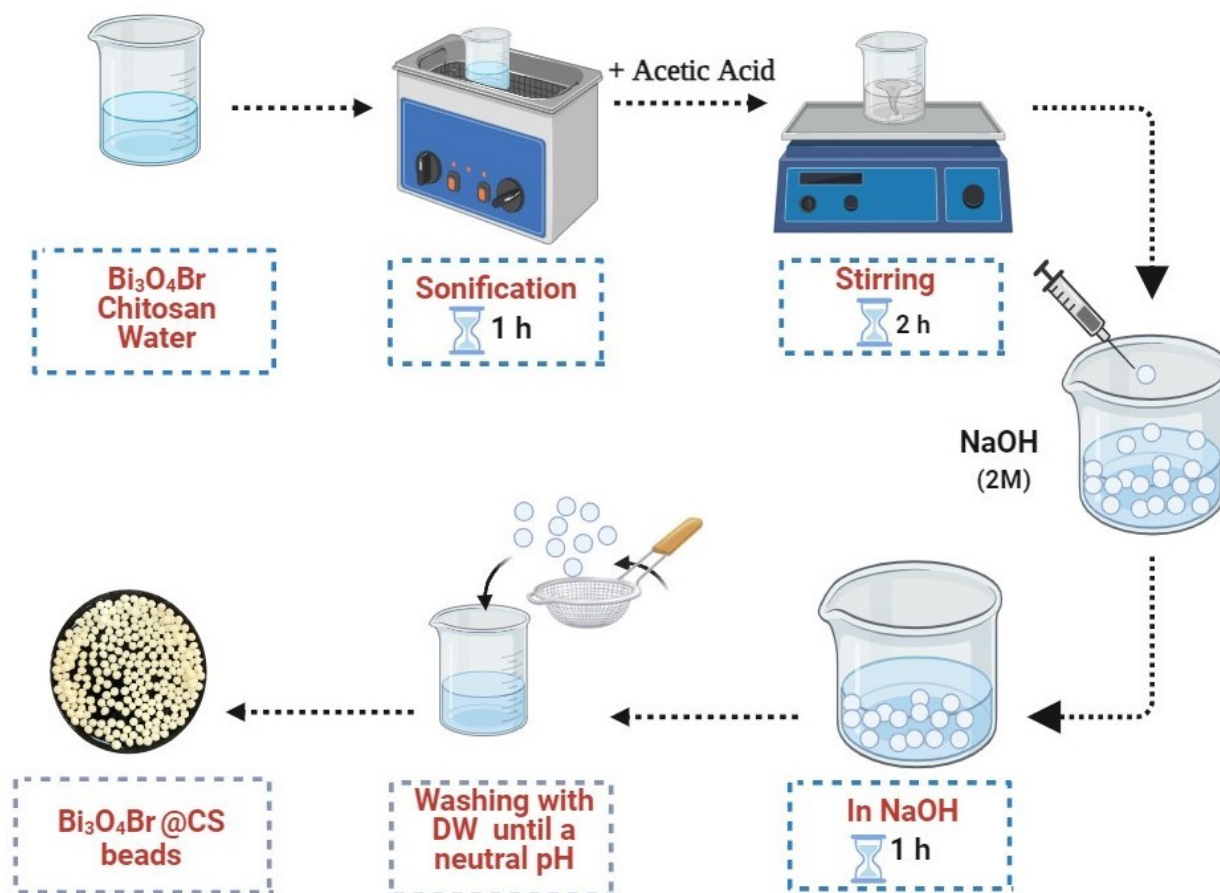


Figure S2 | Schematic illustration for the synthesis of $\text{Bi}_3\text{O}_4\text{Br}@chitosan$ hybrid materials.

Catalytic and Photocatalytic Activity Evaluation

General Conditions for Rhodamine B (RhB) photodegradation

The photocatalytic behavior of the $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials was investigated in the photodegradation of organic dyes under UV light irradiation. For this, RhB was chosen as a model organic dye. These experiments were carried out in a quartz cuvette (25 mL) covered with a Teflon cover. In a typical photodegradation experiment, the quartz cuvette was charged with a certain amount of $\text{Bi}_3\text{O}_4\text{Br}@CB$ and 6 mL of RhB aqueous solution. The reaction was stirred under simulated UV light using a Philips HPL-N 125W lamp with a wavelength of 365 nm as a light source. The progress of the photocatalytic reaction was performed by withdrawing a certain amount of RhB solution at regular intervals and monitoring the absorbance vs wavelength spectra using the UV-Vis spectrophotometer.

General Conditions for Reduction of 4-Nitrophenol to 4-aminophenol

The catalytic performance of $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials in the reduction of 4-NP was performed in an aqueous solution using NaBH_4 as a reducing agent. In a typical reduction process, a mixture of 6 mL of 4-NP aqueous solution (10 mg/L), $\text{Bi}_3\text{O}_4\text{Br}@CSB$ and 2 mL NaBH_4 (0.5, 1 or 2 M) was stirred at room temperature at selected period of time. The progress of the reduction process was determined by monitoring the absorbance band of 4-NP at 402 nm using UV-Vis spectrophotometer. At a regular time interval, samples of 4-NP solution were collected to plot the UV spectra of absorbance vs wavelength at each time.

TGA analysis

The thermal behavior of $\text{Bi}_3\text{O}_4\text{Br}$ sheets and $\text{Bi}_3\text{O}_4\text{Br}@CS$ composite has been studied by thermogravimetric analysis (TGA). The **figure S3** displays the TGA curves of $\text{Bi}_3\text{O}_4\text{Br}$ sheets and $\text{Bi}_3\text{O}_4\text{Br}@CS$ hybrid materials in the temperature range of (~ 20 - 700°C) with a heating rate of $10^\circ\text{C}/\text{min}$. The TGA curve of $\text{Bi}_3\text{O}_4\text{Br}$ sheets revealed that no significant weight loss was observed in all temperature ranges, which confirms the thermal stability of the $\text{Bi}_3\text{O}_4\text{Br}$ sheets in the range (20 - 700°C). Moreover, the absence of weight loss suggests that $\text{Bi}_3\text{O}_4\text{Br}$ sheets have no residual organic compounds nor adsorbed water molecules. On the other hand, the TGA curve of $\text{Bi}_3\text{O}_4\text{Br}@CS$ composite is composed of two regions separated by a significant weight loss in the temperature range of 200 - 300°C . This loss is mainly due to the degradation of chitosan polymeric structure above 250°C . Above $\sim 300^\circ\text{C}$, there is no obvious weight loss which indicates that chitosan has completely decomposed.

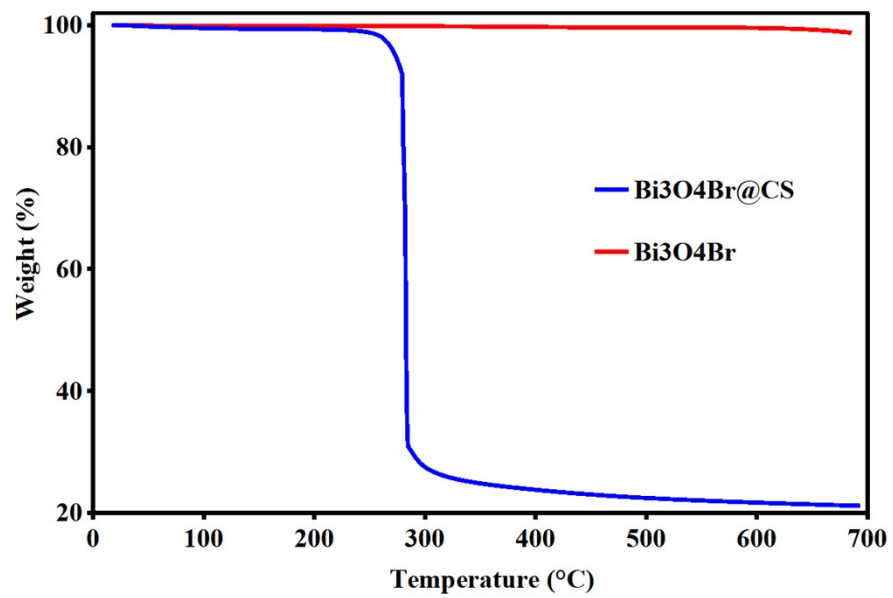


Figure S3 | TGA curves of Bi₃O₄Br sheets and Bi₃O₄Br @CS composite.

Additional SEM images

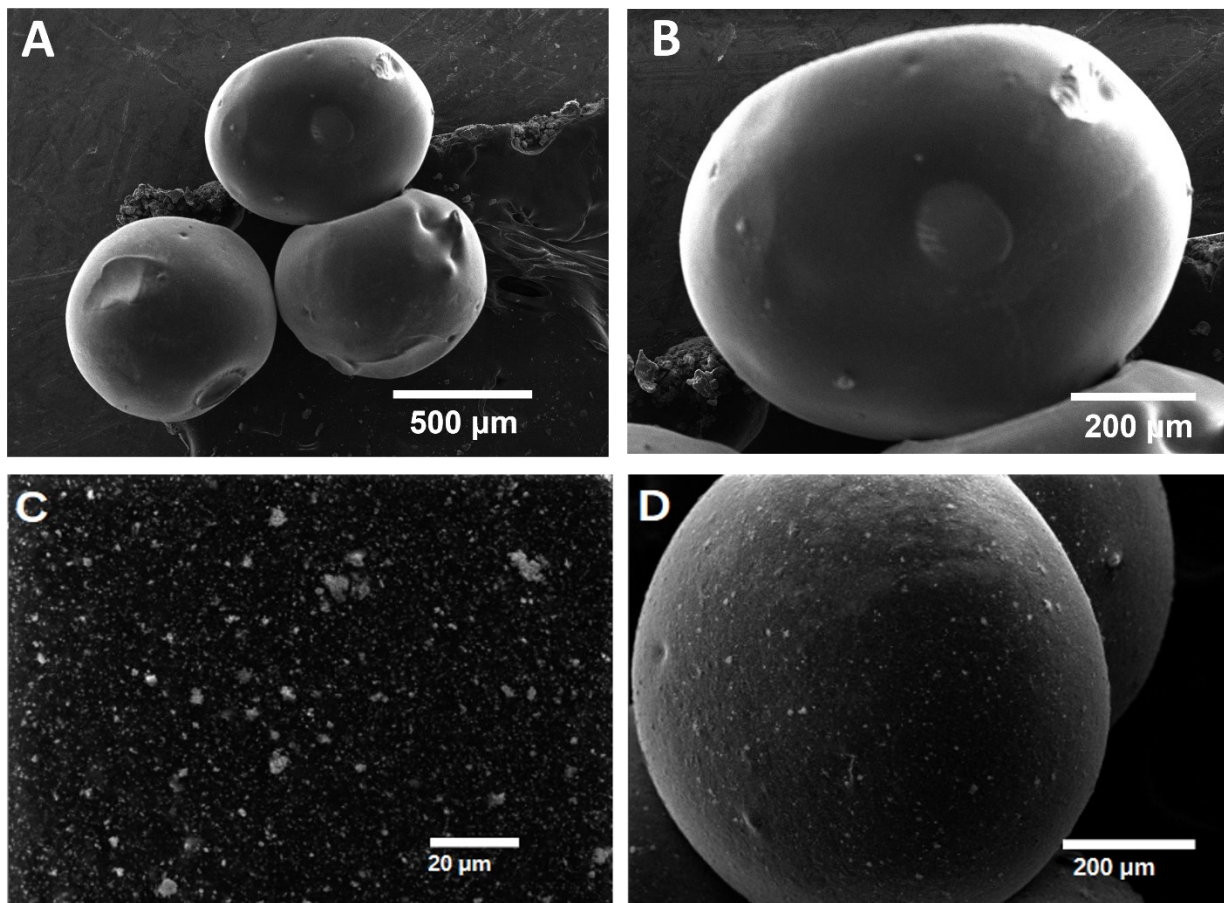


Figure S4 | SEM images of pure chitosan (A and B) and Bi₃O₄Br@Chitosan hybrid materials after three cycles (C and D).

