Supporting Information

Mesoporous TiO_2-BiOBr Microspheres with Tailorable Adsorption Capacities for Photodegradation of Organic Water Pollutants: Probing Adsorption-Photocatalysis Synergy by Combining Experiments and Kinetic Modeling

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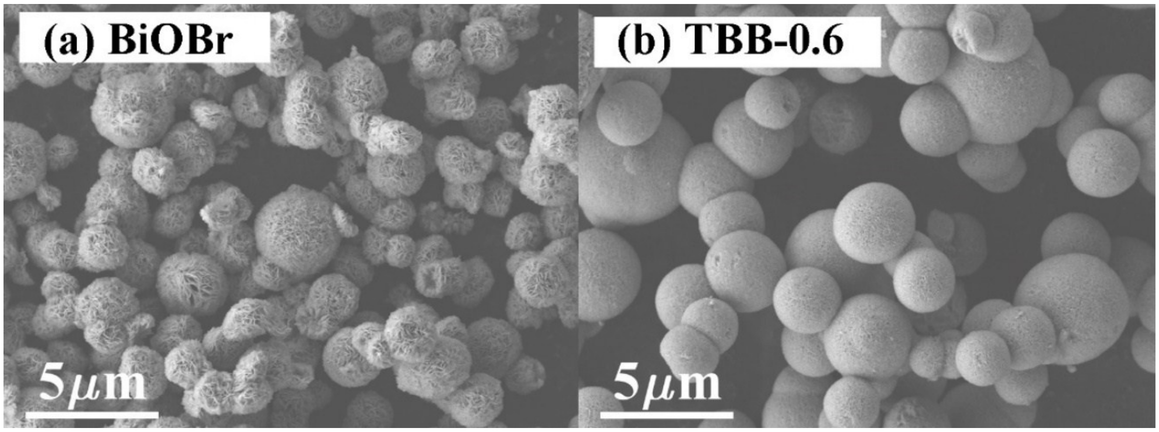

Figure S1. SEM images of BiOBr and TBB-0.6. Compared with BiOBr, TBB-0.6 has more perfect spherical structure.

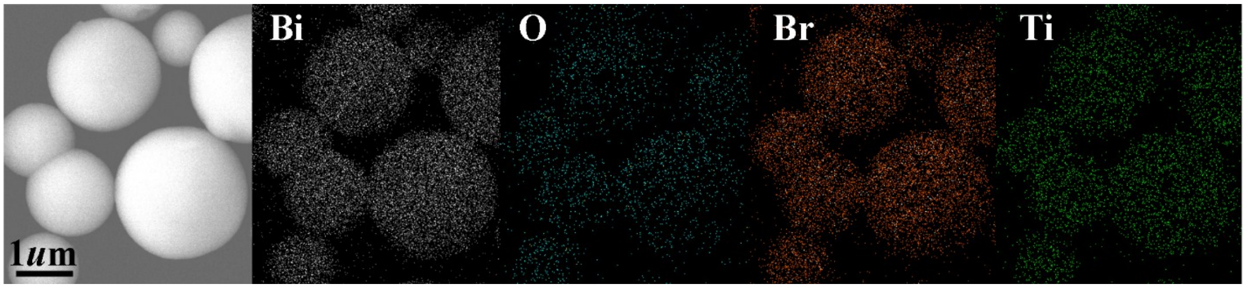

Figure S2. SEM and EDS mapping images of TBB-0.6. The images show uniform distribution of the elements.

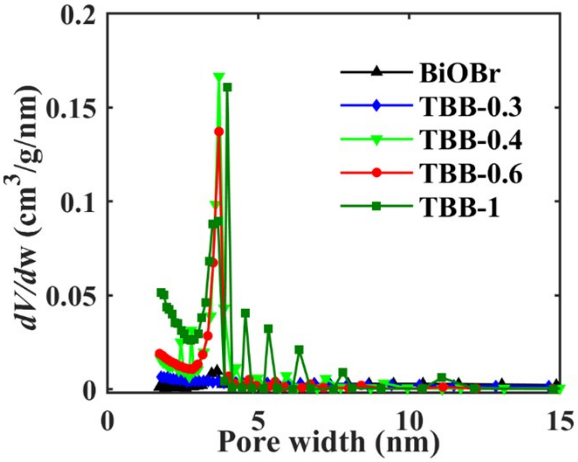

Figure S3. Pore size distributions of the samples. Major pore width is around 3.6 nm.

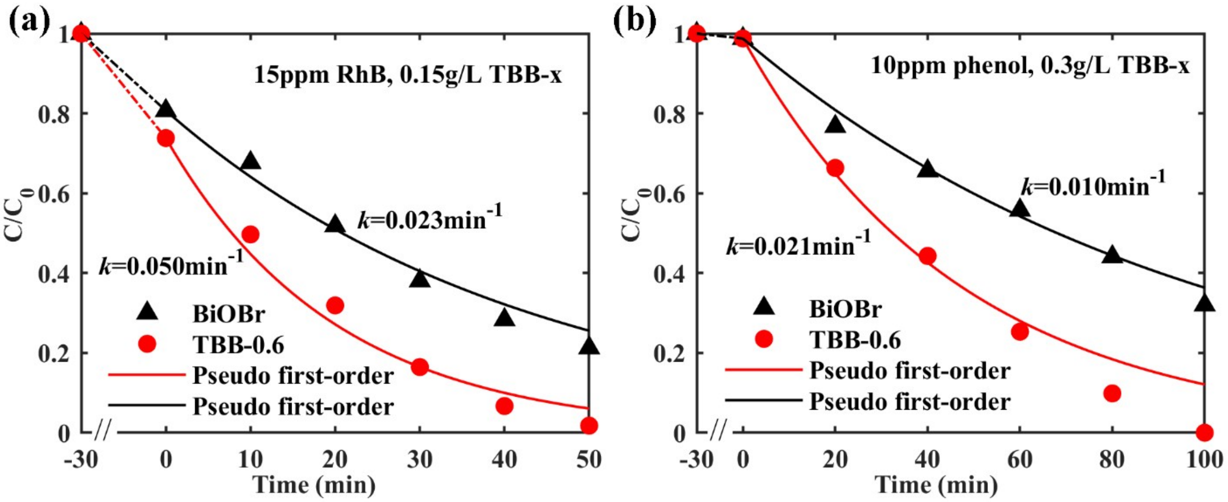

Figure S4. Experimental and fitted photodegradation kinetics of (a) RhB and (b) phenol using BiOBr and TBB-0.6. The rate constants and fittings were derived using the pseudo first-order model. The dose of RhB was 15 mg/L and the concentration of photocatalyst was 0.15 g/L. The dose of phenol was 10 mg/L and the concentration of photocatalyst was 0.3 g/L.

Development of Kinetic Modeling

The exponential decay model based on assumptions of pseudo-first-order kinetics in a completely-mixed, batch reactor ($\ln(C/C_0) = -k_{pfo}t$) is often used to calculate rate constants in order to quantitatively evaluate photodegradation performance. However, this simple model is not appropriate for systems in which the target contaminant is present in more than the solution phase. One example is a system where the target contaminant is strongly adsorbed. In such a system, the amount of contaminant in the adsorbed phase must be considered in the material balance, regardless of what form of rate equation is used [1-5]. Such an approach will be taken here. First, assume that the rate of reaction per unit mass of photocatalyst (r_m) is proportional to the surface concentration of adsorbed target compound (q), that is $r_m = k_s q$, where k_s is the intrinsic reactivity of the photocatalyst. The rate of removal per unit volume of solution (r) can be obtained by multiplying by the photocatalyst concentration solid loading (D), i.e. $r = k_s D q$. If the rate of mass transport from the bulk solution to the surface of the photocatalyst and the rate of adsorption onto the photocatalyst from the adjacent solution are rapid compared to the rate of surface reaction, then the surface concentration can be assumed to be in equilibrium with the bulk solution concentration. Adsorption kinetic data indicate that adsorption of MO onto the photocatalysts was complete within a few minutes, while MO degradation took tens of minutes. Therefore, the assumption of adsorption equilibrium is not unreasonable. However, additional kinetic data may show that transport kinetics play some role in the observed removal kinetics. When substantial adsorption occurs, the material balance needs to consider that the target compound exists in both the solid and solution phases: *d*(mass of target in system/volume of solution)/*dt* = rate of removal:

$$\frac{d}{dt}(C+Dq)=-r \qquad \text{* MERGEFORMAT (1)}$$

Differentiation, application of the chain rule ($\frac{dq}{dt}=\frac{dq}{dC}\cdot\frac{dC}{dt}$) and rearrangement give:

$$\frac{dC}{dt}=-r/(1+D\frac{dq}{dC}) \qquad \text{* MERGEFORMAT (2)}$$

If a linear isotherm applies ($q=K_pC$), this would provide a result that appears to be like that in a system with first-order removal rate without considering adsorption ($dC/dt=k_{app}C$), but the apparent first-order reaction coefficient would include effects of adsorption ($k_{app}=k_sK_pD/(1+DK_p)$).

Since the Freundlich adsorption isotherm ($q=KC^n$) well fits data for equilibrium adsorption on TBB-0.6, it is used to describe adsorption equilibria: $r=k_sDKC^n=k_fDC^n$, where k_f is the overall rate constant ($k_f=Kk_s$). Combining this rate equation with the material balance equation for a batch system when adsorption is important gives:

$$\frac{dC}{dt}=-\frac{k_fDC^n}{1+KnDC^{n-1}} \qquad \text{* MERGEFORMAT (3)}$$

Note that the derivative of the solution concentration is not equal to the rate of MO degradation per volume of solution (k_fDC^n). The denominator on the right side makes the derivative of solution concentration (dC/dt) to be less than the rate of MO degradation, because MO is being removed both from the surface of the solid and from the solution. Simulations of photodegradation kinetics with equilibrium adsorption were then performed by solving Eq.* MERGEFORMAT (3) numerically employing MATLAB function ode45. The overall rate constants were also obtained by nonlinear fitting of the experimental data via MATLAB function nlinfit.

References

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