Supplementary Information

Enhanced Photocatalytic Reduction of Hexavalent Chromium by using Piezo-Photo Active

Calcium Bismuth Oxide Ferroelectric Nanoflakes.

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I. N₂ adsorption-desorption isotherm

The usual type-IV isotherm has a hysteresis loop in the pressure range 0.10-1.0 P/P₀, indicating their mesoporous characteristics. In general adsorption capacity of a photocatalysts is proportional to its surface area (S_{BET}), with larger adsorption capacity allowing the photocatalyst to bind more reactant molecules in the pores for photocatalytic processes. The observed BET surface area and pore volume of CBO is 7.588 m^2/g and 0.039 cm^3/g, respectively, as calculated by the Brunauer-Emmett–Teller (BET) model, as shown in Fig S1. It is well understood that materials with higher S_{BET} values have more active sites and facilitate photogenerated electrons and holes as well as adsorbed molecules to diffuse to a certain extent at the surface, increasing the efficiency of the photoreactions[1].
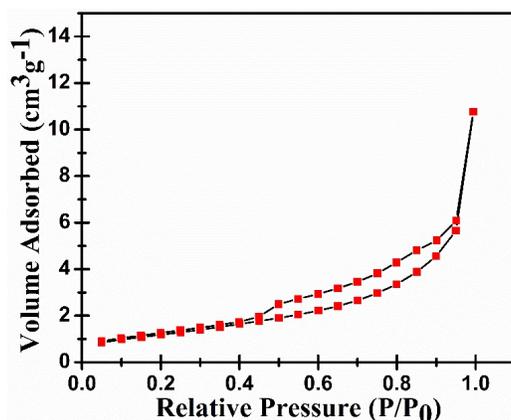

Fig. S1 N₂ adsorption-desorption isotherm of CBO.

II pH effect

We have performed the photoreduction of Cr (VI) by varying pH value from 3 to 11, as shown in Fig S2. The effect of pH of the solution on the photoreduction of Cr (VI) ion was studied by varying the initial pH of the aqueous Cr (VI) ion solution from 3 to 11 with the aqueous HCl and

NaOH solution while keeping all the other experimental condition constant. It is observed that with increase of pH from 3 up to pH 11 the photoreduction rate of Cr (VI) decreases[2, 3].
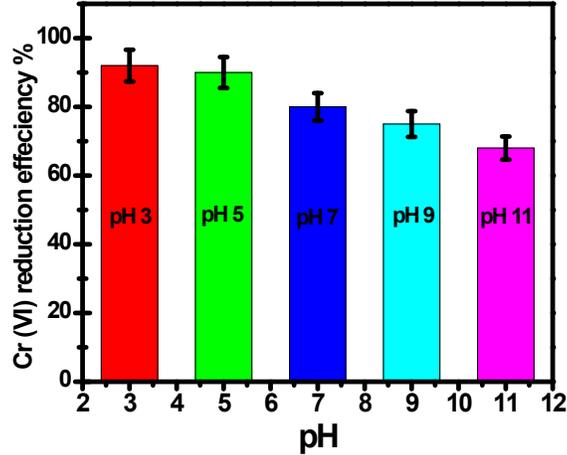
Fig. S2 Effect of pH on photoreduction efficiency of Cr (VI) solution using CBO nanoflakes.

III Mott-Schottky

Fig. S3 shows the results of the Mott-Schottky experiment of CBO performed in 0.5 M Na_2SO_4. CBO has a negative slope, indicating that it is an n-type semiconductor. In n-type semiconductors, the V_{fb} generally exists in the conduction band (CB) region, which may be quantified using the intersection derived from a plot of $1/C^2$ against V $vs.$ Ag/AgCl as followed by the given equation[4];

$$\frac{1}{C^2} = \frac{2}{\varepsilon_r \varepsilon_0 qN_d} \times V\text{-}V_{fb} - \frac{K_B T}{q} \tag{1}$$

where q is the electron charge, ε_r is the dielectric constant, ε_o is the permittivity of a vacuum, N_d is the donor density, V is the applied bias, V_{fb} is the flatband potential, k is the Boltzmann constant, and T is room temperature. The X-axis intercept V vs. Ag/AgCl has been observed as -0.25 V, as illustrated in Fig. S3. Using the equation, $V_{CB} = V_{fb+} \dfrac{KT}{e}$, the V_{fb} is estimated as -0.23 V. According to this result, the CB position of n-type CBO is -0.23 V vs. Ag/AgCl. The valance band

(VB) position can be determined when the bandgap (1.9 eV) is added to the CB using the relationship; $E_{VB} = E_g + E_{CB}$[5]. Therefore, the VB position is observed as +1.67 V *vs.* Ag/AgCl. The observed negative value of the CB position suggests that it straddles the standard redox potential of converting O_2 to $O_2^{-\bullet}$[6], which indicates that CBO can generate more superoxide anion ($O_2^{-\bullet}$) radicals, which assist in enhancing the photoreduction of Cr (VI).
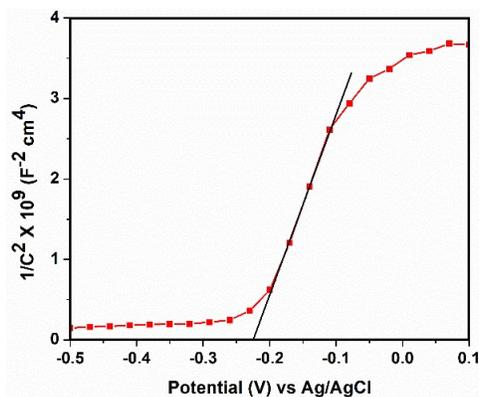

Fig. S3 Mott-Schottky curve of CBO.

IV Scavenging experiment

In order to confirm the participation of $O_2^{-\bullet}$ and $OH^{\bullet}$ in the reduction of Cr (VI) to Cr (III) we have performed the scavenging experiment, as shown in Fig S4. We have studied using ammonium oxalate as hole scavenger and silver nitrate as electron scavenger. The photoreduction of Cr (VI) ion by CBO nanoflakes has been found to be greatly suppressed by an addition of scavengers AO and $AgNO_3$ suggesting that both the photogenerated electron and holes are main active species in the system[7]. However, the rate of photoreduction of Cr (VI) with $AgNO_3$ is higher than that with AO suggesting that the photogenerated electron exhibit greater photoreduction as compared to the holes.
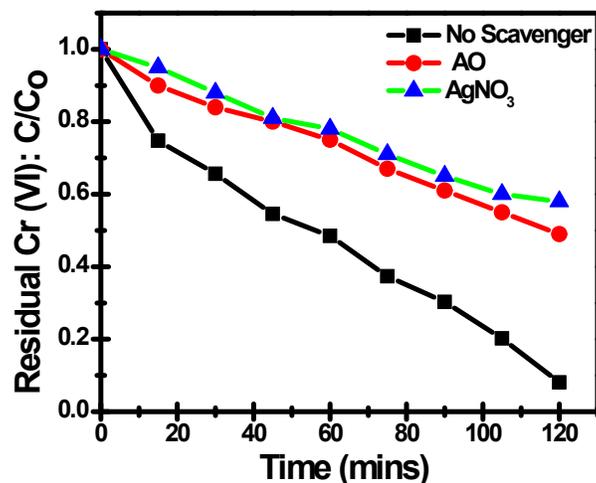
Fig. S4 Degradation rates of Cr (VI) solution using CBO nanoflakes in absence and presence of scavengers.

References:

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