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Enhancement on Degradation of Organic Dye through Piezophotocatalytic Activities by High Entropy Oxide-(CaZrYCeCr)O_2 / $Bi_4Ti_3O_{12}$ Nanocomposite

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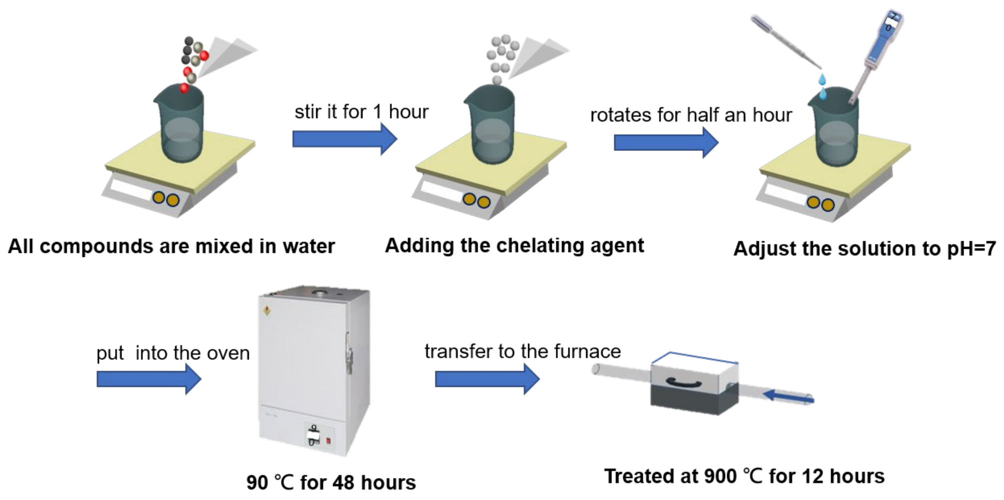
Abstract

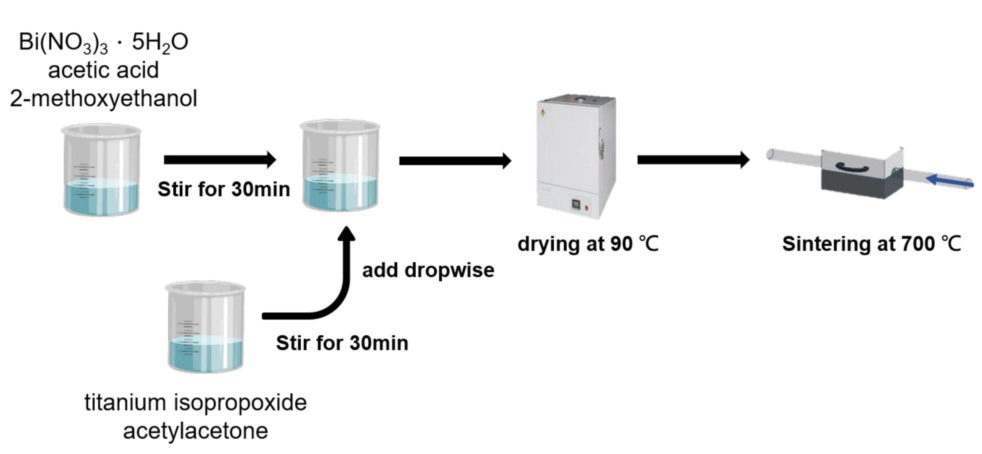
High entropy material demonstrates several effects from multi-component composition, which is potential in the catalytical field. During this decade, combining the mechanical force-driven piezoelectric/ferroelectric catalysts with photocatalysts has attracted much attention due to the separation of photogenerated carriers, leading to synergistic catalytic activities. This study reports a novel composite of high entropy oxide (CaZrYCeCr)O_2 with unique ferroelectric properties mixing with bismuth titanate ($Bi_4Ti_3O_{12}$) microplates, improving the piezo-phototronic catalytic activities.The results show that high entropy oxide catalyst (CaZrYCeCr)O_2 mainly consists of the porous structure with multivalent transition metal substitution, contributing to severe lattice distortion. Consequently, the precipitation of disordered phase $Ca(Zr_{1-x}Cr_x)O_3$(x=0.05~0.1) caused by lattice distortion was decorated on the porous framework. In addition, $Ca(Zr_{1-x}Cr_x)O_3$ with a non-centrosymmetric structure exhibits ferroelectric property and plays a vital role in separating the electron-hole pairs, which performs higher degradation efficiency around 588 % compared to pristine $ZrYCeO_2$. Additionally, the ferroelectric $Bi_4Ti_3O_{12}$ was considered to construct a Z-scheme catalytic activity and form a heterojunction high entropy oxide. Furthermore, we demonstrated that morphotropic phase boundaries between $Bi_4Ti_3O_{12}$ and $CaZr_{1-x}Cr_xO_3$ could dramatically enhance the ferroelectric property and promote the performance of the piezo-phototronic activities, revealing that $CaZrYCeCrO_2$/ $Bi_4Ti_3O_{12}$ could be an innovative catalyst in the future.

Experimental process

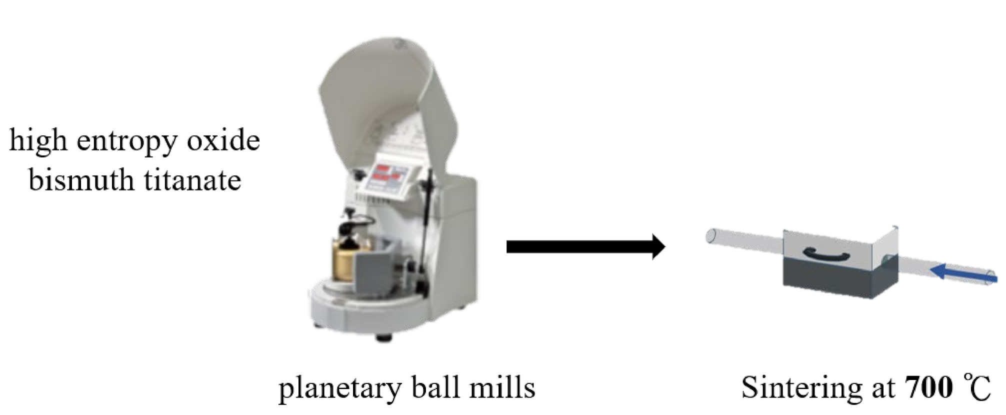
a. Synthesis of high entropy oxide



b. Preparation of bismuth titanate



c. Preparation of high entropy oxide /bismuth titanate nanocomposite



Result and discussion

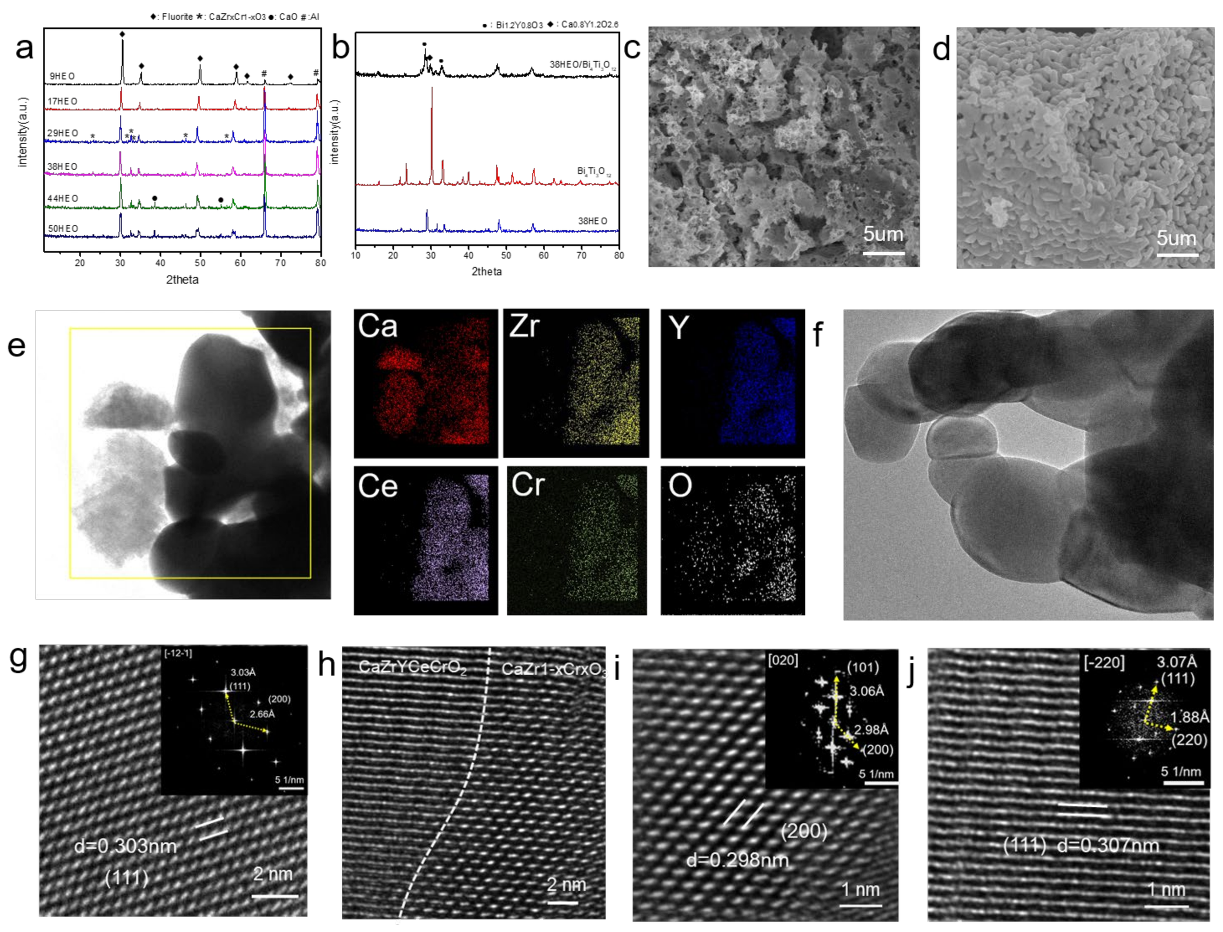


Figure 1. (a,b) XRD pattern of high entropy oxide(HEO) with different calcium content(ex: 9HEO means HEO with 9at% Ca, Al for calibration) and 38HEO/$Bi_4Ti_3O_{12}$ nanocomposite (c) SEM images of the 38HEO and (d) bismuth titanate. (e) TEM EDS mapping of 38HEO. (f) Low-magnitude TEM images of 38HEO. (g) HRTEM image of 9HEO with fluorite structure showing its (111) plane. (h) HRTEM image of 38HEO showing the (i) (200) plane of $CaZr_{1-x}Cr_xO_3$ (j) (111) plane of $CaZrYCeCrO_{2-x}$ and their SAED pattern.

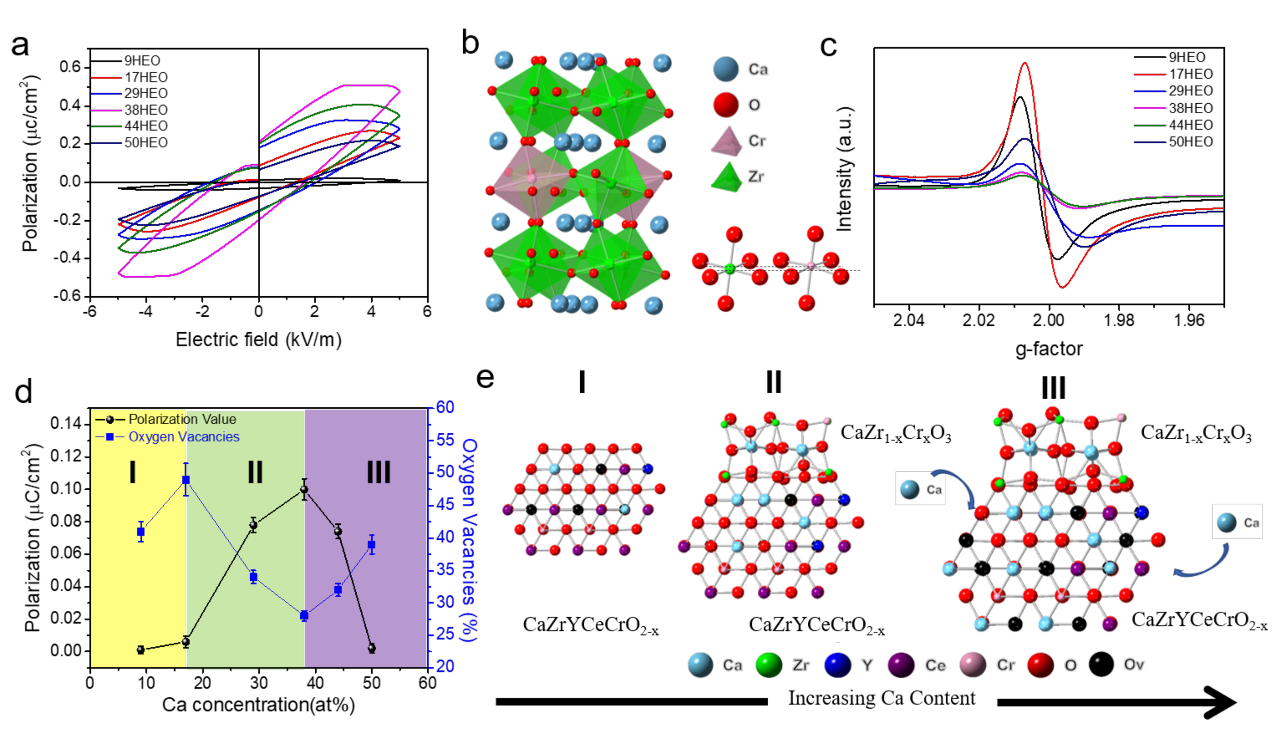


Figure 2. (a) P-E hysteresis loop of HEO with different content of calcium. (b) The schematic diagram of the ZrO_6 and CrO_6 in the $CaZr_{1-x}Cr_xO_3$ crystal structure and its deviation from the octahedral center. (c) EPR spectra of HEO with different content of calcium. (d) The corresponding result of the three stages varied by calcium content derived from (a,c). (e) A schematic of the simplified mechanism of three stages.

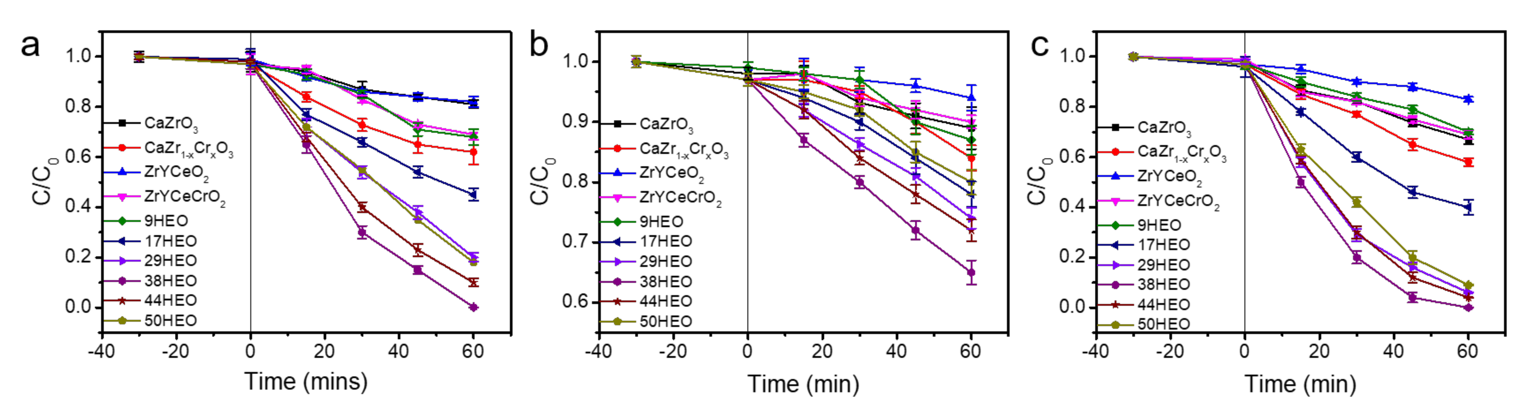


Figure 3. Dye degradation of methylene blue using HEO under (a) applying light irradiation only, (b) applying ultrasonic vibration only and (c) applying light and ultrasonic vibration simultaneously.

Conclusion

1. As increasing Ca content, ferroelectric perovskite structure will precipitate from fluorite structure.
2. HEO with 38at% Ca has the optimal hysteresis loop with the highest polarization and lowest oxygen vacancy concentration, resulting in the highest efficiency in methylene blue degradation activities.
3. 38HEO shows the highest efficiency in MB degradation test