Mechanistic insights for efficient cationic dye degradation via dual Z-scheme CeO_2/BiOCl/Ag_2WO_4 photocatalyst

Kusum Sharma [a] , Pankaj Raizada [a*]

[a] School of Advanced Chemical Sciences, Faculty of Basic Sciences, Shoolini University, Solan (HP), India-173229

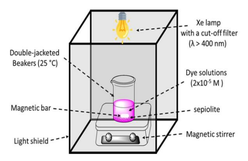
Abstract

A photoactive CeO_2/BiOCl/Ag_2WO_4 heterojunction was successfully constructed using a co-precipitation technique for the degradation of crystal violet (CV) and methylene blue (MB) dyes. It was found through a combination of characterization and experiments that the dual Z-scheme system not only augmented the charge isolation and migration efficiency but also maintained superior redox ability with extended visible light absorption capacity. The ternary hybrid system exhibited 97 % and 98 % degradation efficacy for MB and CV in 75 min. The electron spin resonance (ESR) analysis confirmed that hydroxyl and superoxide radicals (•OH, $•O_2^-$) as the primary reactive species in the degradation process.

Introduction

Methylene blue (MB) and crystal violet (CV) are the two disreputable dyes that are cationic in nature and have intricate structures which makes it difficult to remove them from wastewater, posing serious risks to people's health. Therefore, it is crucial to eradicate these dyes by degrading them into harmless products. Although, various conventional techniques like, precipitation, osmosis, and flocculation were employed out of which, solar-light driven process *i.e.*, photocatalysis has emerged as a promising technique for eliminating a widespread range of toxic contaminants by utilizing unending solar energy. The photocatalytic process undergoes three major steps, photon absorption on solar light irradiation, generation of electron and hole pairs, and surface catalytic reactions.. These oxidative species are capable enough for degrading the toxic contaminants into mineralized products like CO_2 and H_2O.

Set up



1. 100 mL of MB stock solution (50mg/L) + 0.5 g/L photocatalyst = $2x10^{-2}$ mol/L at pH 9 (0.1 M HCl/NaOH)
2. Suspension was placed in a photochemical batch reactor with a double-walled Pyrex container was fitted with cooling circulating water to maintain reaction temperature at 25^0C throughout the degradation process.
3. The suspension was stirred for 30 min under dark conditions to attain adsorption-desorption equilibrium
4. 2 mL aliquot was withdrawn at 10 min regular interval with subsequent photocatalyst separation by 0.22 µm nylon filter and centrifugation at 4000 rpm for 10 min and absorbance measurement using a UV-vis spectrophotometer at λ_{max}=665 nm.
5. Each experiment was conducted in duplicate sets to reduce standard deviation error and the rate constant was calculated.

Results

31/04/24

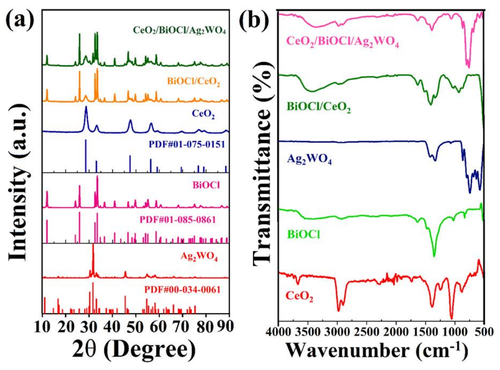


Fig. 1. (a) X-ray diffractogram and**, (b)** FTIR spectra of Ag_2WO_4, CeO_2, BiOCl, CeO_2/BiOCl, CeO_2/BiOCl/Ag_2WO_4 composites

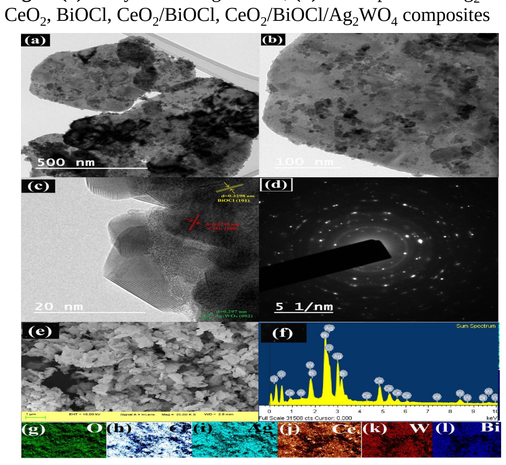


Fig. 2 (a, b) HRTEM image, **(c)** Lattice d-spacing and, **(d)** SAED pattern of CeO_2/BiOCl/Ag_2WO_4 hybrid, **(e)** FESEM pictures of CeO_2/BiOCl/Ag_2WO_4 hybrid with elemental mapping of **(g-l)** O, Cl, Ag, Ce, W, and Bi elements in ternary heterojunction

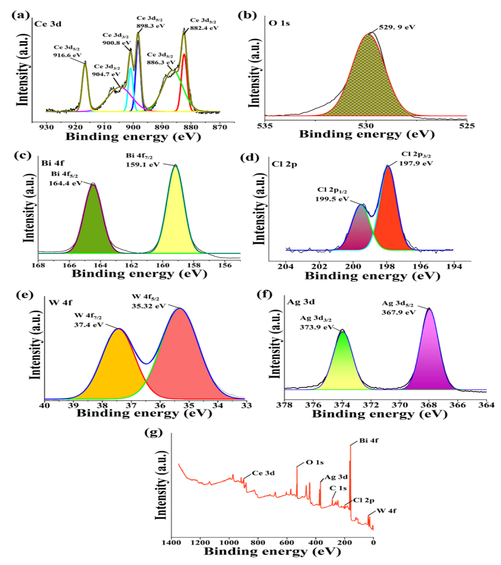


Fig. 3. High resolution XPS spectra of **(a)** Ce, **(b)** O 1s, **(c)** Bi 4f, **(d)** Cl 2p, **(e)** W 4f, **(f)** Ag 3d, **(g)** XPS survey of CeO_2/BiOCl/Ag_2WO_4.

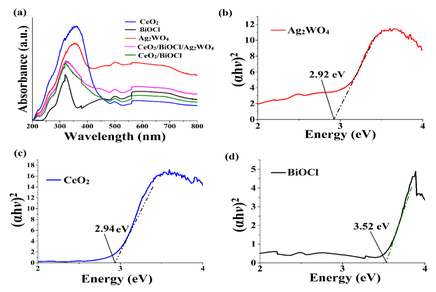


Fig. 4. (a) UV-vis spectra of the fabricated samples**;** Tauc plots of pristine **(b)** Ag_2WO_4**; (c)** CeO_2**;** (d) BiOCl.

Design/Other information

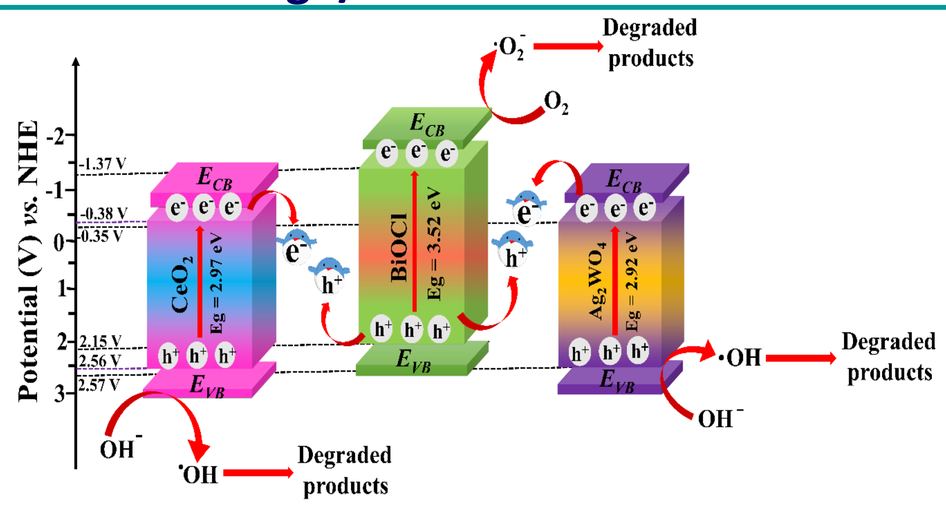


Fig. 5. Plausible charge transferal mechanism of CeO_2/BiOCl/Ag_2WO_4 composite.

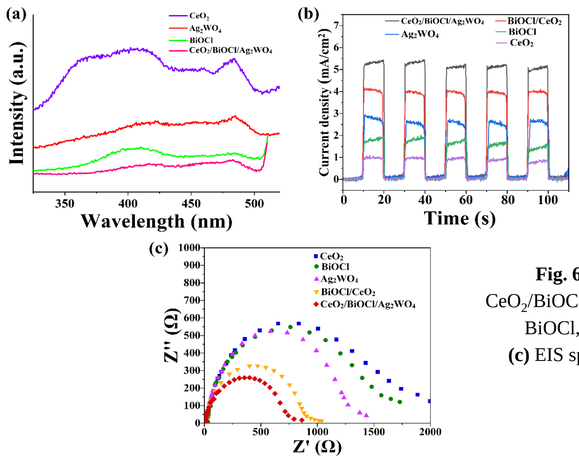


Fig. 6. (a) PL Spectra of CeO_2, Ag_2WO_4, BiOCl, and CeO_2/BiOCl/Ag_2WO_4 hybrid, **(b)** TPR spectra of CeO_2, Ag_2WO_4, BiOCl, BiOCl/CeO_2, and CeO_2/BiOCl/Ag_2WO_4 hybrid, **(c)** EIS spectra of CeO_2, BiOCl, Ag_2WO_4, BiOCl/CeO_2, and CeO_2/BiOCl/Ag_2WO_4 hybrid.

Conclusions

The present work employed a co-precipitation synthetic technique to develop a ternary dual Z-scheme photocatalyst, that exhibited excellent MB and CV degradation. Effective heterojunction formation between CeO_2, BiOCl, and Ag_2WO_4 photocatalysts was proved by the characterization results obtained from XRD, FESEM, HRTEM, and XPS analysis. This remarkable photocatalytic efficacy is attributed to the arrow up dual Z-scheme system that leads to improved migration and spatial isolation of charge carriers, facilitating participation of active radicals in the degradation process.

References

Sarojini, G., P. Kannan, N. Rajamohan, M. Rajasimman,D.-V.N. Vo, Dyes removal from water using polymeric nanocomposites: a review. Environmental Chemistry Letters, 2023. **21**(2): 1029-1058.

Khan, M.E., M.M. Khan,M.H. Cho, Ce3+-ion, surface oxygen vacancy, and visible light-induced photocatalytic dye degradation and photocapacitive performance of CeO2-graphene nanostructures. Scientific reports, 2017. **7**(1): 5928.

Sharma, K., P. Raizada, V. Hasija, P. Singh, A. Bajpai, V.-H. Nguyen, S. Rangabhashiyam, P. Kumar, A.K. Nadda,S.Y. Kim, ZnS-based quantum dots as photocatalysts for water purification. Journal of Water Process Engineering, 2021. **43**: 102217

International Conference on

Composite Materials for Environment Protection & Remediation

(ICCMEPR - 2024) 02-03 July, 2023