Inorganic Sulfide Oxidation Enhanced by Modified Nb-Containing Photocatalysts Utilising Visible Light: A Promising Technological Advancement

POSTER
Ph.D. Student: N
Journal: ESPR

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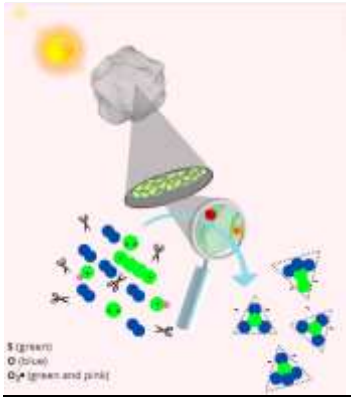

This research thoroughly examines the efficacy of Nb_2O_5-based materials in the photodegradation of aqueous inorganic sulfide, utilising visible light as the energy source. The cobalt-modified materials boast bandgaps ranging from 1.6 to 3.1 eV. The study outcomes demonstrate the highly promising potential of the new materials in eliminating HS^- species. $Nb^{(V)}OCoO$ material stands out due to its exceptional reaction rates, primarily attributed to the Co^{+3} species predominant presence on its surface. The study further reveals that the electron transfer pathway is dominant in inorganic sulfide photooxidation, as confirmed by suppressing reactive oxygen species and charge carriers; consequently, we proposed the formation of an HS• radical intermediate species. Moreover, the study highlights that all materials could generate sulfate and thiosulfates less toxic species during the photoreaction, indicating photocatalysis potential sustainability as an alternative method for treating contaminated effluents.

Introduction

Inorganic sulfide, a pollutant in massive quantities in effluents from food processing, oil refining and paper industry, is an extremely toxic and corrosive contaminant that causes economic and environmental damage. As this problem is not receiving due consideration yet, our research emphasises photocatalysis as a promising technique to convert inorganic sulfides into less toxic forms of sulfur, including sulfate (SO_4^{2-}) and thiosulfates ($S_2O_3^{2-}$). The newly synthesised materials overcome the limitations associated with UV radiation, thereby making the process more accessible and ecologically sustainable [1,2].

Material and Methods

The production process of Nb_2O_5-based materials involves the sol-gel method adapted from the EISA technique [3], which forms $Nb^{(V)}O$ material. In addition to this, we synthesised three chemically modified materials: $Nb^{(V)}OCoO$ was synthesised by wet impregnation of the pure Nb(V)O material, and CoNb(V)O was synthesised by adding the cobalt salt directly at the beginning of the EISA synthesis. Nb(V)OMB was synthesised by wet impregnation with methylene blue dye. A solution containing around 5000 ppm of $Na_2S \cdot 9H_2O$ was exposed to white LED light (150 W) both with and without the photocatalyst materials to determine the materials effectiveness. The sulfide concentration was monitored by UV-Vis spectroscopy at 229.5 nm.

Results and Discussion

The modified materials are indirect gap semiconductors with three absorption regions located in the range between 1.6 and 2.9 eV (Table 1). The textural data and specific BET surface areas of the materials are also shown in Table 1, and some are significantly higher than other Nb_2O_5 materials. The results indicate that the oxidtion reactions are all pseudo-first-order, and the Co-containing photocatalyst with the highest amount of Co^{3+} species showed lowers the activation energy (E_a) (Table 1). The photocatalyst $Nb^{(V)}OCoO$ presented the highest $L_{2,3}$ edge energies, according to EELS analyses (Electron Energy Loss Spectroscopy) shown in Figure 1, suggesting that it has significant Co-species with a higher oxidation state. These results follow the Raman spectrum, indicating Co_3O_4 and CoO(OH) nanoparticles on this material surface.

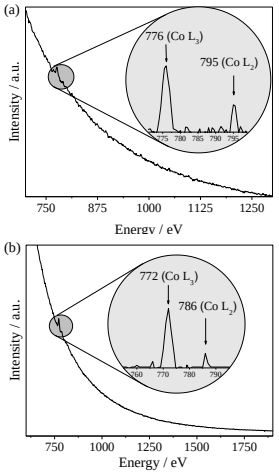

Figure 1. EELS spectra for the materials (a) $Nb^{(V)}OCoO$ and (b) $CoNb^{(V)}O$.

The experiments also showed that Co-materials have more pronounced photocatalytic activities than those photosensitised with MB. Even so, all modified materials present relative photocatalytic efficiency of

more than 84% and significant reusability, maintaining up to 80% of catalytic capacity for six reaction cycles. The best material, $Nb^{(V)}OCoO$, reached almost 100% oxidation in just two hours (Figure 2). After the reactions, Raman analyses confirmed the presence of SO_4^{2-} and $S_2O_3^{2-}$ less toxic species.

Mechanism studies have shown that the essential reactive species for this photooxidation is the superoxide radical (O_2^{-}•), but the reaction occurs through a combination involving these radicals and singlet oxygen species (O_2*).

This way, we can propose a photoreaction mechanism involving the two reactive oxygen species (ROS) working together. However, the main path would be the one that involves the O_2^{-}•.

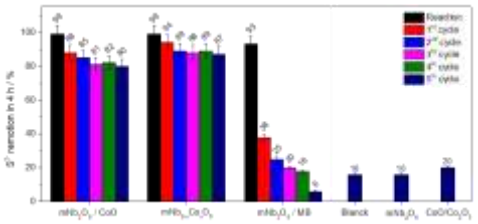

Figure 2. Removal of inorganic sulfide after 5 cycles of reuse, with photocatalysts water washing between cycles.

The separation of charge carriers is essential in the proposed mechanism (Figure 3) because the electrons generated in photoexcitation give rise to superoxide radicals, and the holes manage the creation of hydrogen sulfide radicals (HS•). These species can combine to produce an $HSOO^{-}$-nucleophilic intermediate that is also formed when singlet oxygen reacts with the HS^{-} substrate. The high yield of the photoreaction in water can be achieved to stabilising the $HSOO^{-}$ intermediate through hydrogen bonds.

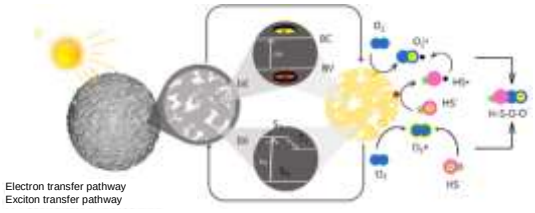

Figure 3. Proposed mechanism for the photooxidation reaction of inorganic sulfides. The involved species are e^{-} (yellow); h^{+} (orange); H (green); O (blue); S (pink).

The adsorption process of the inorganic sulfide on the materials was discarded since at the reaction pH = 12, it is already known, by Zeta potential measurements [4], that the photocatalysts and substrate are negatively charged. Therefore, they are electrostatically repelled, and no strong adsorption takes place.

Table 1. Textural properties of synthesised materials, calculated bandgap values extrapolating energy curves of Kubelka-Munk functions (E_g), and activation energies of photooxidation reactions of inorganic sulfide (E_a).

Material	S_{BET} / m² g^{-1}	$S_{mesopore}$ / m^2 g^{-1}	E_g / eV	E_a / kJ mol^{-1}
$Nb^{(V)}O$	119	95	3.1 ± 0.2	96 ± 10
$Nb^{(V)}OCoO$	50	23	1.64 ± 0.01	15 ± 2
$CoNb^{(V)}O$	134	61	1.64 ± 0.01	34 ± 3
$Nb^{(V)}OMB$	110	76	1.70 ± 0.01	45 ± 2

Conclusions

The study unequivocally proves that heterogeneous photocatalysis using visible light effectively eliminates inorganic sulfide. The material $Nb^{(V)}OCoO$, in particular, stands out for its remarkable ability to remove nearly 100% of the pollutant within two hours of the reaction. Moreover, the process generates less hazardous and toxic sulfur species, making it a sustainable and environmentally friendly alternative to the conventional adsorption method for removing inorganic sulfides from effluents.

Acknowledgements

The authors would like to acknowledge CNPq, CAPES, FAPEMIG and INCT-Midas for financial support.

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