

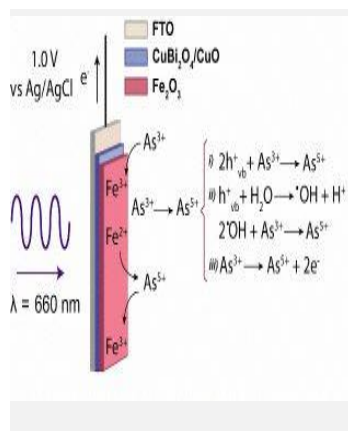
Photoelectrocatalytic oxidation of As (III) to As (V) for adsorption removal using CuBi₂O₄/CuO/Fe₂O₃

POSTER

Ph.D. Student: Y

Journal: NONE

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The presence of arsenic (As) in water indicates a significant environmental concern, necessitating the development of effective removal system. A novel self-standing CuBi₂O₄/CuO/Fe₂O₃ electrode on FTO was synthesized using electrodeposition and dip-coating techniques. Characterization revealed light harvesting and electron transfer capabilities of each layer. The performance electrode in removing 0.5 mg L⁻¹ As (III) was evaluated under various conditions, including adsorption, photocatalysis (PC), electrocatalysis (EC), and photoelectrocatalysis (PEC). PEC treatment at 1.0 V vs Ag/AgCl under visible light irradiation exhibited outstanding As removal efficiency (96.8%), surpassing PC (40.4%) and EC (54.5%). Mechanistic evaluation confirmed As (III) oxidation to As (V) for enhanced adsorption onto iron oxide sites, as revealed by X-ray photoelectron spectroscopy (XPS). These findings underscore the importance of rational design approaches for photoanodes in As adsorption, highlighting the significant role of individual layers.

Introduction

The United Nations aims to ensure access to clean water and sanitation for all by 2030. Researchers are developing water treatment technologies to remove various contaminants, including heavy metals. Heavy metals such as arsenic, chromium, and lead pose significant threats to the environment and human health[1].

Arsenic contamination is a significant barrier to accessing safe drinking water worldwide, affecting an estimated 200 million people globally. Conventional treatment methods are influenced by the speciation of arsenic, which depends on factors such as pH and oxidation state.

Emerging electrochemical technologies, such as electrocoagulation and electrosorption, are promising for removal of arsenic from water. Photoelectrocatalysis (PEC) offers potential advantages like the absence of added chemicals and simultaneous oxidation and adsorption of arsenic species [2].

This study synthesized and characterized a self-standing electrode composed of CuBi₂O₄/CuO/Fe₂O₃ to evaluate its performance for photoelectrocatalytic arsenic removal.

Material and Methods

FTO-coated glass substrate were pre-treated by sonication in ethanol to remove organic impurities, followed by cleaning with a 5% HNO₃ solution and rinsing with ultrapure water. A 1.5 cm x 3.5 cm area on the FTO surface was designated for layer modification. Bi₂O₃ deposition was done via electrodeposition, followed by cyclic voltammetry and chronoamperometry. CuBi₂O₄/CuO surface

synthesis involved electrodeposition with specific concentrations and pH adjustments, followed by thermal treatment. The final CuBi₂O₄/CuO/Fe₂O₃ layer was obtained through dip-coating with Fe(NO₃)₃·9H₂O, citric acid, and ethylene glycol, followed by thermal treatment.

Results and Discussion

The assessment of As (III) photoelectrocatalytic oxidation/adsorption was conducted in 500 $\mu\text{g L}^{-1}$ As³⁺ (NaAsO₂) and 0.1 mol L⁻¹ K₂SO₄ under 660 nm light irradiation at pH 9.0 and 1.0 V vs Ag/AgCl utilizing various synthesized layers. Table 1 depicts the As removal efficiency employing Bi₂O₃, Fe₂O₃, CuBi₂O₄/CuO, and CuBi₂O₄/CuO/Fe₂O₃ under photoelectrocatalytic operation. The initial Bi₂O₃ layer displayed limited activity in As treatment, achieving only 7.5% removal. This poor performance of pristine Bi₂O₃ can be attributed to its high charge transfer resistance (1840 K Ω) and a high band gap of 2.94 eV, rendering it minimally photo-active under visible light. Evaluation of Fe₂O₃ as a unique layer resulted in 40.4% As removal, showcasing the impact of its lower band gap (2.12 eV) and enhanced electron transfer capabilities. However, it fell short of the complete removal achieved by the composite layer system CuBi₂O₄/CuO/Fe₂O₃. Furthermore, CuBi₂O₄/CuO demonstrated superior performance to Fe₂O₃ with 55.0% removal, highlighting its lower band gap (1.46 and 1.76 eV) and reduced charge transfer resistance (60 K Ω).

The CuBi₂O₄/CuO/Fe₂O₃ inter-layer exhibited the highest efficiency at 96.8%, indicating a synergistic effect of the p-n heterojunction. It is essential to note that the removal capacity of each layer (CuBi₂O₄,

CuO, and Fe₂O₃) cannot be considered additive, as the exposed geometrical area to the solution remains constant across all conditions, with the external layer playing a crucial role in defining the overall removal capacity of the system. Subsequently, the desorption of As (V) species follows an adsorption process over Fe³⁺ sites, regenerated by the applied potential during the process.

XPS analysis was employed to evaluate changes in oxidation states and As speciation before and after treatment, as shown in Figure 1. The Fe 2p XPS analysis revealed a shift in the Fe³⁺:Fe²⁺ ratio from 1.6:1 to 16.2:1, indicating the significant role of Fe³⁺ in As adsorption. The prevalence of Fe³⁺ post-treatment suggests the oxidation of Fe²⁺ sites by the applied potential. Additionally, the O 1s XPS analysis demonstrated the impact of pH and applied potential, resulting in a decrease in lattice oxygen (O1) and an increase in oxygen vacancies (O2) post-adsorption. Oxygen associated with adsorbed H₂O (O3) and H₂O multilayer (O4) exhibited higher intensity after treatment. According to these findings the proposed mechanism involves the following processes on electrode surface:

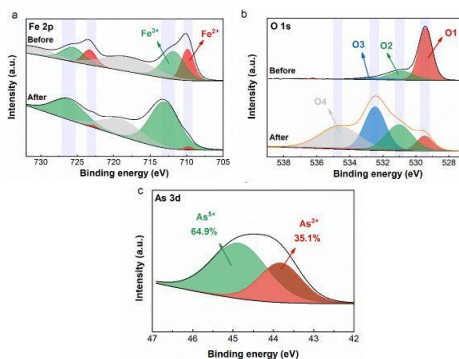
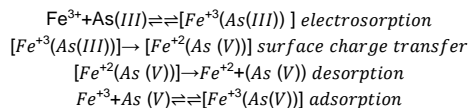


Figure 1. High-resolution XPS spectra of (a) Fe 2p and (b) O 1s before and after As adsorption using CuBi₂O₄/CuO/Fe₂O₃. (c) As oxidation state identification after adsorption treatment with CuBi₂O₄/CuO/Fe₂O₃.

Table 1. Removal efficiency bias photoelectrochemical activity.

Electrode	Removal Efficiency (%)
Bi ₂ O ₃	7.5
Fe ₂ O ₃	40.4
CuBi ₂ O ₄ /CuO	55.0
CuBi ₂ O ₄ /CuO/Fe ₂ O ₃	96.8

Conclusions

This study focused on synthesizing self-standing electrodes for efficient photoelectrocatalysis. The CuBi₂O₄/CuO/Fe₂O₃ p-n heterojunction demonstrated superior arsenic removal performance and enhanced charge carrier accumulation under visible light. These results highlight the potential of rationally designed electrocatalysts for specific environmental treatments, emphasizing material composition and configuration in achieving enhanced performance.

Acknowledgments

This work has been supported by the Research Institute of the Universidad de Lima – IDIC – project. We acknowledge the use of facilities within the Eyring Materials Center at Arizona State University, supported partly by NNCI-ECCS -2025490.

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