Moxifloxacin photoelectrocatalytic degradation on $CuWO_4/g-C_3N_4$ photoanode

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The presence of antibiotic residues in water is a major concern for scientists. Traditional water treatment methods have proven to be ineffective in removing these pollutants. In response, advanced water treatment techniques (POAs) have been developed to address this issue. In this study, CuWO₄/g-C₃N₄ photoanodes (CuWO₄/g-CN 5, 10, and 20 %) were used to break down the antibiotic Moxifloxacin in water. The materials were characterized using XRD, and their photoelectrochemical properties were examined in a PEC. When an external potential (0.7 V vs. Ag/AgCl) was applied, the materials demonstrated excellent photocatalytic performance compared to CuWO₄ pure. The CuWO₄/g-CN 20 photoanode exhibited a degradation rate of 49.89 % for the antibiotic moxifloxacin while maintaining chemical stability over four consecutive cycles.

Introduction

Environmental concerns are a critical focus in modern society due to environmental issues affecting our planet. Many alternatives have been developed to tackle the environmental impacts caused by human activity, particularly the contamination of rivers and lakes. Among the several options available, semiconductor oxides have been widely used as a remedy for environmental pollution as reported in the literature [1,2].

One of the standout semiconductor oxides is the Copper Tungstate (CuWO₄) from the metallic tungstates family. It exhibits *n*-type behavior and a narrow band gap (2.0 to 2.4 eV), which makes it an attractive option for photocatalytic applications [3]. Despite this, the high rate of pair recombination (electron/hole) limits CuWO₄ in solar energy conversion processes [4,5]. Some studies explore ways to enhance electron/hole pair recombination time in CuWO₄, such as modifying its structure (e.g., introducing oxygen vacancies), morphology, or combining it with other semiconductor materials (Type II heterojunction and Scheme Z) [6,7,8].

Graphitic carbon nitride $(g-C_3N_4)$ is a promising candidate that can potentially assist CuWO₄ in overcoming this limitation. $g-C_3N_4$ exhibits n-type behavior, is metal-free, has low electron/hole pair recombination rate, and absorbs visible light (band gap 2.5 - 2.9 eV)[9,10].

In this study, the photoelectrocatalytic efficiency of $CuWO_4/g-C_3N_4$ photoanodes in removing Moxifloxacin from aqueous media was evaluated.

Material and Methods

The CuWO₄ synthesis and composite preparation follow a known methodology [1]. The scheme in

Figure 1 briefly demonstrates the synthesis of materials and photoanode preparation.



Figure 1. Synthesis and preparation of photoanodes.

Results and Discussion

The XRD patterns of CuWO₄, g-C₃N₄, and CW-gCN (5, 10, and 20 %) composites are presented in Figure 2. The diffraction peaks of CuWO₄ correspond to ICSD No. 16009, indicating a Triclinic structure with high periodicity [3]. On the other hand, g-C₃N₄ displays the presence of the main plane (002) at 27.86°.



Figure 2. XRD pattern of CuWO₄, g-C₃N₄, and CW/gCN (5, 10, and 20 %).

In Figure 3a, it was observed that there was a decrease in the photocurrent density signals of the CW/gCN photoanodes (at 5%, 10%, and 20% concentrations) as the amount of g-C₃N₄ in the mixture increased, in comparison to the photocurrent density of pure CuWO₄. The photocurrent density of pure CuWO₄ was found to be 28 μ A cm.₂ at 0.70 V vs. Ag/AgCl. This was expected as g-C₃N₄ has a low photocurrent density, which is attributed to its high charge transfer resistance[10]. On the other hand, the recombination time of 83.20 s, which is much longer compared to the time of CuWO₄ (58.38 s) (Figure 3b).



Figure 3. (a) Photocurrent transient (b) and recombination time of CuWO₄, g-C₃N₄, and CW/gCN (5, 10, and 20 %) photoanodes at 0.7 V vs. Ag/AgCl in 0.1 M of Na₂SO₄.

The study evaluated the use of photoanodes in the photoelectrodegradation of MOX (10^{-5} M) under polychromatic light irradiation for 180 minutes at 0.7 vs. Ag/AgCl. The composites demonstrated superior photoelectrocatalytic performance in MOX degradation as compared to pure materials, with CW/gCN 20 displaying the highest rate of approximately 49.89% (Figure 4a).



Figure 4. The degradation rate of pure materials and CW/gCN composites (5, 10, and 20%) (b) and stability test with CW/gCN 20.

It is interesting to note that mixing CuWO₄ with g-C₃N₄ resulted in a significant improvement in adsorption, which exposed more active sites to interact with the pollutant. Additionally, the recombination time was longer for CW/gCN 20, which may have favored more reactive species, thereby explaining its superior performance in MOX degradation. Finally, recycle tests were carried out with CW/gCN 20, and it proved to be stable over four consecutive cycles, as shown in Figure 4b.

Table 1 presents the degradation rate values and kinetic constants (k) using the pure photoanodes and the composite that showed the best photoelectrocatalytic performance.

Table 1. Photoanode degradation rate and kinetic constants (k).

Photoanodes	Degradation rate (%)	k (10 ⁻³ min ⁻¹)
$g-C_3N_4$	23.10	1.46
CuWO ₄	31.00	2.08
CW/gCN 20	49.89	3.84

Conclusions

In this study, we evaluated the photoelectrocatalytic performance of $CuWO_4/g-C_3N_4$ photoanodes in the degradation of Moxifloxacin. Our results showed that the CW/gCN composite loaded with 20% g-C₃N₄ exhibited a longer recombination time than pure CuWO₄. This resulted in a higher degradation rate of MOX. Additionally, CW/gCN 20 demonstrated stable degradation efficiency over four consecutive cycles. We believe that our findings can provide evidence for the improvement of visible light-powered photocatalysts for environmental remediation.

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