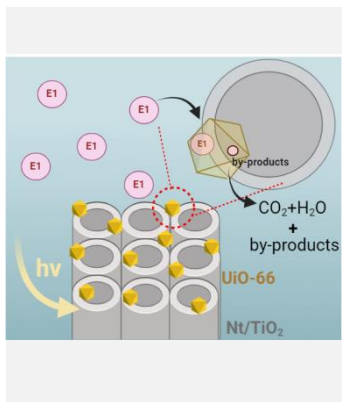


Enhanced Photoelectrocatalytic Degradation of Hormonal Pollutants Using TiO₂ Nanotubes Modified with Electrodeposited UiO-66 MOF

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Recent discussions have centered on the environmental impact of emerging pollutants, driven by their significant adverse effects. Photoelectrocatalytic processes have shown promise in enhancing the removal of these contaminants. The electrodeposition of zirconium metal-organic framework (UiO-66 MOF) nanoparticles on TiO₂ nanotubes offers a promising approach for modifying the photoelectrode, providing advantages such as improved capture and pre-concentration of dispersed contaminants for subsequent oxidation, in addition to promoting MOF nanoparticle more firmly anchored and distributed on oxide layer. This study aims to synthesize TiO₂ nanotubes modified with UiO-66 MOF nanoparticles via electrodeposition and solvothermal method and evaluate their efficacy in the degradation of estrone (E1) and 17 α -ethinylestradiol (EE2) hormones. Comparative studies demonstrated that TiO₂ nanotubes modified via the electrodeposition process were more efficient and stable due to better distribution and anchoring of the MOF in the oxide layer.

Introduction

In recent years, there has been a growing concern about the environmental impact of emerging pollutants, driven by their significant adverse effects [1]. Endocrine disrupting compounds (EDCs), a subset of these pollutants, have garnered particular attention due to their resistance to conventional wastewater treatment methods and their potential risks as endogenous drugs [2]. Notably, hormones like estrone (E1) and 17 α -ethinylestradiol (EE2) have been identified as problematic contaminants in surface waters, contributing to endogenous alterations in aquatic organisms [2].

To address the challenge of removing these contaminants, advanced oxidative processes (AOP), photocatalysis (PC) and photoelectrocatalysis (PEC), have emerged as effective methods[4]. Catalyst selection in PC and PEC emphasizes efficient light absorption and surface interaction with target compounds, making TiO₂ a particularly attractive candidate due to its stability, low toxicity, and versatility [2].

However, the low pollutant concentration often requires long treatment times for large volumes of water. One promising approach to mitigate this challenge involves modifying the photoelectrode with high-efficiency adsorbents, such as metal-organic frameworks (MOFs) like UiO-66 [5]. MOFs have gained interest for their large surface area, robust interactions, and exceptional chemical stability. In addition, UiO-66 is standing out as a promising option due to its Zr-based composition [3]. Furthermore, electrochemical synthesis of UiO-66 on TiO₂ nanotubes (NT/TiO₂-UiO 66) offers several advantages, including uniform nanoparticle distribution more firmly anchored on the oxide layer and enhanced catalytic active surface area [3].

Material and Methods

Synthesis and characterization of TiO₂ oxide nanotubular electrode

Electrodes were obtained from the anodization

process of Ti substrates using F⁻ ions. The constant potential at 20 V was applied for 2 h. After the nanotube synthesis, the samples were annealed at 450°C. The morphology, structure, and photoelectrocatalytic properties of this electrode were investigated by SEM-FEG, XRD, UV-Vis spectroscopy, and linear sweep voltammetry under irradiation.

Synthesis and characterization of UiO-66 and modifications of nanotubes

UiO-66 nanoparticles were synthesized by the solvothermal method in a Teflon-coated stainless-steel autoclave for 12 h and subjected to a heat treatment at 120°C. The particles were deposited along the nanotube wall via spray-coating for comparison with those prepared by the electrochemical process.

For the electrochemical synthesis, a potential of 6V was applied for 2 h, using NT/TiO₂ as the anode and platinum as the cathode. The electrodes were immersed in a solution containing 0.005 mol.L⁻¹ of 2-aminobenzenedicarboxylic acid and 0.005 mol.L⁻¹ of zirconium chloride in ethanol, dimethylformamide and glacial acetic acid. The morphology, structure, and photoelectrocatalytic properties of this system (UiO-66 MOF + NT/TiO₂) were investigated by SEM-FEG, XRD and photocurrent curves.

Photoelectrocatalytic Oxidation

The degradation experiments of E1 and EE2 hormones were carried out under the photolysis, and photocatalytic and photoelectrocatalytic processes using a borosilicate cell with irradiation of 100 mW/cm². NT/TiO₂ or NT/TiO₂-UiO-66 photoanode and a platinum grid cathode were placed in parallel inside of the reactor in a 40 mL of working solution consisting of deionized water with added E1 or EE2 (10 mg L⁻¹) at pH 6. The concentration of hormones was controlled by High Performance Liquid Chromatography. Anchoring test and stability of UiO 66 in NT/TiO₂ were investigated for different flow rate of the solution concerning both methods to modify the TiO₂ nanotubes. The efficiency of

the methods was analyzed using photocurrent curves obtained before and after the flow tests.

Results and Discussion

The SEM-FEG images revealed the formation of nanotubular structures from TiO_2 after the anodization process. In contrast, UiO-66 nanoparticles exhibited an octahedral morphology, as illustrated in Figure 1. The nanotube matrix displayed an internal diameter of approximately 70 nm, while the MOF nanostructures had dimensions of about 10 nm for the electrochemically deposited nanoparticles and 40 nm for the nanoparticles deposited via spray-coating. The presence of UiO-66 MOF was also confirmed by the presence of the peak in XRD on $2\theta = 7,34^\circ$. The deposition of MOF nanoparticles on the electrode surface, increased the adsorption capacity of the semiconductor. However, the photocatalytic activity was reduced due to the presence of UiO-66 nanoparticles on the nanotubes, as indicated by the voltammetric curves shown in Figure 2b. Nonetheless, maintaining the pollutant close to the TiO_2 nanotubes may facilitate a more efficient degradation process.

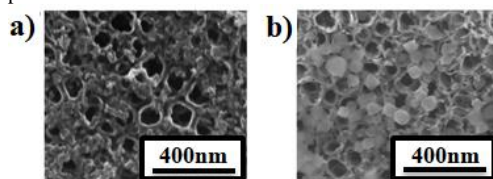


Figure 1. FEG- SEM images of TiO_2 nanotube layer modified with octahedral nanostructures of UiO-66 by (a) electrodeposition and (b) spray-coating deposition.

Comparing the photocatalytic activity among the electrodes (NT/ TiO_2 , NT/ TiO_2 -UiO-66 (spray-coating), NT/ TiO_2 -UiO-66 (electrochemically)), the E1 and EE2 solution were degraded more efficiently by the PEC process, using NT/ TiO_2 modified with UiO-66 electrochemically deposited. The superior performance of the NT/ TiO_2 -UiO-66 (electrochemically) electrode can

Conclusions

The electrochemical synthesis of UiO-66 on TiO_2 nanotubes has proven to be a promising approach to enhancing the efficacy of catalytic materials in water treatment applications. The presence of UiO-66 increased the electrode's adsorption capacity, in comparison to the NT/ TiO_2 no modified. Electrodeposition synthesis offers a uniform distribution of nanoparticles and strong substrate adherence, addressing challenges related to nanoparticle stability. Therefore, this strategy has the potential to optimize the electrode's efficiency in pollutant degradation in wastewater treatment systems.

Acknowledgments

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be attributed to its strong absorption capacity due to the presence of large and stable conjugated systems. In the spray-coating deposition, there is no anchoring of nanoparticles, as evidenced by the increased photoactivity when the electrode was subjected to flow rates between 200 ml/min (laminar flow) and 1500 ml/min (turbulent flow). It was also observed that the degradation efficiency of the electrode subjected to leaching testing at a flow rate of 1500 ml/min decreased by 24% as shown in Figure 2a. This decreasing was attributed to nanoparticle loss.

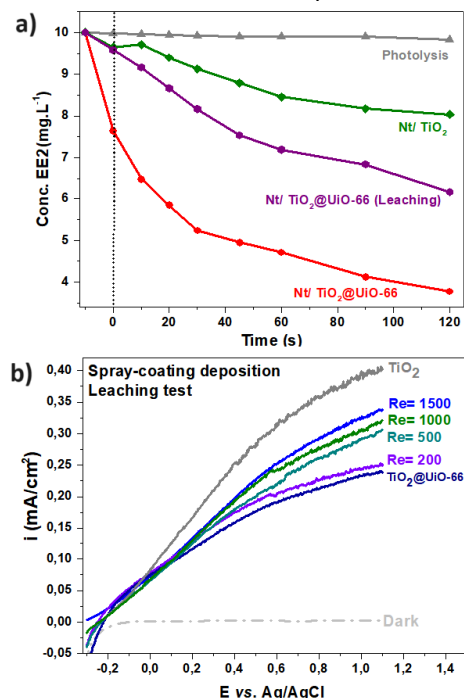


Figure 2. (a) Photoelectrocatalytic degradation of EE2 under UV-Vis irradiation using NT/ TiO_2 -UiO-66 (spray-coating) before and after leaching test at 1500 mL/min. (b) Photocurrent curves obtained before and after leaching test using NT/ TiO_2 -UiO-66 (spray-coating).