Photoelectro-reduction of nitrates from flexible Cu_2O/ITO/PET photoelectrodes

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Cu₂O/ITO/PET films

The concentration of nitrates in water resources has increased due to the use of fertilizers in agriculture, potentially exceeding the maximum permissible limits and affecting both aquatic ecosystems and human health. This study proposes the sustainable photoelectrochemical reduction of nitrates to produce ammonia using flexible photoelectrodes based on Cu_2O/ITO/PET. The films were synthesized through electrodeposition and subsequently grown via a chemical bath process. Characterization was performed using X-ray diffraction and UV-Vis spectroscopy. The produced ammonia will be identified using the indophenol colorimetric method at 655 nm. The electrode allowed for the reduction of nitrate with a ammonia yield rate of 0.52 mg cm^{-2} h^{-1} and ammonia selectivity of 19.5% at −1.0 V vs. Ag/AgCl. The goal was to develop an improved flexible material activated in the visible region that selectively converts nitrate ions to ammonia.

Introduction

Nitrate is one of the most frequently occurring anthropogenic groundwater contaminants. The concentration of nitrates in water resources has increased globally due to the use of fertilizers in agriculture. Additionally, nitrogen oxyanions can affect human health by causing methemoglobinemia. The World Health Organization (WHO) regulates nitrate in drinking water at a maximum level of 50 mg/L NO_3^- (Tugaoen et al., 2017). An attractive method for nitrate removal is photoelectrochemical reduction, which has the advantage of high activity and utilizes solar energy, unlike electrochemical reduction that typically requires a large overpotential and noble metals. This approach also allows allows the production of fossil-free ammonia through nitrogen recycling (Cerrón et al., 2022). In the literature, the Cu_2O/TiO_2 heterojunction is noted for its complementary electronic properties and effective use of the solar spectrum. TiO_2 is a stable, low-cost, and low-toxicity n-type semiconductor, though it has limitations such as high e^-/h^+ recombination and photon capture limited to UV light (Matamala et al., 2023). Cu_2O is a p-type semiconductor with a high photochemical response to the solar spectrum, low cost and non-toxic, although is unstable and can be oxidized by the photogenerated h+, limiting its activity. Cu_2O injects photogenerated e^- into TiO_2, while h^+ remains in Cu_2O, preventing recombination and photocorrosion (Matamala et al., 2021). Flexible supports like ITO/PET are lighter, easier to handle, and allow greater design variation in photoelectrochemical cells (Okumura & Iwata, 2011). This work proposes a simple, scalable and low-cost method for synthesizing Cu_2O/ITO/PET capable of reducing nitrates in water to valuable products like ammonia.

Material and Methods

Materials

Copper (II) acetate ($Cu(CH_3COO)_2.H_2O$) of analytical grande, purchased from Sigma-Aldrich. Copper (II) sulphate pentahydrate ($Cu(SO_4).5H_2O$) and sodium sulfite (Na_2SO_3) were acquired from Merck. Mannitol was supplied by Merck. ITO/PET was used as electrode support material (Solaronix, 18 Ω/sq, 0.125 mm).

Electrosynthesis of nanostructured photo-cathode

The first composite layer consisted of a thin Cu_2O film synthesized via electrodeposition in a 0.02 M $Cu(CH_3COO)_2$ and 0.1 M mannitol solution at pH 12, using a three-electrode system. The ITO/PET substrate served as the working electrode under a continuous potential of -0.4 V vs Ag/AgCl for 600 s at 55 °C. The film was then washed with Milli-Q water. Crystal seeds were grown chemically for 3 h in a 0.04 M $CuSO_4$ solution with 0.2 M Na_2SO_3 at pH 7.2 at 90 °C. The synthesized composite electrode was washed with Milli-Q water and dried at room temperature. The geometric area of working electrode was 5 cm^2.

Characterization of Cu_2O/ITO/PET thin films

Structural analysis of the thin films was performed with X-ray diffraction (XRD) to verify the Cu_2O structure and absence of metallic copper or cupric

oxide impurities.

Generate ammonia from a synthetic nitrate solution using photoelectrocatalysis

Nitrate reduction was conducted using an H-type electrochemical cell with $Cu_2O/ITO/PET$ as the cathode, a Pt wire as the counter electrode, and Ag/AgCl (3.5 mol L^{-1}) as the reference electrode. The cell contained 0.1 mol L^{-1} Na_2SO_4 with 100 mg L^{-1} $NaNO_3$ (pH 5.89), and a constant potential was applied using a potentiostat (Matamala et al., 2021). Potentials -1.0 V were applied under 1 h of illumination (LED lamp 440 nm, 50 W). Initial nitrate concentration for ammonia generation was 100 mg L^{-1}. Ammonia determination was carried out using the indophenol colorimetric method. The formation of the indophenol dye was determined using the UV-Vis spectrophotometer at a wavelength of 655 nm. Nitrogen species (NO_3^- and NO_2^-) in solution were determined using colorimetric methods. The absorption intensities at wavelengths of 220 nm and 275 nm were measured for the final samples.

Nitrate conversion was calculated using Ec (1).

$$Nitrate\ conversion\ (\%) = \frac{C_{nitrate,i} - C_{nitrate,t}}{C_{nitrate,i}} x\ 100$$

where $C_{nitrate,i}$ is the nitrate concentration in mg NO_3^--N L^{-1} before treatment, and $C_{nitrate,t}$ is the nitrate concentration at time (t). The selectivity (S_X) towards ammonia was calculated using Eq. (2).

$$S_{NH_3}(\%) = \frac{C_{ammonia}}{C_{nitrate,i} - C_{nitrate,t}} x\ 100$$

where $C_{ammonia}$ represents the concentration of ammonia (mg NH_3-N L^{-1}), produced over time.

Results and Discussion

X-ray diffraction analysis (Figure 1) identified different crystallographic peaks of Cu_2O and PET grown on $Cu_2O/ITO/PET$ films. The characteristic peak at 36.4° corresponds to the crystalline plane (111) of cuprite structure of Cu_2O, indicating epitaxial growth during the chemical bath. Peaks at 25.5° and 53.5° correspond to the ITO coated PET substrate.

Regarding the catalytic photoelectric process, after 1 h of treatment, the conversion of nitrates resulted in 46%. The production of nitrites was 19 mg L^{-1}, and ammonia production was 8.97 mg L^{-1}. The selectivity (S_x) was 19.5%. Increasing the reaction time from 30 min to 60 min decreased the nitrate concentration while increasing the concentrations of ammonia and nitrite. This suggests the conversion of NO_3^- to NO_2^- and NH_4^+. The conversion yield resulted in 0.52 mg cm^{-2} h^{-1}. The determination required the preparation of a calibration curve considering the dilution factor when applicable.
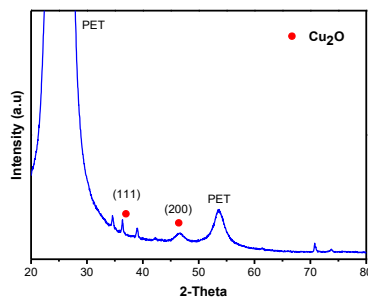

Figure 1. XRD pattern of the $Cu_2O/ITO/PET$ film.

Conclusions
$Cu_2O/ITO/PET$ electrodes were successfully synthesized via electrodeposition and subsequent chemical bath growth. The Cu_2O growth on the surface improved the electrocatalytic response of the electrodes, presenting nitrate conversion than Cu_2O seed electrodes. $Cu_2O/ITO/PET$ presented nitrate conversion 0.52 mg cm^{-2} h^{-1} and Sx of 19.5% in 1 h.

References
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