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Rapid and ultrasensitive electrochemical detection of ammonia nitrogen in groundwater by a core-shell Cu_2O@UiO-66 modified electrode

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Ammonia nitrogen(NH_3 and NH_4^+, NH_4-N), as an important chemical indicator reflecting the quality of the water environment, plays a vital role in ecosystem stability. Especially in complex and variable low-quality groundwater environments, it is necessary to develop high-sensitive and selective NH_4-N detections to provide technical support for investigating its migration and remediation mechanism. The most-used detection method for NH_4-N is Nessler's reagent method, which suffers from a highly toxic substance, interference with other components, as well as only being used on-site instead of in-situ. Thus, the urgent key issue in this field is to develop a highly selective, environmentally friendly, and rapid in-situ detection method for ammonia nitrogen in groundwater where multiple components coexist.

In this study, a three-electrode detection system for NH_4-N with core-shell MOF(Cu_2O@UiO-66) as the working electrode was constructed. The functionalized Cu_2O@UiO-66 was synthesized by a facile hydrothermal method, followed by an in-situ growth on conductive carbon cloth (CC) to fabricate an electrochemical sensor (Cu_2O@UiO-66/CC). Under optimized conditions, the Cu_2O@UiO-66/CC electrochemical sensor demonstrated a response time of only 12 seconds for detecting ammonia nitrogen through cyclic voltammetry (CV), with a low detection limit of 0.231 μM, sensitivity of 5.75 $\mu A \cdot \mu M^{-1}$, strong anti-interference ability, and a long service life. The detection mechanism was investigated as the presence of oxygen vacancies created by carboxylate ions and the nanoconfinement effect resulting from the pores of UiO-66 in the “shell” structure, which captures more ammonia nitrogen to the “core” Cu_2O to complete the subsequent electrocatalytic oxidation. Spiked water and real groundwater samples analysis showed that the sensor exhibited reliable recoveries (98.47% to 100.39%) and relative standard deviation (RSD) (<3 %). This study offers a novel approach for swift and accurate in-situ detection of ammonia nitrogen in groundwater, indicating a great potential for practical application.

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