

Very efficient yet durable urea electrosynthesis *via* carbon dioxide and nitrate over the defect-rich In_2O_3 nanotube

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Significance and Relevance

A Vo-rich In_2O_3 nanotube was fabricated by thermally treating a MOF precursor and employed as an electrocatalyst for highly efficient and durable urea synthesis via the EC-CO₂/NO₃⁻. The In_2O_3 -NT-500 electrode shows a urea formation rate of 1441 µg h⁻¹ mg_{cat}⁻¹ and a FE of 60.3%, outperforming the most reported EC-CO₂/NO₃⁻ systems towards urea electrosynthesis. The defect-engineered catalyst not only stabilizes the *CO₂NH₂ intermediate, but also reduces the energy barrier for the rate-determining step during the C-N coupling processes, thus enhancing the efficiency and selectivity of urea production.

Introduction and Motivations

Urea is widely used as nitrogen fertilizer and also a fundamental feedstock for the manufacture of resins, plastics, etc. ^{1,2} At present, the industrial urea production is dominated by the conventional Bosch-Meiser process. It is considerably energy- and pollution-intensive; in contrast, the electrochemical conversion of CO_2 and nitrate (NO_3^-) pollutants into urea at mild conditions provides a promising alternative to the practical route, not only benefiting global carbon/nitrogen neutrality, but also reforming urea synthesis industry. ³

Materials and Methods

In₂O₃-NT was fabricated by calcination of the MOF (MIL-68 (In)) precursor at different temperatures. The finally obtained catalysts were denoted as In₂O₃-NT-400, In₂O₃-NT-500, In₂O₃-NT-600, accordingly, where 400, 500, and 600 represent the annealing temperatures adopted. The bulk In₂O₃ (In₂O₃-B) was prepared by one-step calcination without using the MOF precursor. The resulting In₂O₃-B was also subject to a ball-milling treatment, and the sample was denoted as milled In₂O₃-B. The urea electrosynthesis test was performed on a CHI 660E electrochemical analyzer equipped with three electrode configurations, using a two-chamber cell as a reactor, Pt sheet as a counter electrode, Ag/AgCl-saturated KCl as a reference electrode, and carbon paper (CP) with loaded catalyst as a working electrode. The catalysts were characterized by various techniques and the DFT simulation was also performed to better understand the nature of catalysts and the reaction pathways.

Results and Discussion

Herein, a Vo-rich In_2O_3 -NT catalyst was obtained from thermally treating an organic metal framework (MOF), namely, MIL-68 (In), and used for urea electrosynthesis through co-reduction of CO₂ and NO₃⁻. By calcination of MIL-68 (In) at setting temperatures for 2 h, the MOF ligands in the precursor are removed to form a special three-dimensional porous structure. Compared to the In(OH)₃ nano-cube and the InOOH nanorod with typical solid structure, the current porous In_2O_3 -NT assembled by smaller nanoparticles can not only enhance the exposure of active surface for electrocatalytic reaction, but also improve the electrolyte diffusion and mass transfer, thus boosting the catalytic kinetics of urea electrosynthesis. The derived In_2O_3 -NT-500 electrode affords a highest urea production rate of 1441 µg h⁻¹ mg_{cat}⁻¹, a maximal Faraday efficiency (FE) of 60.3% and robust stability for durable urea formation. This exceptional performance of In_2O_3 -NT-500 outperformed all of the In-based systems as well as other EC-CO₂/NO₃⁻ systems reported so far. The mechanism investigation disclosed that the Vo specimen in the catalyst can not only stabilize the *CO₂NH₂ intermediate, but also effectively reduce the reaction energy barrier of the rate-determining step (RDS), thereby significantly enhancing the overall urea production of the defect-engineered In_2O_3 -NT.





Figure 1 In-situ ATR-FTIR spectra of (a) In_2O_3 -NT-500 and (b) In_2O_3 -B; difference in charge density for *NO₃ adsorption on (c₁) Vo-rich In_2O_3 (222) and (c₂) Vo-deficient In_2O_3 (222) surface, difference in charge density for *CO₂ adsorption on (c₃) Vo-rich In_2O_3 (222) and (c₄) Vo-deficient In_2O_3 (222) surface (the yellow area corresponds to a higher electron density, whereas the blue area represents a lower electron density); (d) free energy diagrams of the C-N coupling process on the Vo-deficient and Vo-rich In_2O_3 (222) surfaces.



Figure 2 Defect-rich In_2O_3 electrocatalyst highly efficient yet durable for sustainable urea synthesis *via* co-reduction of CO_2/NO_3^- at mild conditions.

References

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