Ambient electrosynthesis of urea with nitrate and carbon dioxide over iron-based dual-sites

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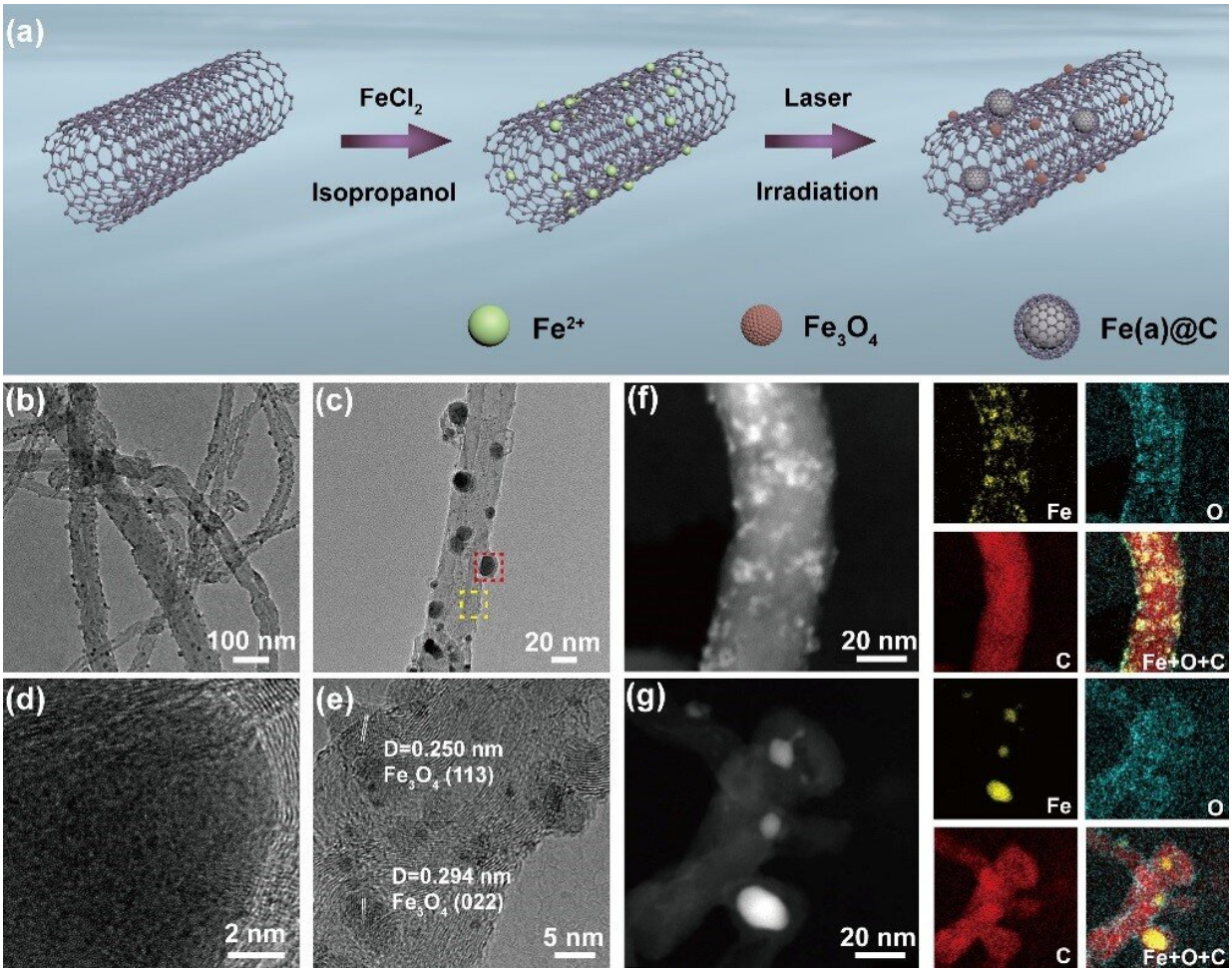

(a). Schematic illustration of the synthetic process of Fe(a)@C-Fe3O4/CNTs; (b). Low- and (c) high-magnification TEM images of Fe(a)@C-Fe3O4/CNTs. HRTEM images of Fe(a)@C (d) (from the red dashed box in c) and Fe3O4 NPs (e) (from the yellow dashed box in c); (f), (g) HAADF-STEM images and corresponding elemental mapping images of Fe3O4 and Fe(a)@C. Credit: Geng

Jing

Urea ($CO(NH_2)_2$) has been applied both in agricultural and pharmaceutical field. The widely used Bosch-Meiser process has high energy consumption and CO_2 emission. Therefore, it is imperative to explore energy-saving and economical routes for urea synthesis under mild conditions.

The electrosynthesis of urea with CO_2 and NO_3- under ambient conditions is an efficient way, but it is far from application. This is because the key step needs an efficient electrocatalyst enabling adsorption and activation of NO_3- and CO_2 to accomplish the C-N coupling.

Researchers from the Hefei Institutes of Physical Science of the Chinese Academy of Sciences have now developed a liquid-phase laser irradiation route to fabricate symbiotic carbon encapsulated amorphous iron (Fe(a)@C) and iron oxide nanoparticles (Fe_3O_4 NPs) on carbon nanotubes (denoted as Fe(a)@C-Fe_3O_4/CNTs).

The as-fabricated Fe(a)@C-Fe_3O_4/CNTs contained two Fe-based active components, namely, Fe@C NPs with the particle sizes of 10~20 nm and Fe_3O_4 NPs with the particle sizes of 1~5 nm.

The presence of two different structural units in Fe(a)@C-Fe_3O_4/CNTs made it possible to synergistically electrocatalytic activate CO_2 and NO_3- to realize the C-N coupling for urea synthesis.

As expected, Fe(a)@C-Fe_3O_4/CNTs exhibited superior activity toward the electrocatalytic coupling of CO_2 and NO_3- for urea synthesis, affording a urea yield of 1341.3±112.6 μg h-1 mgcat-1 and a faradic

efficiency of 16.5±6.1% at -0.65 V (vs. RHE) in 0.1 M KNO3 electrolyte.

Both experimental and theoretical results unveiled that Fe(a)@C was mainly responsible for the electrocatalytic reduction of NO_3- to form *NH_2 intermediates, while Fe_3O_4 was more beneficial for the electrocatalytic reduction of CO_2 to form *CO intermediates.

The synergistically catalytic effect contributes to the excellent electrocatalytic performance of urea synthesis at ambient conditions.

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More information: Jing Geng et al, Ambient Electrosynthesis of Urea with Nitrate and Carbon Dioxide over Iron-Based Dual-Sites, *Angewandte Chemie International Edition* (2022). DOI: 10.1002/anie.202210958

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