Uniform single atomic sites anchored in graphdiyne for benzene hydroxylation to phenol

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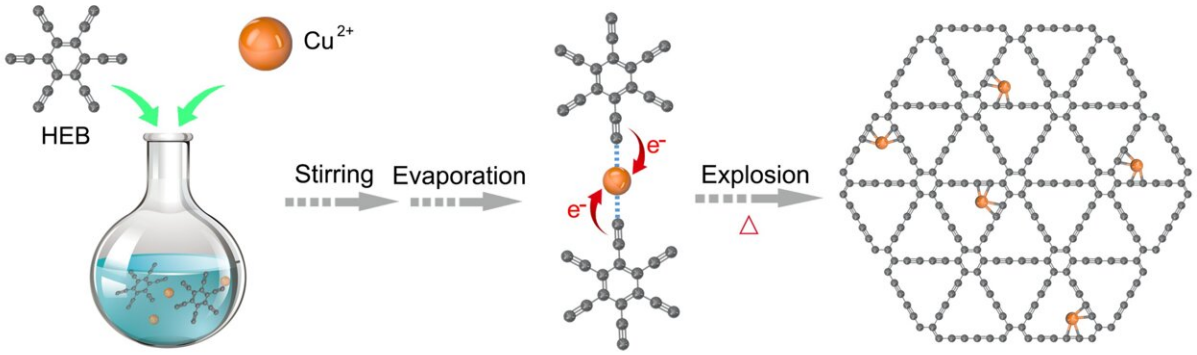


Copper ions are complexed with the graphdiyne monomer (HEB) to form copper-alkyne complexes. During the monomer coupling process, copper ions are reduced and anchored by graphdiyne. Credit: Science China Press

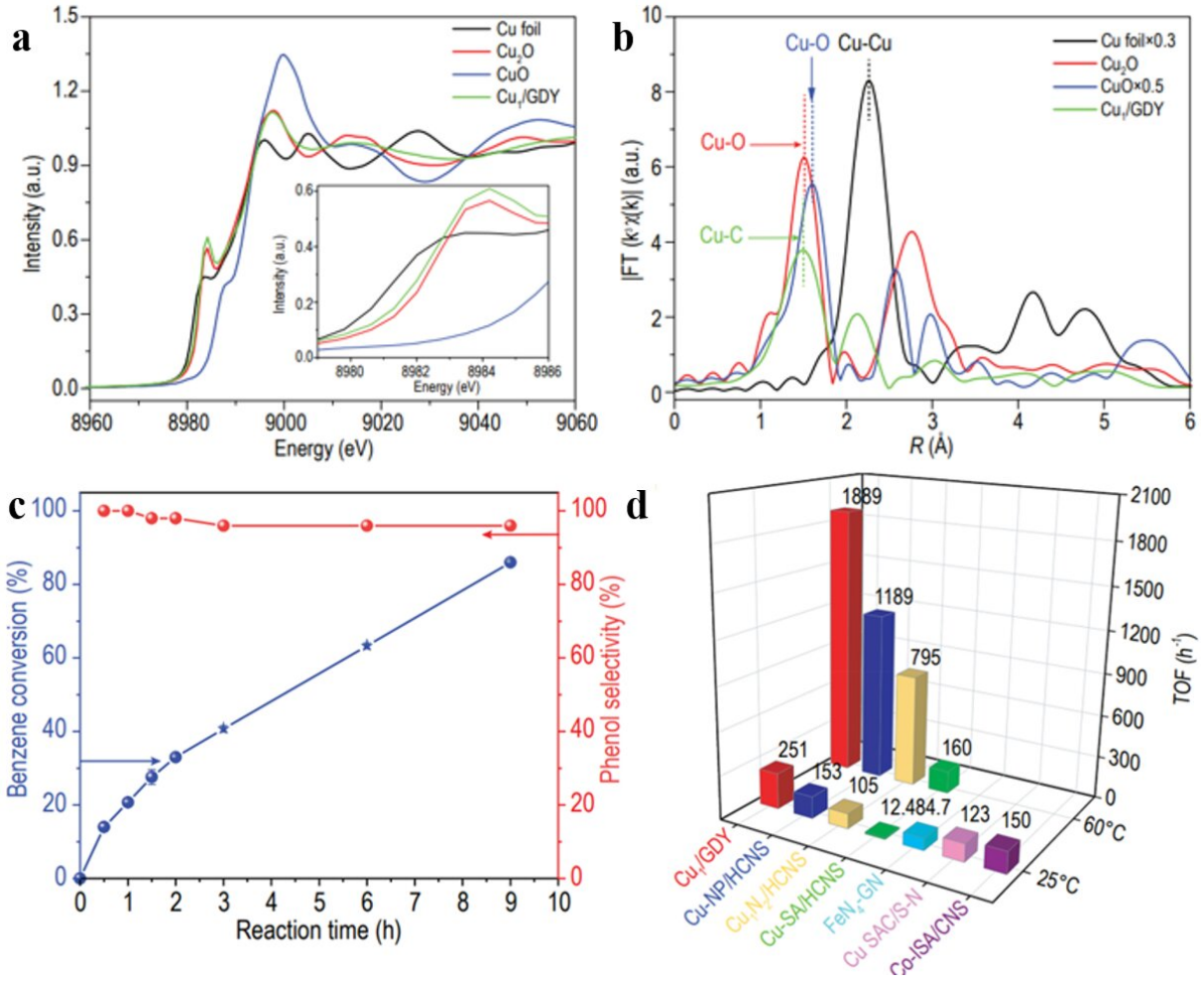
For single-atom catalysts (SACs), the catalyst supports are not only anchors for single atoms, but also modulators for geometric and electronic structures, which has an important impact on the catalytic performance. Selecting an appropriate support to prepare SACs with uniform coordination environments is critical for achieving optimal performance and clarifying the relationship between the structure and the property of SACs.

Graphdiyne (GDY), a new two-dimensional periodic carbon allotrope with an atom-thick layer, which was first synthesized by Prof. Yuliang Li in ICCAS, China, is composed of sp-hybridized carbon atoms in diacetylenic and sp^2-hybridized carbon atoms in benzene rings. The unique alkyne-rich structure of GDY makes it an ideal support for anchoring single atoms due to the uniformly distributed pores and large binding energies to metal atoms via the strong d-π interaction. Taking advantage of the above characterizations of GDY, Dr. Changyan Cao and Dr. Feng He from ICCAS present an efficient and simple strategy for fabricating Cu single atoms anchored on GDY (Cu_1/GDY) with uniform Cu_1-(sp)C_4 single sites under mild conditions.

By using synchrotron radiation X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, and density functional theory (DFT) calculation, it is proved that $Cu^{\delta+}$ (0_1-(sp)C_4 coordination environment. Cu_1/GDY demonstrated excellent catalytic performance for benzene oxidation to phenol using H_2O_2. The calculated turnover frequency (TOF) is approximately 251 h^{-1} at room temperature and 1889 h^{-1} at 60 °C, which is significantly higher than previously reported catalysts under the same reaction conditions.

Furthermore, even with a high benzene conversion of 86% , high phenol selectivity (96%) is maintained, which can be ascribed to the hydrophobic and oleophilic surface nature of Cu_1/GDY for benzene adsorption and phenol desorption. Synchrotron X-ray absorption spectroscopy, Fourier transform infrared absorption spectroscopy and density functional theory show that the Cu_1-C_4 active site can more effectively activate H_2O_2 to form Cu=O bond, which is an important active intermediate for the oxidation of benzene to phenol. The intrinsic higher activity of Cu_1/GDY compared with other Cu SACs with nitrogen coordination structures is clarified by DFT calculations of Cu-3d band center.

This work not only presents an efficient route for fabricating GDY-supported metal SACs with uniform metal-C_4 centers, but also provides a promising benzene hydroxylation catalyst for phenol production with H_2O_2.



a) Cu K-edge XANES spectra of Cu_1/GDY and reference samples; b) Fourier transformed (FT) k3-weighted χ(k)-function of the EXAFS spectra for Cu K-edge; c) Conversion and selectivity vs reaction time curves of Cu_1/GDY for benzene oxidation to phenol with H_2O_2 ; d) TOF comparison of Cu_1/GDY and other metal SACs. Credit: Science China Press

The research was published in *National Science Review*.

More information: Jia Yu et al, Uniform Single Atomic Cu1-C4 Sites Anchored in Graphdiyne for Hydroxylation of Benzene to Phenol, *National Science Review* (2022). DOI: 10.1093/nsr/nwac018