

Laser-driven synthesis of advanced carbon-based catalysts from aerosolized organic precursors

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Highlights

- Laser-assisted pyrolysis enables tunable carbon catalysts with atomically dispersed metals and controlled doping with heteroatoms.
- Post-treatment improves (Fe/Co)-NC structure and tunes ORR selectivity (2e⁻ or 4e⁻).
- Metal-free and Fe/Co carbons exhibit enzyme-like activity for the selective detection of glucose and glutathione.

1. Introduction

Carbon-based nanomaterials (CBM) have become central to modern catalysis owing to their large surface area, chemical tunability, and outstanding stability under diverse reaction conditions. Their applications span energy conversion (e.g., oxygen reduction and hydrogen evolution reactions), environmental remediation, and (bio)sensing technologies, where their ability to host active sites, facilitate electron transfer, and interact with substrates via π - π or electrostatic interactions is highly advantageous [1]. Beyond electrocatalysis, and motivated by their excellent electron-transfer capabilities, an increasing number of studies have demonstrated that CBMs, particularly when heteroatom-doped, exhibit redox enzyme-like (nanozyme) activity using small oxygenated species—mainly O₂ and H₂O₂—as substrates, thereby mimicking peroxidase, oxidase, and catalase functions [2]. Laser-driven methodologies have recently been recognized as an excellent bottom-up approach for the synthesis of advanced carbon-based materials through the pyrolysis of organic precursors [3,4]. This innovative technique enables precise control over the composition of the resulting materials by adjusting the organic molecule used as the feedstock. As a result, we can achieve tailored doping with heteroatoms like N and O or even incorporate metals such as Fe or Co into the structure as Single-Atom catalysts (SACs). The synthesized materials demonstrated remarkable catalytic performance in both the Oxygen Reduction Reaction (ORR) and as enzyme-like surrogates, highlighting the versatile catalytic capabilities of carbon materials synthesized through laser-pyrolysis.

2. Methods

Materials were synthesized by laser-assisted pyrolysis in a continuous-flow reactor using pyridine solutions of phthalocyanine precursors (Fe and Co) and ferrocene (Fe) dissolved in mesitylene. The aerosolized precursor mixture was decomposed by a CO₂ laser in the presence of SF₆ as a photosensitizer and argon as a carrier gas, producing carbon-based nanoparticles collected on cellulose filters. The obtained materials were calcined at 300 °C, with or without subsequent thermal treatment under NH₃/N₂ atmospheres at 900 °C. Electrocatalytic performance of mesitylene-derived samples toward the oxygen reduction reaction (ORR) was evaluated using an Autolab PGSTAT302N potentiostat in a three-electrode configuration in 0.1 M KOH at room temperature, employing Ag/AgCl (3 M NaCl) as the

reference electrode and a Pt wire as the counter electrode. The oxidase- and peroxidase-like activities of pyridine-derived nanozymes were investigated through TMB oxidation monitored by UV–vis spectroscopy, and kinetic parameters were determined using the Lineweaver–Burk model. Based on this catalytic activity, a colorimetric glucose sensing platform employing glucose oxidase (GOx) was developed, and the glutathione (GSH) depletion capability was evaluated, demonstrating its potential for redox-related biosensing applications.

3. Results and discussion

Electrocatalytic oxygen reduction plays a central role in electrochemical energy technologies and in hydrogen peroxide production. Achieving selective control over the two-electron ($2e^-$) and four-electron ($4e^-$) ORR pathways within a single catalyst platform, however, remains challenging. Laser-driven synthesis of Fe–C nanostructures from ferrocene/mesitylene aerosols enables tunable ORR selectivity through controlled post-treatment. Air annealing at 300 °C produces catalysts with high H_2O_2 selectivity, attributed to oxygen-containing surface groups and well-developed mesoporosity. Using this optimized $2e^-$ catalyst, 80 ppm of H_2O_2 with 94% faradaic efficiency was obtained after 24 h of electrolysis. In contrast, NH_3/N_2 treatment at 900 °C promotes nitrogen incorporation and microporosity, favoring selective water production. The resulting $4e^-$ catalyst delivers power output and stability comparable to Pt/GC in a primary zinc–air battery. These findings demonstrate a practical strategy to tune ORR selectivity in Fe-containing nanocarbons with trace Fe (<0.1 wt%) present as atomically dispersed active sites.

In parallel, carbon-based nanozymes with distinct enzyme-like activities were obtained from phthalocyanine-derived precursors. A metal-free nitrogen-doped carbon exhibits exclusive peroxidase-like activity, whereas Fe- or Co-containing nanocarbons (~0.55 wt% metal) form atomically dispersed Fe/Co– N_x sites that provide oxidase-like activity. The versatility of laser-assisted pyrolysis enables precise control over nanocarbon composition and the formation of single-atom metal centers. These nanozymes enable selective colorimetric detection of glucose and glutathione, showing good selectivity against structurally related metabolites and reliable performance in artificial samples. Future studies will focus on developing direct electrochemical biosensors for glucose and GSH based on these nanocarbon catalysts.

4. Conclusions

Laser-assisted pyrolysis provides a versatile platform for the synthesis of carbon-based catalysts with tunable composition and functionality. By selecting appropriate molecular precursors and post-treatments, the resulting nanocarbons can be tailored either for electrocatalytic ORR applications or for enzyme-like activity in biosensing systems. The approach enables the generation of atomically dispersed metal active sites as well as heteroatom-doped carbon structures, providing versatile catalysts for a range of applications, including sustained H_2O_2 production, energy conversion in zinc–air batteries, and colorimetric detection of biologically relevant molecules. These results highlight the potential of laser-driven synthesis for designing multifunctional carbon nanomaterials.

References

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Keywords

Carbon nanomaterials; Laser-assisted pyrolysis; Oxygen reduction reaction; Nanozymes