Highlight

Advanced electrosynthesis of hydrogen peroxide on oxidized carbon electrocatalyst

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A R T I C L E   I N F O

Article history:
Received 3 September 2018
Accepted 5 September 2018
Available online 8 September 2018

Keywords:
Hydrogen peroxide electrosynthesis
Oxygen reduction reaction
Carbon nanotubes
Electrocatalysis
Oxygen functional groups

Hydrogen peroxide (H₂O₂) is one of the 100 most important chemicals involved in multiple chemical processes including paper and textile manufacturing, waste degradation, and pharmaceutical production [1]. Compared with the current industrial process to produce H₂O₂ following the anthraquinone oxidation/reduction method, electrochemical reduction of oxygen to H₂O₂ through a two-electron pathway constitutes an environmental friendly alternative route [2–4]. Unfortunately, the electrogneration of H₂O₂ from two-electron reduction of oxygen feedstock is kinetically sluggish and therefore requires electrocatalysts with high reactivity, high selectivity, and good stability [5,6]. Carbon-based materials are promising candidates for H₂O₂ electrosynthesis because of their superb mechanical and chemical stability, electronic conductivity, earth abundance, and versatility in composition and structure [7–9]. For instance, Liu et al. reported a porous carbon material with abundant defects and large surface area that exhibits satisfactory H₂O₂ selectivity over 90.0% in acid conditions [10]. Fellinger and co-workers synthesized a mesoporous nitrogen-doped carbon and the nitrogen dopants are identified as active sites for selective H₂O₂ electrogneration [11]. In addition, oxygenated acid species on carbon materials also demonstrate promising reactivity and selectivity of 88% [12]. However, mechanistic investigation regarding to selective reduction of oxygen to H₂O₂ remains insufficient with neither deep understanding of the origin of H₂O₂ selectivity nor rational design principles to construct active sites for H₂O₂ electrosynthesis. Complicated synthetic procedures of H₂O₂ electrocatalysts further hinder the practical application of electrochemical synthesis of H₂O₂.

In order to address the above issues, Cui and co-worker from Stanford University reported a facile surface oxidation approach to modify multiple carbon materials with highly-reactive oxygen functional groups that significantly enhances the selectivity of H₂O₂ electrogneration from oxygen [13]. Multiple commercial carbon materials were oxidized by nitric acid to fabricate oxygen functional groups. For instance, oxidized carbon nanotubes (O-CNTs) demonstrate excellent performance for H₂O₂ electrochemical production in both basic and neutral electrolytes. Compared with pristine carbon nanotubes, O-CNTs significantly reduce the overpotential by ~130 mV at 0.2 mA (Fig. 1a) and simultaneously increase the selectivity to ~90% (Fig. 1b). Long-term durability evaluation indicates superior stability of O-CNTs during H₂O₂ electrosynthesis with negligible changes in reactivity or selectivity for 10 h. X-ray photoelectron spectroscopy (XPS) results verify the existence of both C–O and C=O functional groups on the surface (Fig. 1c, d). The reactivity and selectivity are proved to be in linear relationship with the oxygen content of O-CNTs (Fig. 1e), validating that the oxygen functional groups contribute to the superior performance of H₂O₂ production. Further theoretical simulations suggest the carbon atoms adjacent to the oxygen functional groups are the active sites for oxygen reduction through the two-electron pathway to produce H₂O₂ (Fig. 1f). Therefore, surface oxidation of carbon materials effectively constructs oxygen functional groups.
groups as H₂O₂ active sites and significantly improves the electrocatalytic performance for H₂O₂ production.

Surface oxidation of carbon materials affords a facile approach to large-scale synthesis H₂O₂ electrocatalysts with great potential for practical applications. The oxygen functional groups were unambiguously identified as active sites for selective H₂O₂ electrochemical production from oxygen by employing various experimental methods and theoretical simulations. The strategy of producing chemicals through environmentally friendly electrochemical approaches represents advanced manufacture and green chemistry of our sustainable nature.

Acknowledgments

This work was supported by the National Key Research and Development Program (2016YFA0202500 and 2016YFA0200101), the National Natural Science Foundation of China (21676160), and Tsinghua University Initiative Scientific Research Program.

Supplementary materials


References