



## Highlight

## Advanced electrocatalysis of hydrogen peroxide on oxidized carbon electrocatalyst

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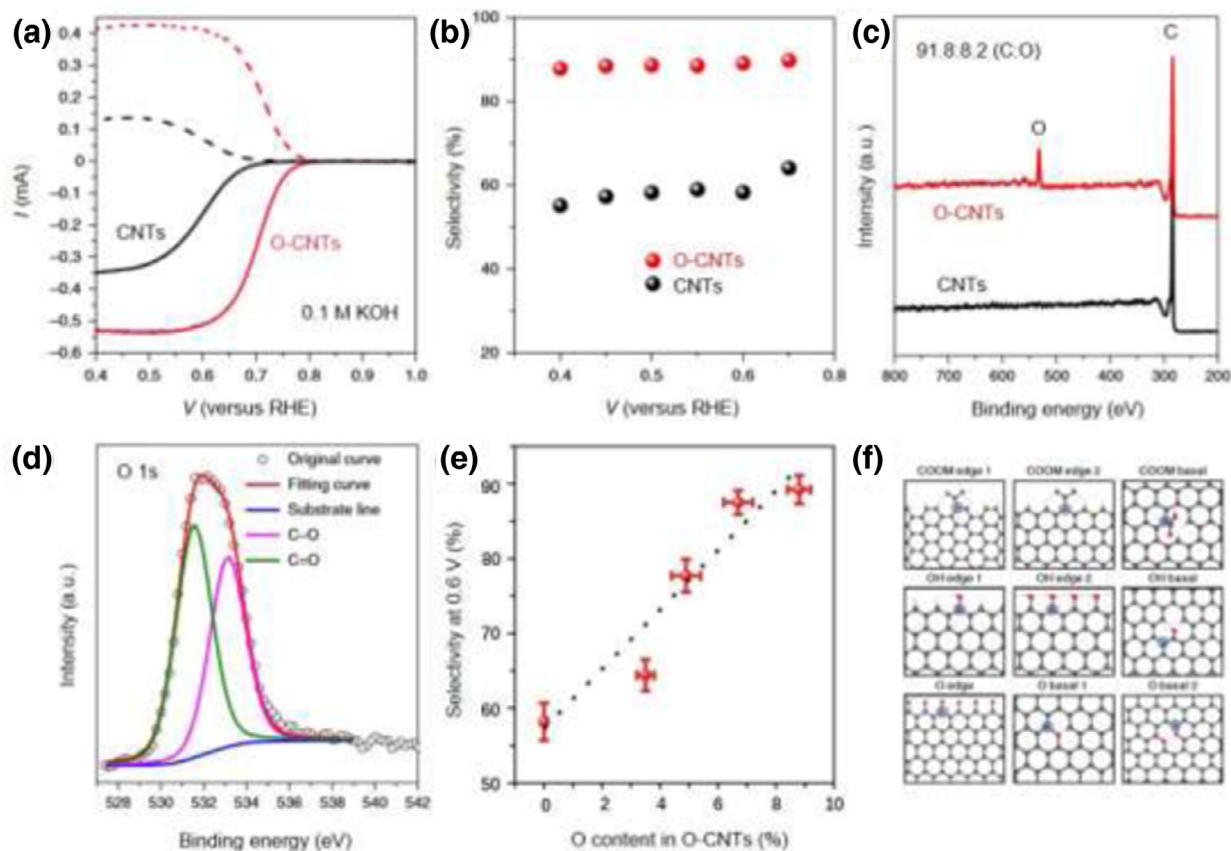
Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is one of the 100 most important chemicals involved in multiple chemical processes including paper and textile manufacturing, waste degradation, and pharmaceutical production [1]. Compared with the current industrial process to produce  $\text{H}_2\text{O}_2$  following the anthraquinone oxidation/reduction method, electrochemical reduction of oxygen to  $\text{H}_2\text{O}_2$  through a two-electron pathway constitutes an environmental friendly alternative route [2–4]. Unfortunately, the electrogeneration of  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  electrocatalysis 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  $\text{H}_2\text{O}_2$  selectivity over 90.0% in acid conditions [10]. Fellingner and co-workers synthesized a mesoporous nitrogen-doped carbon and the nitrogen dopants are identified as active sites for selective  $\text{H}_2\text{O}_2$  electrogeneration [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  $\text{H}_2\text{O}_2$  remains insufficient with neither deep understanding of the origin of  $\text{H}_2\text{O}_2$  selectivity nor rational design principles to construct active sites for  $\text{H}_2\text{O}_2$  electrocatalysis. Complicated

synthetic procedures of  $\text{H}_2\text{O}_2$  electrocatalysts further hinder the practical application of electrochemical synthesis of  $\text{H}_2\text{O}_2$ .

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  $\text{H}_2\text{O}_2$  electrogeneration 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  $\text{H}_2\text{O}_2$  electrochemical production in both basic and neutral electrolytes. Compared with pristine carbon nanotubes, O-CNTs significantly reduce the overpotential by  $\sim 130$  mV at 0.2 mA (Fig. 1a) and simultaneously increase the selectivity to  $\sim 90\%$  (Fig. 1b). Long-term durability evaluation indicates superior stability of O-CNTs during  $\text{H}_2\text{O}_2$  electrocatalysis 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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  (Fig. 1f). Therefore, surface oxidation of carbon materials effectively constructs oxygen functional

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**Fig. 1.** (a) Linear sweep voltammetry profiles of O-CNTs and CNTs at a scan rate of 10.0 mV s<sup>-1</sup> in O<sub>2</sub>-saturated 0.10 M KOH, where solid lines and dashed lines are the disc currents and ring currents, respectively; (b) calculated selectivity at various potentials based on (a); (c) XPS survey spectra of O-CNTs and CNTs; (d) oxygen 1s XPS spectra of O-CNTs; (e) Plots of H<sub>2</sub>O<sub>2</sub> selectivity at 0.6 V of O-CNTs with different oxygen contents; (f) different oxygen functional groups examined by theoretical simulations [13]. Copyright 2018, Springer Nature.

groups as H<sub>2</sub>O<sub>2</sub> active sites and significantly improves the electrocatalytic performance for H<sub>2</sub>O<sub>2</sub> production.

Surface oxidation of carbon materials affords a facile approach to large-scale synthesis H<sub>2</sub>O<sub>2</sub> electrocatalysts with great potential for practical applications. The oxygen functional groups were unambiguously identified as active sites for selective H<sub>2</sub>O<sub>2</sub> electrochemical production from oxygen by employing various experimental methods and theoretical simulations. The strategy of producing chemicals through environmental friendly electrochemical approaches represents advanced manufacture and green chemistry of our sustainable nature.

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### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jechem.2018.09.002.

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