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Efficient oxygen reduction to H$_2$O$_2$ in highly porous manganese and nitrogen co-doped carbon nanorods enabling electro-degradation of bulk organics

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**A B S T R A C T**

The direct synthesis of hydrogen peroxide using sustainable energy and molecular oxygen is a promising alternative approach to the conventional batch synthesis. Here we present a manganese and nitrogen co-doped carbon material which catalyzes the selective reduction of dioxygen in an acidic environment to hydrogen peroxide. The onset potential is close to 0.7 V, with >98% H$_2$O$_2$ selectivity in the range of 0.7 – 0.5 V vs RHE. This is the highest reported to date, outperforming many bimetallic noble metal catalysts. Besides, this doped carbon material is hierarchically porous, featuring both a large mesopore volume (4.54 m$^3$/g$^1$) and a high specific surface area (1333 m$^2$/g$^1$). This enables the effective adsorption of bulky organics such as methylene blue (385 mg/g$^1$). Combined with the formation of hydroxyl radicals during electrochemical H$_2$O$_2$ generation, this material also enables the efficient electrochemical degradation of methylene blue, as evidenced by in situ UV−vis spectrometry.

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1. Introduction

Industrial wastewater often contains toxic organic pollutants. Traditional water treatment traps these contaminants in the sludge, incurring a large environmental footprint [1–4]. Recently, electrochemical methods using electrons as “clean reagents” have attracted much attention [5–10]. In particular, the oxygen reduction reaction (ORR) takes advantage of the readily-available oxygen dissolved in the water to produce hydrogen peroxide. This reaction is often associated with the formation of hydroxyl and peroxy radicals at the electrode [11–13]. These radicals can break up even the most resistant organic compounds. Yet converting O$_2$ electrocatalytically into H$_2$O$_2$ is no easy task. The state-of-the-art platinum catalysts often facilitate the 4-electron transfer reaction, producing mainly water with little H$_2$O$_2$ [14–16]. Alloying Pt with suitable transition metals such as Au and Hg can catalyze the 2-electron transfer reaction and boost the H$_2$O$_2$ selectivity to >90% [17], but these catalysts are expensive and their working potential at the benchmark 1 mA cm$^{-2}$ is often below 0.4 V vs RHE. As we and others recently showed carbon catalysts have excellent ORR activity in alkaline media [18–25]. But most of these are not H$_2$O$_2$-selective and show poor activity under acidic conditions [26]. There are exceptions: a carbon-based catalyst tailored to produce H$_2$O$_2$ selectively in an acidic electrolyte was reported by Liu et al. [27]. Their material, made from MOF-5, showed a 0.42 V vs RHE onset potential and a H$_2$O$_2$ selectivity of 90%. Elsewhere, Fellinger et al. used acetic acid for their mesoporous nitrogen-doped carbon, reporting an onset potential of 0.55 V vs RHE and 95% H$_2$O$_2$ selectivity (other high-performance H$_2$O$_2$ catalysts are listed in Table S1 in the supporting information).

Because the reactive hydroxyl radicals are short-lived, the organic contaminants must be adsorbed and held at the electrode in close proximity to the radical-generating sites. This means that the H$_2$O$_2$-formation catalyst should be a porous material, allowing the capture of the organic pollutants. Pollutants come in all sizes, and the pore structure of the electrode must be designed appropriately. For instance, simple aromatics such as benzene, toluene and xylene have kinetic diameters < 8 Å, fitting easily in micropores. But many dyes [28–31], surfactants [32,33] and pharmaceutical compounds [34,35] can be > 2 nm in size, requiring larger pores for effective adsorption and mass transfer. Ideally, we want hierarchically porous electrodes with a high micropore volume and...
a high mesopore volume. Carbon materials are suitable electrode materials, due to their high conductivity, low cost and tunable pore structure. Many groups are working on this topic (see also Table S2 in the supporting information for details); Schuster et al. prepared a spherical mesoporous carbon with 2.32 cm$^3$ g$^{-1}$ pore volume and SSA of 2445 m$^2$ g$^{-1}$ via a complex double ‘hard’ templating method [36]. Elsewhere, Xu et al. reported the synthesis of hollow N–C nanospheres with a surface area of 3022 m$^2$ g$^{-1}$ and pore volume of 2.43 cm$^3$ g$^{-1}$ N–C using a ‘soft’ templating technique [37]. Using MOF-5 as the precursor, a hierarchically mesoporous carbon with a SSA of 2734 m$^2$ g$^{-1}$ and pore volume of 5.53 cm$^3$ g$^{-1}$ was reported by Srinivas et al. [32] We also reported a series of N–C nanos with hierarchical porosity showing excellent catalytic activities using the same approach [18]. Yet making hierarchically porous carbons with a high surface area and a large mesopore volume remains a challenge [38,39].

Based on our recent research into nitrogen-doped carbon (N–C) catalysts, we hypothesized that an active and selective catalyst for reducing O$_2$ to H$_2$O$_2$ with a high pore volume would both capture bulky organic pollutants from water and catalyze their degradation. Here we report a facile synthesis of hierarchically Mn and N co-doped carbon nanorods (Mn–N–C) starting from nitrilotriacetic acid. This material, with its large pore volume of 4.54 cm$^3$ g$^{-1}$ and a high specific surface area of 1333 m$^2$ g$^{-1}$, can adsorb 385 mg g$^{-1}$ of methylene blue (MB, a dye with many industrial applications) [33–37]. Importantly, our catalyst converts O$_2$ selectively into H$_2$O$_2$, exhibiting a high onset potential of ca. 0.7 V vs RHE in 0.1 M HClO$_4$. The hydroxyl radicals degrade the adsorbed MB in the adjacent area within the porous electrode (see schematic in Fig. 1). This combined adsorption and electrocatalytic activity opens new opportunities for wastewater treatment as well as for electrocatalysis applications.

2. Results and discussion

2.1. Synthesis and physical properties of Mn–N–C nanorods

The Mn–N–C nanorods were prepared by adapting our previously published method [detailed experimental procedures are included in the supporting information] [21]. Briefly, nanorods of the manganese nitrilotriacetate precursor were synthesized hydrothermally. Subsequent pyrolysis and acid-washing removed the MnO particles, yielding the Mn and N co-doped carbon (see Fig. 2a). Scanning transmission electron microscopy (STEM) measurements confirmed that all of the MnO particles were removed (Fig. 2b). The nanorods have abundant mesopores (D < 20 nm) which are visible in the magnified SEM image in Fig. 2c. These mesopores vary in size, enabling the adsorption of different contaminants. By comparing the high-resolution transmission electron microscopy (HRTEM) images in Fig. 2e and f, we confirmed that these mesopores were templated by the MnO nanoparticles. The pore walls are made of graphitic carbon shells. They are typically less than 20 layers in thickness, containing many worm-like micropores. This connectivity creates a hierarchical pore structure (vide infra).

Fig. 3a compares the powder XRD patterns of MnO/Mn–N–C and the Mn–N–C nanorods. Three strong peaks in MnO/Mn–N–C at 2θ = 35.0°, 40.7° and 58.8° correspond to the (111), (200) and (220) planes of MnO, respectively. The Mn–N–C nanorods had no residual MnO. The broad peak at 2θ = 25° was assigned to the graphite (002) plane. From the Raman spectrum in Fig. 3b we infer that the Mn–N–C nanorods contain both ordered and disordered carbon domains, (cf. the D- and G-band at 1351 and 1588 cm$^{-1}$, respectively) [40]. Again, no MnO signal (typically below 800 cm$^{-1}$) was observed. The presence of Mn and N moieties in the carbon was verified by X-ray photoelectron spectroscopy (XPS, Fig. 3c). It revealed a 1.5% nitrogen content including graphitic, pyridinic and oxidized N, of which ca. 20% was pyridinic nitrogen [21].

We then studied the pore structure using both nitrogen adsorption and mercury intrusion porosimetry. The nitrogen adsorption isotherm (Fig. 4a), shows a combination of a H3 and H4 hysteresis loops, implying the presence of micro-, meso- and macropores [41]. A BET analysis gave a high specific surface area of 1333 m$^2$ g$^{-1}$. We used the Saito and Foley model to examine the micropore volume and micropore size distribution (see Fig. 4b). This model indicated a micropore volume of 0.76 mL g$^{-1}$, with most pores > 0.6 nm. As CO$_2$ is produced during the pyrolysis, these pores might be created by the typical CO$_2$ activation process [42]. For comparison, we measured under the same conditions a control sample of commercial activated carbon. This had a similar specific surface area of 1301 m$^2$ g$^{-1}$ and a micropore volume of 0.64 mL g$^{-1}$.

In the middle region of the isotherm, our Mn–N–C differs from the commercial carbon sample. The adsorption-desorption hysteresis of Mn–N–C nanorod suggests the existence of mesopores. Analysis of the isotherm using Gurvich model revealed a pore volume of 4.54 mL g$^{-1}$ at 0.99 p/p$_0$ [43]. This value surpasses most of the porous carbon materials reported to date (for a detailed comparison see Table S2 in the supporting information). Most of the mesopores in our material are < 10 nm in diameter (see Fig. 4c). This well matches the observations from the TEM micrographs. The mesopore volume calculated from the mercury intrusion porosimetry (Fig. 4d) reached 3.45 mL g$^{-1}$, derived from the intruded volume between pore sizes 3.6–50 nm (ρ = 29.6 MPa for 50 nm, θ = 140°, γ = 0.48 N m$^{-1}$). This is slightly lower than that obtained from N$_2$ adsorption. Most likely, the difference is caused by ink-bottle shaped pores where the pore opening is too small for mercury to enter. The pore size distribution shows that most of the
pores are < 15 nm in diameter (inset of Fig. 4d, a high-resolution image is shown in Fig. S3).

2.2. Methylene blue adsorption

To evaluate the performance of our porous nanorods in the adsorption and electrocatalytic degradation of methylene blue (MB) illustrated in Fig. 1, we initially studied their capability of removing 50 ppm MB from an aqueous solution. This was compared to a commercial activated carbon which is essentially microporous with similar surface area (see Fig. 4a, b, c and Table 1 for the N₂ adsorption comparisons). After adding 5 mg of either Mn–N–C or activated carbon to 25 mL 50 ppm MB solution (pH was adjusted to 4 using HCl) and shaking gently, the blue color in the Mn–N–C suspension disappeared almost instantly. The complete removal of MB was confirmed by UV–visible spectroscopy (Fig. 5b). In contrast, the activated carbon suspension still displayed a light blue color even after 12 h agitation (see Fig. 5a). This implies that the carbon was already saturated by MB and could not remove the residual MB from the suspension.

To quantify the MB uptake, we measured its adsorption from solutions with varied concentrations, from 25 ppm up to 300 ppm. In each case, the amounts of adsorbed MB on the material and remaining MB in solution at equilibrium were measured and denoted as \( q_e \) (mg g\(^{-1}\)) and \( C_e \) (mg L\(^{-1}\)), respectively. Fitting the \( q_e - C_e \) plot using established adsorption models can reveal the adsorption mechanism and maximum uptake of MB for each
maximized by increasing its specific surface area that is mainly attributed by the micropore. This principle has been applied in developing high-performance materials for supercapacitors and CO2 adsorption [45-53]. However, when the molecular dimension of the adsorbate is large, such as that of dyes and surfactants, the adsorbate will transfer slowly in the adsorbent and can easily block the small micropores during the adsorption process (see the schematic comparison in Fig. S4). In this case, the material with more mesopores is much advantageous in capturing and accommodating these bulky molecules [31,54,55]. The large MB molecules (1.3–1.8 nm diameter [29,56,57]) may block the micropores of the commercial activated carbon [31,54,55]. In addition, the commercial activated carbon would also suffer from a lower mass transport. Consequently, our hierarchically porous Mn−N−C nanorods with high specific surface area and mesopore volume showed a superior capability in adsorbing MB.

2.3. Electrochemical production of H2O2

We studied the catalytic activity of Mn−N−C nanorods in producing H2O2 from the dissolved O2 through the electrocatalytic oxygen reduction reaction. The ORR activity and selectivity of both the Mn−N−C nanorods and commercial activated carbon were tested in a 0.1 M HClO4 electrolyte. Cyclic voltammetry using a rotating disc electrode in the N2-saturated electrolyte only showed capacitive behaviors for both materials (Fig. S5). In the O2-saturated electrolyte, reduction peaks at ca. 0.6 and 0.3 V vs RHE were observed for the Mn–N−C nanorods and commercial activated carbon, respectively, which confirmed that ORR has occurred at these potentials.

We then used a rotating ring disk electrode (RRDE) for evaluating the ORR activity and H2O2 selectivity. Fig. 6a compares the linear sweep voltammograms (LSVs) of the disk for three different samples: commercial activated carbon (red), Mn−N−C nanorods (black) and 20 wt% Pt/C (blue). The Mn−N−C nanorods have an onset potential of ca. 0.7 V vs RHE. This agrees with the observed potential from the ring when H2O2 oxidation starts (see Fig. 6b). This value is close to the standard reduction potential E0(H2O2/H2O) = 0.7 V and is among the highest reported for the O2−H2O2 conversion [17,27,58–61]. Moreover, unlike many excellent carbon-based ORR catalysts [18,23,62,63], our Mn−N−C nanorods showed not only high activity in acidic media, but also exceptionally high H2O2 selectivity (98%) at potentials > 0.5 V vs RHE (see

| Carbon                        | SSA (m2 g−1) | Micropore volume (mL g−1) | Gurvich pore volume (mL g−1) | Hg intrusion mesopore volume (mL g−1) |
|-------------------------------|-------------|---------------------------|------------------------------|--------------------------------------|
| N−C nanorods                  | 1333        | 0.76                      | 4.54                         | 3.45                                 |
| Commercial activated carbon   | 1301        | 0.64                      | 0.75                         | n.a.                                 |

* Gurvich volume calculated with p/p0 = 0.95.

Fig. 5. (a) Photo of three vials containing 25 mL of a 50 ppm MB solutions after the addition of 5 mg Mn−N−C nanorods, 5 mg commercial activated carbon and nothing; (b) The UV−Vis spectrum of a 50 ppm MB solution before and after adding 5 mg Mn−N−C nanorods; Experimental data and fittings of the adsorption isotherm of MB for (c) Mn−N−C nanorods and (d) the commercial activated carbon. (A colour version of this figure can be viewed online.)

Fig. 6. (a) Disk current density and (b) ring current from the RRDE experiments; (c) the H2O2 selectivity at different potentials. The measurements were performed in a O2-saturated 0.1 M HClO4, with a scan rate of 10 mV s−1 and the rotating speed of 1600 rpm. (A colour version of this figure can be viewed online.)
the onset potential barely changed. This is most likely due to the adsorption of MB molecules covering active sites and reducing the electrocatalytic activity. The electrocatalytic activity in the 18 h longevity test (see Fig. S6). Additionally, the Mn–N–C nanorod showed that all of the MB disappeared after only 5 s. However, this was not because of the electrocatalytic degradation of MB, but was ascribed to the rapid adsorption of MB on the working electrode. To exclude this artefact, we first immersed the Mn–N–C nanorod working electrode in 10 ppm electrolyte with sufficient volume. Then the MB-saturated working electrode, denoted as treated Mn–N–C, was then mounted in the in situ cell. A clear MB concentration decrease was observed progressively only when the potential was applied, confirming the electrocatalytic decomposition.

3. Conclusions

The decomposition of organic pollutants in water can be done efficiently if one combines adsorption, electrocatalysis, and free-radical reactions. Hierarchically porous carbon nanorods doped with manganese and nitrogen are ideal for this purpose, as they have both a large surface area and a high pore volume, as well as good active sites. These materials can adsorb large amounts of methylene blue from water (385 mg g⁻¹, 46% higher compared to a commercial activated carbon with a similar surface area). Importantly, they also catalyze the electrochemical reduction of dioxygen to hydrogen peroxide with >98% selectivity. In situ generation of hydroxyl free-radicals at the catalyst surface enables the efficient decomposition of methylene blue. The catalysts are made from abundant elements, and can be produced on gram scale. We hope that the results reported here will stimulate researchers to use these materials in a variety of applications.

Acknowledgement

We thank the financial support from the Netherlands Organisation for Scientific Research NWO-GDST Advanced Materials program (project No. 729.001.022), and the research fund through Wuhan University for the in-situ UV–vis spectrometric study using a three-electrode cell. The electrolyte was also O₂-saturated 0.1 M HClO₄ containing 10 ppm MB and the working electrode was biased at 0.4 V vs RHE (see supporting information for details). Because the Pt wire reference electrode can catalyze the generation of hydroxyl radicals through eq. (1), we limited the test time to <30 s. We anticipated that this can avoid the contact between the generated H₂O₂ and Pt wire. In the Pt working electrode test, the concentration of MB remained constant in time (see Fig. 7c). Interestingly, the test with pristine Mn–N–C nanorod showed that all of the MB disappeared after only 5 s. However, this was not because of the electrocatalytic degradation of MB, but was ascribed to the rapid adsorption of MB on the working electrode. To exclude this artefact, we first immersed the Mn–N–C nanorod working electrode in 10 ppm electrolyte with sufficient volume. Then the MB-saturated working electrode, denoted as treated Mn–N–C, was then mounted in the in situ cell. A clear MB concentration decrease was observed progressively only when the potential was applied, confirming the electrocatalytic decomposition.

2.4. Electrochemical degradation of methylene blue

H₂O₂ can hardly oxidize many “robust” organic pollutants directly (such as the aromatics and MB) [12,65]. Typically, the oxidation can only occur via the scission of the peroxy bond and the generation of active free-radicals (eq (1)). Transition metal ions are often applied as the catalysts [66–68], as is the activated carbon [69,70]. Remarkably, the advantage of converting O₂ into H₂O₂ electrochemically is the formation in situ of these hydroxyl and peroxyl radical intermediates [11–13]. A 3-electron transfer process and a mono-electron reduction of H₂O₂ have been proposed as the two possible pathways (eqs (2) and (3)):

\[ 2\text{H}_2\text{O}_2 \rightarrow \text{HOO}^- + \text{HO}^- + \text{H}_2\text{O} \] (1)

\[ \text{O}_2 + 3\text{H}^+ + 3e^- \rightarrow \text{HO}^- + \text{H}_2\text{O} \] (2)

\[ \text{H}_2\text{O}_2 + e^- + \text{H}^+ \rightarrow \text{HO}^- + \text{H}_2\text{O} \] (3)

With the presence of hydroxyl radicals, the complete oxidation of MB can be achieved following eq (4) with minimal toxic products release [71]. As the hydroxyl radicals can be rapidly reduced to hydroxyl ions, it is critical that MB is pre-adsorbed in the porous structure where the radical-generation sites are nearby (see Fig. 1).

\[ \text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}^5 \text{H}^+ + 16\text{CO}_2 + 6\text{H}_2\text{O} + \text{H}_2\text{SO}_4 + \text{3HNO}_3 + \text{HCl} \] (4)

Before studying the electrocatalytic degradation of MB, we first examined whether the adsorption of MB will cause the poison of our catalyst. Fig. 7a compares the performances of Mn–N–C nanorods with and without the presence of 25 ppm MB. Despite the fact that the current reduction has shifted a little to lower voltages due to the MB addition, the onset potential barely changed. This is also reflected by the unchanged onset potential, recorded at the ring in Fig. 7b, at which the production of H₂O₂ starts. The current drops in both the ring and disk after adding MB can be ascribed to (1) blockage of active site by adsorbed MB molecules and (2) the consumption of peroxy or hydroxyl radicals by MB.

To study the electrocatalytic degradation of MB, we performed an in-situ UV–vis spectrometric study using a three-electrode cell. The electrolyte was also O₂-saturated 0.1 M HClO₄ containing 10 ppm MB and the working electrode was biased at 0.4 V vs RHE (see supporting information for details). Because the Pt wire reference electrode can catalyze the generation of hydroxyl radicals through eq. (1), we limited the test time to <30 s. We anticipated that this can avoid the contact between the generated H₂O₂ and Pt wire. In the Pt working electrode test, the concentration of MB remained constant in time (see Fig. 7c). Interestingly, the test with pristine Mn–N–C nanorod showed that all of the MB disappeared after only 5 s. However, this was not because of the electrocatalytic degradation of MB, but was ascribed to the rapid adsorption of MB on the working electrode. To exclude this artefact, we first immersed the Mn–N–C nanorod working electrode in 10 ppm electrolyte with sufficient volume. Then the MB-saturated working electrode, denoted as treated Mn–N–C, was then mounted in the in situ cell. A clear MB concentration decrease was observed progressively only when the potential was applied, confirming the electrocatalytic decomposition.

Appendix A. Supplementary data

Supplementary data to this article can be found online at
