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Straightforward synthesis of nitrogen-doped carbon nanotubes as highly active bifunctional electrocatalysts for full water splitting

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ABSTRACT

The success of intermittent renewable energy systems relies on the development of energy storage technologies. Particularly, active and stable water splitting electrocatalysts operating in the same electrolyte are required to enhance the overall efficiency and reduce the costs. Here we report a precise and facile synthesis method to control nitrogen active sites for producing nitrogen doped multi-walled carbon nanotube (NMWNT) with high activity toward both oxygen and hydrogen evolution reactions (OER and HER). The NMWNT shows an extraordinary OER activity, superior to the most active non-metal based OER electrocatalysts. For OER, the NMWNT requires overpotentials of only 320 and 360 mV to deliver current densities of 10 and 50 mA cm^{-2} in 1.0 M NaOH, respectively. This metal-free electrocatalyst also exhibits a proper performance toward HER with a moderate overpotential of 340 mV to achieve a current density of 10 mA cm^{-2} in 0.1 M NaOH. This catalyst also shows high stability after long-time water oxidation without notable changes in the structure of the material. It is revealed that the electron-withdrawing pyridinic N moieties in the NMWNTs could serve as the active sites for OER and HER. Our findings open up new avenues for the development of metal-free electrocatalysts for full water splitting.

1. Introduction

Fossil fuels are currently the dominating energy source and form the basis of the world economy. However, in the future energy supply based on clean and renewable energy will dominate over the dependency on fossil fuels and this addresses challenges for technology development [1,2]. Water electrolysis is a promising method for storing intermittent electrical energy from renewable resources, such as sun and wind, in the form of hydrogen fuel [3]. Electrochemical water splitting in alkaline media includes two half reactions: the hydrogen evolution reaction (HER, $4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$) and the oxygen evolution reaction (OER, $4OH^- \rightarrow 2H_2O + 4e^- + O_2$). Currently, Ir or Ru-based compounds have shown high activity toward OER in acidic and alkaline media [4,5], and among the non-noble metal OER electrocatalysts, nickel (Ni) based electrocatalysts have shown very promising performance for OER in alkaline media [6–10]. For HER, Pt based materials are known as the most efficient HER catalysts in both acidic and alkaline media [4,11]. However, platinum group metals suffer from high costs and scarcity resulting in difficulties in the long-term availability. Hence, to ensure availability of catalysts innovative breakthroughs are needed in order to develop affordable, sustainable and efficient catalytic materials for both HER and OER. In order to reduce/replace noble metal based electrocatalysts, various non-precious metal water-splitting catalysts have been developed [12].

In recent years, clear progress has been made in the development of efficient electrocatalysts with earth-abundant materials for HER [13,14] and OER [3,4,15] in alkaline media. Substantial research efforts have been put on developing versatile bifunctional catalysts with satisfying activity toward both HER and OER, enabling operation in the same electrolyte [8,16]. However, developing such active bifunctional electrocatalysts is challenging due to the incompatibility of pH ranges in which catalysts are stable and active. In this view, various efficient bifunctional catalysts based on transition-metal based compounds of Ni [6,8,17–20], Co [4,16,21] and doped heteroatoms [22–24] in alkaline media have been proposed. However, the transition metal oxide materials suffer from intrinsically low conductivity limiting their performance at high current densities. To circumvent this issue, conductive materials such as carbon nanomaterials, graphene and carbon nanotubes (CNTs) are usually used as catalyst supports for transition metal oxide nanoparticles [25,26]. Such carbon supports are inactive toward most of the electrochemical reactions. However, the graphite or carbonaceous materials can be doped by heteroatoms

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such as nitrogen [24,27], boron [28] or phosphorous [22] to form active metal-free electrocatalysts. Carbonaceous doped materials can be used either as metal-free electrocatalysts [29,30] or as catalyst supports [31] for active metal nanoparticles to get the advantage of synergistic catalytic activity. The chemical and electronic properties of these doped materials can significantly alter their OER and HER performance because of the induced changes in the local charge density and asymmetry spin density of the carbon lattice [32]. Among the carbonaceous doped-materials, nitrogen doped CNTs (NCNTs) have recently gained notable attention as low-cost metal-free catalysts with excellent durability, unique structure and earth-abundant element based catalytic active sites [24,27,33–36]. Bin Yang et al. [37] have shown that pyridinic nitrogens serve as the active sites for OER. However, the vast challenge in the NCNTs electrocatalysts is to find a synthesis process enabling control of the final nitrogen types as well as the interaction of nitrogen moieties with the CNTs. Despite tremendous efforts, great challenges exist for developing metal-free electrocatalysts for full water splitting exhibiting the above mentioned features. Hence, only few successful materials have been achieved so far [38].

In this study, nitrogen doped multi-walled carbon nanotubes (NMWNT) are synthesized by a simple, cost-effective and scalable method. These NMWNTs exhibit superior electrocatalytic activity as bifunctional metal-free catalysts toward both OER and HER with excellent stability. Interestingly, the NMWNTs not only show much higher catalytic performance compared to corresponding single-heteroatom-doped counterparts but also show comparable, or even higher, activity than the most active metal-based electrocatalysts, especially the ones reported for OER so far.

2. Results and discussion

The NMWNTs were synthesized as depicted in Fig. 1. The synthesis method is explained in detail in the Supplementary Information. Scheme S1 shows the chemical structure of the emeraldine salt. Shortly, to enhance interaction of MWNTs with emeraldine salt (ES), both commercial MWNTs and ES are first dispersed in 0.0025 M HCl solution (pH 2.6) to create a stable solution [39]. The mixture is then sonicated for 20 h via an ultrasonic bath to provide a very thin and highly interconnected layer of the ES on the surfaces of the MWNT. During this step, the positively charged nitrogen moieties in the polymer induce intimate interaction between ES and MWNT and facilitate the formation of a hybrid material [40]. Thus, the polymer is wrapped simply around the surfaces of the nanotubes through physical adsorption requiring no additional functional group or pretreatment for the nanotubes (see Fig. 2a). Subsequent centrifugation process eliminated the excess polymer and led to separation of the MWNT/ES materials with a low amount of nitrogen of (0.5 at.%). For the comparison two samples with shorter sonication times of 5 and 10 h were prepared leading to nitrogen contents of 1.2 at.% and 1 at.%, respectively, and also one sample with longer sonication time of 30 h were prepared (see Experimental section in Supporting Information).

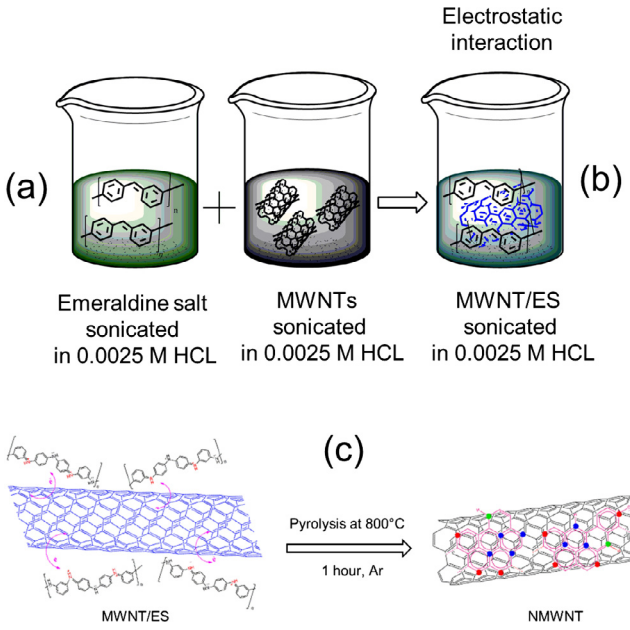

Fig. 1. Schematic illustration of the synthesis procedure of the NMWNT materials. Steps: (a) dispersing emeraldine salt and MWNTs in 0.0025 M HCl; (b) preparing MWNT/ES with electrostatic interaction; and (c) pyrolysing MWNT/ES to form NMWNT.

The MWNT/ES materials were then pyrolyzed at 800 °C in argon, leading to the formation of surface doped NMWNTs. The final products were denoted as 5, 10, 20 and 30-NMWNT referring to the NMWNTs prepared with different sonication times of 5, 10, 20 and 30 h, respectively.

To investigate the properties of the NMWNT material high-resolution transmission electron microscopy (HRTEM) is utilized to observe the polymer wrapping around the MWNT surface in 20-MWNT/ES before pyrolysis (Fig. 2a) and the changes in the graphitic structure of the 20-NMWNT after pyrolysis (Fig. 2b). Fig. 2a illustrates the presence of thin layer of the residual polymer on the surface of the MWNTs that plays a crucial role in obtaining the material with a high electrocatalytic activity. Moreover, as shown in Fig. 2b the graphite structure of the MWNTs still exhibits a relatively high degree of crystallinity indicating that the sonication and pyrolysis processes do not significantly affect the quality of the nanotubes (see also Fig. S1). This is in agreement with the graphite structure of the 20-NMWNT shown in Raman results (see discussion below).

2.1. OER electrocatylitic activity

The electrocatalytic activity of the 20-NMWNT samples for the OER is investigated by rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) measurements using a standard three and four-electrode systems, respectively, in 0.1 and 1 M NaOH. Fig. 3a exhibits polarization curves for OER on the 20-NMWNT material compared with the pristine MWNT, IrO_2, and 20 wt% Pt/C electrodes in 0.1 M NaOH saturated with O_2. All the studied catalysts are measured on a glassy carbon (GC) electrode and with a similar loading of ~0.2 mg cm^{-2}. The 20-NMWNT sample shows a superior OER catalytic activity with an onset potential of 1.54 V versus reversible hydrogen electrode (RHE) in 0.1 M NaOH. The pristine MWNT shows almost no catalytic activity for OER indicating that the activity is induced by the functionalization.

The observed current on the studied electrodes can result from the desired four electron transfer OER (OER pathway: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$) or from the undesirable two electron transfer reaction ($3OH^- \rightarrow HO_2^- + 2e^- + H_2O$) resulting in peroxide formation. Moreover, oxidation of the catalyst material can take place as an unwanted side reaction. To investigate the origin of the high current on 20-NMWNT, RRDE measurements in N_2-saturated 0.1 M NaOH are performed as shown in Fig. 3b. In the RRDE measurements, the oxygen evolved at the catalyst covered glassy carbon disk is subsequently reduced at the surrounding Pt ring electrode hold at 0.4 V. Meanwhile, the ring current resulting from oxygen reduction reaction (ORR) is recorded. Similarly, the Pt ring is held at 1.4 V to reduce any formed H_2O_2 [41,33,42]. In alkaline solution any formed CO_2 (from the catalyst material oxidation) would react