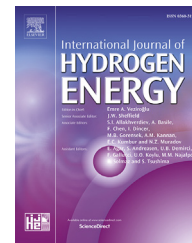




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Simultaneous water recovery and hydrogen production by bifunctional electrocatalyst of nitrogen-doped carbon nanotubes protected cobalt nanoparticles

Jiayuan Yu ^{a,b,1}, Guixiang Li ^{a,1}, Hui Liu ^{a,b}, Aili Wang ^{a,b}, Linjing Yang ^a, Weijia Zhou ^{a,*}, Yongyou Hu ^{a,**}, Benli Chu ^b

^a The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou Key Laboratory for Surface Chemistry of Energy Materials, New Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Centre, Guangzhou 510006, PR China

^b School of Physics and Telecommunication Engineering, South China Normal University, Guangzhou Higher Education Mega Center, Guangzhou, Guangdong, 510006, China

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ABSTRACT

Cobalt nanoparticles encapsulated in nitrogen-doped carbon nanotubes (Co@N-C) are obtained by a simple pyrolysis of Co-MOF (ZIF-67) for the bifunctional water recovery and hydrogen production. The results showed that calcination temperature of ZIF-67 significantly affected the morphology and catalytic performance. Wastewater are effectively recovered in the presence of the Co@N-C and oxidant, which is promoted by anodic oxidation reactions. Co@N-C as the cathode catalyst exhibited excellent hydrogen evolution reaction catalytic activity with a low onset potential of -51 mV (vs. RHE, current density of 0.5 mA/cm²), Tafel slope of 96.73 mV/dec and extraordinary long-term durability. Finally, as a proof of concept, a home-made two-electrode device employed Co@N-C as both anode and cathode catalyst for continuous water recovery and simultaneous hydrogen production, which possesses the possibly applications in solving the environmental pollution and energy crisis.

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Introduction

Recently, the increasing of water pollution and energy crisis have been sparked great interest in developing novel

technologies for water treatment and energy recovery (e.g., H₂ production) [1–3]. Several methods of water treatment (such as physical absorption [4], advanced oxidation processes [5–7], biodegradation [8,9], and photocatalytic degradation [10–13], etc) have been actively applied in wastewater

* Corresponding author.

** Corresponding author.

E-mail addresses: eszhouwj@scut.edu.cn (W. Zhou), ppyyhu@scut.edu.cn (Y. Hu).

¹ These authors contributed equally to this work.

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management system. However, the water treatment performance of conventional catalyst is normally limited by low efficiency and secondary pollution [14]. On the other hand, in order to ease the energy crisis, the usage of clean and sustainable hydrogen energy is an effective approach. An effective and promising approach for hydrogen production is based on the electrolysis of water. To date, platinum-based materials are the most efficient catalysts for hydrogen production, but the high cost and low abundance significantly hamper their broad utilization [15]. Therefore, it is highly attractive to look for suitable catalyst with low cost and high active simultaneous apply to water treatment and energy recovery.

Advanced oxidation processes (AOPs) are desirable as efficient methods to deal with the wastewater [16–19]. The most famous catalysts for AOPs are Fenton and Fenton-type catalysts [20–22]. Transition metal (especially zero-valent Fe, Co, and Ni) catalysts are typical Fenton-type catalysts with advantages of abundant source and low cost, which efficiently activate oxidant (such as peroxymonosulfate (PMS) or H_2O_2) to produce free radicals with highly oxidizing power [23,24]. The disadvantages of homogeneous transition metal catalytic process give rise to secondary pollution due to the dissolved of transition metal in acid condition, and also leading to decrease of the catalytic activity. In order to solve the aforementioned drawbacks, developing novel transition metal catalysts have been tried to effectively improve the activity, stability and environmental benignancy. Prof. Wang reported that magnetic metals (Fe, Co, or Ni) embedded in N-doped carbon were fabricated using additional dicyandiamide as a carbon and nitrogen source [23]. The obtained $M@N-C$ ($M = Fe, Co, \text{ or } Ni$) was employed as catalyst for water purification.

Hydrogen, as a clean and renewable energy, is expected to be a promising alternative energy resource [25]. The platinum-based material is the most excellent electrocatalyst for hydrogen production, but it possesses the characteristics of high price and low reserves, which severely limit its practical application [25,26]. Development of non-precious, low-cost and earth-abundant catalysts to replace platinum is an important way to achieve mass electrical hydrogen production [27–30]. In the past few years, transition-metal nanoparticles embedded into carbon shell (transition-metal@carbon core-shell structures) were widely employed as non-precious electrocatalysts for efficient water splitting [15,31–33]. For example, prof. Asefa reported that cobalt-embedded nitrogen-rich carbon nanotubes significantly promoted electron penetration and enhanced the catalytic activity for HER [34]. The ultrathin carbon layers wrapped the transition-metal particles not only protected the transition-metal from dissolving in acidic condition, but also had no effect on the catalytic activity of the transition-metal as a result of interfacial charge transfer. However, the oxygen evolution reaction (OER) is more difficult than the hydrogen evolution reaction, which limits the application of water splitting [35–38]. It is an efficient method that utilizing thermodynamically more favorable oxidation process (such as oxidizing harmful contaminated in the process of water recovery [39,40]) instead of OER to increase the energy conversion efficiencies [41,42]. Therefore, it is practical that non-noble metal

catalysts can be applied to combine water treatment and hydrogen production [43].

Herein, MOFs (ZIF-67) with diverse composition and controllable porous structures are assembled by metal ions and organic ligands as both templates and precursors, which was used to synthesize functional carbon-wrapped cobalt nanoparticles ($Co@N-C$) via direct pyrolysis process. As known to our knowledge, this study is a first attempt to combine simultaneous hydrogen production with water recovery by using metal@carbon catalyst derived from MOFs in acidified contaminants water. Benefiting from the synergetic effect between metal cobalt as core and N-doped carbon as shell, the as-prepared $Co@N-C$ as a multifunctional catalyst exhibited a better efficiency of water treatment and high activity for HER in acidified contaminated water.

Experiment

Chemicals

All reagents were of analytical grade and used without further purification. Cobaltous nitrate ($Co(NO_3)_2 \cdot 6H_2O$), 2-Methylimidazole ($C_4H_6N_2$), absolute ethanol (C_2H_5OH), methanol (CH_3OH), peroxymonosulfate ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), and sulfuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagents Beijing Co. Deionized water was supplied with a Barnstead Nanopure Water System (18.2 $M\Omega$ cm) and was used throughout this experiment.

Synthesis of Co nanoparticles embedded into N-doped carbon nanotubes ($Co@N-C_X$ composites, X is the final heating temperature)

First, the synthesis process of ZIF-67 particles was according to the literature with a modification [44]. In a typical synthesis process, 2-Methylimidazole (1.95 g) was added into a 100 mL round bottomed flask with 40 mL methanol. $Co(NO_3)_2 \cdot 6H_2O$ (1.75 g) was dissolved in another 40 mL methanol. The former solution was poured into the latter one, and then mixed under continuous vigorous stirring for 10 min. The final purple solution was obtained by keeping at room temperature for 24 h without interruption. Then the purple precipitate was collected by centrifugation under 6000 rpm for 5 min, and washed with absolute ethanol at least six times, finally dried at 80 °C overnight to obtain the precursors (ZIF-67). Second, the synthesis process of $Co@N-C_{600}$ was as following steps. The dried sample of ZIF-67 (500 mg) was placed in ceramic boat with a seal cover, then heated to 450 °C in 20 min and maintained for 2 h. Then the temperature in the furnace further raised to the target temperature (600 °C) at a ramp rate of 2 °C/min and maintained at this temperature for 2 h. After that, the furnace was cooled down to room temperature naturally. During the pyrolysis process, the furnace was under 10% Ar/H_2 (10 vol% H_2) with a 10 sccm flow rate. The as-prepared black powder products were treated in 1 M HCl solution for 12 h to remove the uncovered cobalt particles, as shown in Fig. S1a. The resulting samples were collected by centrifugation under 8000 rpm for 10 min, and then washed with deionized water three times, finally dried at 60 °C. Other

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