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# Three-dimensional functionalized graphene networks modified Ni foam based gold electrode for sodium borohydride electrooxidation

Dongming Zhang<sup>a,1</sup>, Guiling Wang<sup>a,\*</sup>, Yao Yuan<sup>a,1</sup>, Yuguang Li<sup>b,\*\*</sup>,  
Sipeng Jiang<sup>b</sup>, Yongkuo Wang<sup>b</sup>, Ke Ye<sup>a,1</sup>, Dianxue Cao<sup>a,1</sup>, Peng Yan<sup>a,1</sup>,  
Kui Cheng<sup>a,1</sup>

<sup>a</sup> Key Laboratory of Superlight Materials and Surface Technology of Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin, 150001, PR China

<sup>b</sup> 101 Institute of the Ministry of Civil Affairs, PR China

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## ABSTRACT

Three-dimensional (3D) reduced graphene networks (RGN) were successfully fabricated on Ni foam without any conductive agents and polymer binders by dipping commercial Ni foam into graphene oxide (GO) suspension and subsequent an electroreduction process in a buffer solution. Au nanoparticles were then deposited on the RGN through an electrodeposition process to form a novel reduced graphene networks-Au (RGNA) electrode. The morphology and phase structure of the RGNA electrode are characterized by scanning electron microscope, transmission electron microscope and X-ray diffraction spectrometer. The NaBH<sub>4</sub> electrooxidation performance on the RGNA electrode is investigated by means of cyclic voltammetry and chronoamperometry. The RGNA electrode owns special hierarchical porous structure, rapid electron and ion transport, and large electroactive surface area due to the intrinsic electronic conductivity, mesoporous nature of graphene. The RGNA electrode exhibits a good stability during the electrochemical process and the oxidation current density at RGNA electrode reached 500 mA cm<sup>-2</sup> at 0 V in the solution containing 0.1 mol dm<sup>-3</sup> NaBH<sub>4</sub> and 2 mol dm<sup>-3</sup> NaOH, which is higher than that at bare Au–Ni foam without graphene. The excellent structural stability and high catalytic performance for NaBH<sub>4</sub> electrooxidation make the RGNA a promising material for future energy systems.

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## Introduction

Direct borohydride fuel cells (DBFCs) employing NaBH<sub>4</sub> directly as fuel exhibits many outstanding advantages, such as high energy density (9.3 Wh g<sup>-1</sup>), high hydrogen contents

(10.6 wt.%), high chemical stability in alkaline solution, non-toxic, and easy handling [1–13]. Furthermore, the complete electrooxidation of NaBH<sub>4</sub> release 8 e<sup>-</sup> (Eq. (1)), which is much higher than the electrooxidation of H<sub>2</sub> (2 e<sup>-</sup>) [14], CH<sub>3</sub>OH (6 e<sup>-</sup>) [15], N<sub>2</sub>H<sub>4</sub> (4 e<sup>-</sup>) [16], NH<sub>3</sub>BH<sub>3</sub> (6 e<sup>-</sup>) [17], H<sub>2</sub>O<sub>2</sub> (2 e<sup>-</sup>) [7,18] and so on.

\* Corresponding author. Tel./fax: +86 451 82589036.

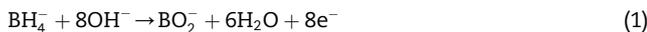
\*\* Corresponding author.

E-mail addresses: [wanguiling@hrbeu.edu.cn](mailto:wanguiling@hrbeu.edu.cn) (G. Wang), [liyuguang@126.com](mailto:liyuguang@126.com) (Y. Li).

<sup>1</sup> Tel./fax: +86 451 82589036.

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In general, the catalysts for  $\text{NaBH}_4$  electrooxidation include hydrogen storage alloys (EG.  $\text{AB}_5$ -,  $\text{AB}_2$ - type alloys) [5,6], transition metals (EG. Ni, Co, Co–Ni) [7–9], noble metals and their alloys (EG. Pt, Pd, Au, PtCo, Pt/Ni, AuCo, Au–Ni) [10–13]. Among these catalysts, the investigation of noble metals is still the main trend due to their outstanding catalytic activity toward  $\text{NaBH}_4$  oxidation. However, the drawback of limited reserves and high cost restrict their extensive utilization. Nowadays, depositing noble metals on 3D porous foam materials possesses distinctive structural features and superior properties have been a hot topic [20–27], which is an interesting and useful way to reduce the loading mass and electrode price [16,18–27]. For example, V. Pérez-Herranz et al. [20] and Xia et al. [21] prepared 3D ringent metal electrodes through simple hydrogen template synthesis approach for catalytic reactions; Cui et al. [22,23] electrodeposited nano Pt and  $\text{MnO}_2$  on 3D porous carbon nanotubes (CNTs) modified flexible textile and sponge for microbial fuel cells and supercapacitor and achieved high electrochemical performance. In recent, our team designed and fabricated 3D ringent metal material [13], CNTs modified porous sponge and textile [8,9,16,18] as the substrate for the deposition of metals towards the electrocatalysis of  $\text{NaBH}_4$ ,  $\text{H}_2\text{O}_2$  and  $\text{N}_2\text{H}_4$ , all of which have achieved excellent catalytic activity. Lately, graphene supported on Ni foam, giving a 3D architecture and favorable property without aggregation and restacking of graphene nanosheets, have attracted scientists' attention and been prepared in many ways (EG. chemical vapor deposition, dipping and drying approaches) [24–27] for energy storage. Unfortunately, almost none of them are employed in fuel cells.

In this paper, we fabricated a reduced graphene networks (RGN) on Ni foam by a simply dipping and electroreduction process. The RGN substrate keeps a 3D structure and the surface of Ni skeleton is coated by graphene nano-sheets uniformly. The existence of graphene increases the specific surface area of Ni foam, which is benefit for the diffusion of the electrolyte and the contact between the electrode surface and fuel, and produces more electroactive sites. More importantly, the formation of graphene network structure doesn't employ any binder, which not only provides a good electronic conductivity for the electrode, but also improves the utilization efficiency of graphene and catalysts. According to the previous studies [1–4], compared with Pt and Pd, Au owns the better selectivity to electrooxidation with weaker catalytic activity towards  $\text{NaBH}_4$  hydrolysis (Eq. (2)) [1–13], leading a higher  $\text{NaBH}_4$  utilization efficiency, benefiting for the fuel cell system. Here, the Au nanoparticles were electrodeposited on the surface of graphene sheets and both of the Au and graphene tightly get in touch with the skeleton of Ni foam and serve as the effective catalysts for  $\text{NaBH}_4$  electrooxidation. As a result, the RGN supported Au electrode exhibits an incremental catalytic activity compared to the bare AuNi foam electrode without the modification of graphene.



## Experimental

All the chemicals are of analytical grade and were used without further purification. All aqueous solutions are prepared with ultrapure water (Milli-Q, 18  $\text{M}\Omega$  cm).

First, the GO was synthesized from spectral graphite by the modified Hummers method [28] in our experiment. After that, the as-synthesized GO was suspended in water to offer a brown suspension, then was ultrasonic and centrifugal processing for a period of time to remove any unexfoliated graphite oxide.

The RGNA electrode was prepared by a three-step process (Fig. 1): In the first step, a piece of commercial Ni foam ( $1 \times 1 \text{ cm}^2$ ), which have been treated by acetone,  $\text{C}_2\text{H}_5\text{OH}$  and HCl to remove the oil and oxide layer (eg. NiO) [29], was dipped in an ultrasonic uniform suspension containing  $1 \text{ mg mL}^{-1}$  GO to form GO–Ni foam (a  $\rightarrow$  b). In the second step, the 3D reduced graphene networks (RGN) was obtained by electroreduction of the as-prepared GO–Ni foam using the Autolab PGSTAT302 (Eco Chemie) electrochemical workstation in a conventional three electrode electrochemical cell with a saturated Ag/AgCl, KCl reference electrode and Pt foil counter electrode at  $-1.0 \text{ V}$  for 30 min in potassium biphthalate ( $\text{C}_8\text{H}_5\text{KO}_4$ ) buffer solution (b  $\rightarrow$  c). At present, the yellowish-brown GO–Ni foam gets black and forms the RGN substrate (f). In the last step, Au nanoparticles were electrodeposited on the RGN with the same three electrode system in  $0.01 \text{ mol dm}^{-3}$   $\text{HAuCl}_4$  at a stable potential (c  $\rightarrow$  d).

$\text{NaBH}_4$  electrooxidation was also performed in the same three-electrode electrochemical cell using the  $1 \text{ cm}^2$  RGNA electrode as working electrode and employing NaOH as electrolyte. All potentials were referred to the saturated Ag/AgCl, KCl reference electrode. The morphology of the electrodes was determined using a scanning electron microscope (SEM, JEOL JSM-6480) equipped with an energy-dispersive X-ray (EDX) analyzer and transmission electron microscope (TEM, FEI TeccaiG2S-Twin, Philips). The structure was analyzed by a powder X-ray diffractometer (XRD, Rigaku TTR-III) equipped with Cu  $K\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ). Raman spectra were characterized by an XploRA PLUS Raman spectrometer (HORIBA JOBIN YVON S.A.S.) with 532 nm wavelength incident laser light. Fourier transform infrared spectroscopy (FT-IR) analyses were obtained on a Perkin Elmer SP-100 spectrometer (KBr pellet technique).

## Results and discussion

The morphologies of Ni foam (a – c), RGN substrate (d – f) and RGN electrode (g) were examined by SEM, the detailed microstructures of graphene sheets and Au nanoparticles were further demonstrated by TEM (h) and the results are shown in Fig. 2. It is obvious that the Ni foam owns a 3D structure (a) and the surface of the skeleton is smooth (b – c). After dipping in the graphene suspension, the graphene sheets closely coat on the skeleton of Ni foam, implying good contact between the graphene and Ni foam (e – f). Interestingly, the RGN substrate maintains specific porous structure as the bare Ni foam, which is benefit for the diffusion of electrolyte during the react

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