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Controlling the adsorption behavior of hydrogen at the interface of polycrystalline CVD graphene

Yanru Guo ^{a,d,e,1}, Dong Han Seo ^{b,*,1}, Jungmi Hong ^b, Dawei Su ^c,
Hongxia Wang ^{d,e}, Jie Zheng ^{a,**}, Xingguo Li ^{a,***}, Anthony B. Murphy ^b,
Kostya (Ken) Ostrikov ^{a,d,e}

^a Beijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

^b CSIRO Manufacturing, P.O. Box 218, Lindfield NSW 2070, Australia

^c School of Mathematical and Physical Sciences, University of Technology Sydney, NSW 2007, Australia

^d Institute for Future Environments and Institute for Health and Biomedical Innovation, School of Chemistry, Physics, and Mechanical Engineering, Queensland University of Technology, Brisbane, QLD 4000, Australia

^e CSIRO – QUT Joint Sustainable Processes and Devices Laboratory, P. O. Box 218, Lindfield, NSW, Australia

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ABSTRACT

Polycrystalline graphene films were synthesized from renewable biomaterials in ambient air using a facile and rapid thermal chemical vapour deposition technique. Characterization of the graphene reveals a large surface area, the presence of nanoscale domains and open edges, atomic-level stacking, and high electrical conductivity, which are favorable features for electrochemical hydrogen evolution reactions (HERs). The numerous boundaries and open edges accelerate the gas diffusion process and enlarge the effective reactive surface area for gas evolution, which is responsible for a significant improvement of HER performance and stability compared to a commercial graphene film. The hydrogen adhesion behavior is investigated for both bare Ni foil/foam and graphene grown on Ni foil/foam samples. The hydrogen gas bubbles adhere to the polycrystalline graphene for a long period of time before detaching, in contrast to their behavior on the pristine Ni foil surface. Post treatment of the graphene film using plasma treatment increases the desorption rate of hydrogen bubbles from the surface. The results indicate a wide range of possibilities for use of graphene-based catalysts in electrocatalytic gas evolution reactions.

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Introduction

Electrocatalytic gas evolution reactions such as the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)

are attracting increasing attention in the past few years as an alternative energy conversion and storage processes [1–3]. To date, most of the research efforts have been devoted to exploring new kind of catalysts with high HER activity [4].

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: Michael.Seo@csiro.au (D.H. Seo), zhengjie@pku.edu.cn (J. Zheng), xgli@pku.edu.cn (X. Li).

¹ These authors contributed equally to this work.

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Interactions at the material–gas–electrolyte interface that occurs on electrodes have received very limited attention until recently [5–8]. However, the formation of hydrogen gas at the catalyst–electrolyte interface and the behavior of hydrogen gas bubbles in the electrolyte are of great importance as they dictate the eventual HER activity and the performance of assembled devices [9–12]. In HER systems, factors including the apparent surface area, conductivity and adhesion of as-formed gas bubbles on catalysts are crucial, affecting the electrolyte diffusion, exposure of active sites and actual surface area, and eventually determining their HER performance.

As a result, understanding of catalyst interface properties and electrolyte interactions is now attracting increasing attention. Recently, Li et al. demonstrated the importance of wetting and dewetting properties of catalysts with aerophobic surfaces; HERs on surfaces of different aerophobicity exhibited obvious differences in hydrogen gas formation and adsorption behavior [13]. They prepared superaerophobic MoS_2 with low adhesive forces, from which hydrogen bubbles could easily be driven, showing the vital connection between surface properties and electrode performance. The adhesion behavior of gas bubbles depends strongly on the surface properties, as indicated by the “bursting state” [14], in which air bubbles burst quickly on a lotus leaf surface, and “pinning state” [15], in which air bubbles pin themselves on a superhydrophobic rose petal surface. A lubricant-infused slippery (LIS) surface with water-repellent properties is another way to manipulate bubbles in an aqueous environment, which demonstrates the possibility to transport and control hydrogen gas bubbles [12].

Graphene is a widely studied two-dimensional (2D) HER catalyst that possesses many favorable properties for HERs, including high conductivity, excellent mechanical properties and abundant electrochemically active sites [8,16–19]. Moreover, significant enhancement of its electrocatalytic ability is observed when doped with heteroatoms such as N, P or I [20–26]. However, most of the research effort has been directed towards using graphene-based powders and their dispersion [16,18,20,21,27]. There has been limited attention to utilization of graphene films and fundamental investigation of the interactions between graphene, electrolyte and hydrogen gas [28]. Recently, Sun et al., demonstrated the HER activity of pristine graphene film grown on copper substrate via CVD process. They showed that graphene thickness and the structural quality of the film were dominant factors influencing the HER performance of these graphene films [29]. Moreover, investigation shows many important challenges need to be addressed for pristine graphene film to be implemented in HER processes. For example, the impermeable nature of graphene means that it acts as a barrier film, which deteriorates the HER performance when it is grown on metallic substrates. Moreover, the poor stability of graphene film during vigorous HER reactions limits its usage.

In this work, we used a single-step ambient-air synthesis of polycrystalline graphene film derived from renewable biomaterial (soybean oil) grown on the commonly-used substrates Ni foil and Ni foam. The properties of the graphene film are characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The HER

performance is compared to a bare Ni film, and a commercial graphene film on Ni foil. The growth and detachment of hydrogen bubbles is investigated in detail, and the influence of surface modification using an atmospheric-pressure plasma is investigated.

The importance of grain boundaries and domain sizes in determining the interactions between hydrogen gas and the graphene surface as well as providing effective sites for the HER process are considered. The understanding of interface properties between graphene, electrolyte and gas that is developed provides a wide range of possibilities for use of graphene-based catalysts as high efficiency catalysts in electrocatalytic gas evolution reactions.

Results and discussion

Polycrystalline graphene synthesis on Ni foil and its structural, atomic morphological features

We used simple, single-step, low-cost, thermal CVD strategy to prepare graphene film in an ambient-air environment that was free from compressed gases. In this process, renewable sources such as soybean oil are the sole precursor [30]. Polycrystalline graphene was formed on a Ni substrate as a result of this unique growth process. The experimental and morphological features were then analyzed and described in Fig. 1. The morphological features of bare Ni foil and polycrystalline graphene film on Ni foil were characterized by SEM (Fig. 1c–h). Bare Ni foil exhibited microscopic metallic grain boundaries under low magnification (Fig. 1c–d) and a nanoscopically smooth surface under high magnification (Fig. 1e). Polycrystalline graphene exhibited different colouration of the surface on the Ni foil at low magnification, revealing the presence of graphene films with different thicknesses (Fig. 1f–g). Unlike bare Ni foil, the polycrystalline graphene surface had a rough surface with randomly stacked graphene and numerous, sharp, open edges (Fig. 1h).

Such difference in morphologies of the two electrodes (bare Ni foil and Polycrystalline graphene on Ni foil) induced significantly different HER activity, which will be discussed later. Confocal Raman areal mapping of the graphene film, especially I_D/I_G and I_{2D}/I_G intensity ratios, were used to determine the areal defect variation as well as relative thickness uniformity of the graphene films (Fig. 2a, b) [31]. The intensity ratio I_D/I_G ranged from 0.1 to 0.2, and the average I_D/I_G ratio was 0.15. The low I_D/I_G ratio confirmed good structural quality of the graphene film. Similarly the I_{2D}/I_G ratio ranged from 0.6 to 1.5, with an average ratio of 0.8. Areal mapping also revealed that the graphene film had low defect levels, with variation in graphene thicknesses occurring over a large area. A Raman spectrum of the graphene film was shown in Fig. 2c, in which three distinct peaks were clearly visible. The peak located at $\sim 1350\text{ cm}^{-1}$ as a disorder peak (D peak) which arises from the defects in the sp^2 carbon. The peak located at $\sim 1580\text{ cm}^{-1}$ was a graphitic peak (G peak) caused by the in-plane vibrational E_{2g} mode of the sp^2 carbon and the peak located at $\sim 2700\text{ cm}^{-1}$ represents the second-order 2D-band arising from the inter-planar stacking of the hexagonal carbon network [32].

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