Effects of Growth Temperature on Electrocatalytic Properties of Three-dimensional Sulfur-doped Graphene Foam

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Abstract: Three-dimensional sulfur-doped graphene (3DSG) has been grown by chemical vapor deposition (CVD) using nickel foam as substrate and thianthrene as the solid carbon and sulfur source. The results show that the growth temperature of 3DSG has significant influence on the electrocatalytic activity for hydrogen evolution reaction (HER). The 3DSG sample under optimal growth temperature of 800 °C has the best electrocatalytic activity. The excellent electrocatalytic activity can be attributed to its well-designed porous, conductive and flexible 3D sulfur-doped graphene structure.

1. Introduction
Design and engineering of high-efficiency electrocatalysts for hydrogen evolution reaction (HER) is of importance for hydrogen energy research [1]. Pt-based electrocatalysts as the most active HER catalysts are expensive which hindered their applications [2]. Therefore, transition-metal-based catalysts such as Fe, Co, Ni, Mo, W and transition-metal sulfides, selenides, phosphide have been intensively studied as the promising HER catalyst [3-7]. Recently, metal-free carbon-based catalysts have been studied as promising HER catalysts [8]. Among them, graphene have been drawn much attentions due to its high electronic conductivity, high mechanical strength and large surface area [9]. Furthermore, it has been demonstrated that doping graphene with heteroatoms such as B, N, S, P is an effective strategy to improvement its electrocatalytic activity [10-13]. On the other hand, most of graphene-based catalysts are based on 2D graphene sheets and the ineffective packing of 2D graphene sheets inevitably decreases the number of catalytically active sites. Therefore, design and fabrication graphene with 3D porous structures as well as heteroatoms doping still remains challenge.

Herein, we demonstrated a facile method to prepare three-dimensional sulfur-doped graphene (3DSG). The 3DSG was synthesized by chemical vapor deposition (CVD) using nickel foam as substrate and thianthrene (C_{12}H_{8}S_{2}) as the solid carbon and sulfur source. The free-standing 3DSG can be directly used as binder-free electrocatalyst and it exhibited significant improvement HER performance than pristine graphene foam. The excellent electrocatalytic activity can be attributed to its well-designed porous, conductive and flexible 3D sulfur-doped graphene structure. Furthermore, the effects of growth temperature on the electrocatalytic performance of 3DSG was also studied.
2. Experimental

2.1. Synthesis of 3DSG and 3DGF

The 3DSG was synthesized by CVD which is similar with our previous reports [14, 15]. Briefly, the commercial nickel foams were firstly washed in dilute HCl and deionized water, then dried and loaded onto a tube furnace. The thianthrene (C₁₂H₈S₂) with 200 mg was placed in the upstream of the tube furnace. The nickel foams were annealed at 1000 °C for 30 min under H₂ (30 sccm) and Ar (270 sccm) and then cooled down to the growth temperature. Then the thianthrene was heated up to 140 °C and introduced to the substrate for 30 min growth. The 3DGF was synthesized using 50 sccm CH₄ as carbon source. The Ni foam template was etched away using etching solution contains 1 M FeCl₃ and 0.5 M HCl. The 3DSG synthesized at growth temperature 700, 800, 900 °C denote as 3DSG700, 3DSG800 and 3DSG900, respectively.

2.2. Characterizations

The morphologies, structures and elemental compositions of the samples were characterized with field emission scanning electron microscope (SEM, JSM-7000F, JEOL), transmission electron microscope (TEM, Tecnai F20 at 200 kV), Raman spectrometer (Renishaw, 532 nm) and X-ray photoelectron spectroscopy (XPS, Kratos XSAM800, Al Kα radiation (144 W, 12 mA, 12 kV)).

2.3. Electrochemical Measurements

The electrochemical measurements were carried on by using CHI 660D electrochemical workstation (CH Instruments, Inc.). A saturated calomel electrode (SCE) and graphite rod were used as reference and counter electrodes, respectively. The as prepared graphene foams were directly used as binder-free working electrodes. The effective electrochemical geometric area was 0.78 cm² and the mass loading was 2.68 mg/cm². The electrolyte was 0.5 M H₂SO₄ and degassed by bubbling with Ar for 2 h. The polarization curves were collected with linear sweep voltammetry at a sweep rate of 0.5 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) test was performed at a potential of -0.35V versus RHE with the frequency ranging from 0.1 Hz to 0.1 MHz.

3. Results and Discussion

The morphologies and microstructures of 3DSG800 was characterized by SEM and TEM. As shown in Figure 1a, the 3DSG possess porous structure and the pore diameter is between 200 and 600 μm. The corresponding HRTEM image (Figure 1b) shows one to few layer of the graphene film folded over itself, indicating that the graphene foam comprises of less than 10 atomic layer of carbon.

Figure 1. SEM image (a) and TEM image (b) of 3DSG
Raman was utilized to characterize the structure and defect level of the prepared graphene foams. As shown in Figure 2, the Raman spectrum of all the prepared samples shows a typical G-band (ca. 1580 cm\(^{-1}\)) and 2D-band (ca. 2710 cm\(^{-1}\)) which represents the carbon sp\(^2\) bonding in graphene [16]. The D-band is related to the disorder and defect and it was not observed in 3DGF which indicates its perfect graphitic structure with a high crystallinity [26]. In contrast, the D-band at ca. 1343 cm\(^{-1}\) appeared in all the 3DSG samples, which can be mainly attributed to the introduction of sulfur atoms. Furthermore, the intensity of D-band becomes larger with lower growth temperature, indicates that the 3DSG contains more disorder or defects at lower growth temperature.

![Figure 2. Raman spectra of 3DGF and 3DSG at different synthesized temperature.](image)

The XPS measurements were performed to investigate the elemental composition in 3DSG. Figure 3a shows the high-resolution C 1s spectra of 3DSG800 which has a strong band of C-C species (284.6 eV) with a weak shoulder of C-S/C-O groups (285.2 eV) [17-19]. The high-resolution S 2p spectra of 3DSG800 (Figure 3b) can be deconvoluted into S-H (161.8 eV), C-S-C (163.5 eV), C=S (164.7 eV), C-SO\(_2\)-C (168.2 eV) and C-SO\(_3\)-C (169.4 eV) [17-21]. The S contents of 3DSG800 were measured to be 2.8 at%. These results confirm that S atoms have been successfully doped into the graphitic structures of graphene foam.
To evaluate the effects of growth temperature on the HER performances of the 3DSG, the free-standing graphene foams were directly used as binder-free working electrodes and were tested in typical three-electrode setup. For reference, HER performance of 3DGF and commercial Pt catalyst (20 wt% Pt/C load on glassy carbon electrode) was also investigated. As shown in Figure 4a, all of the 3DSG samples show more positive onset potential than that of 3DGF, indicating that the catalytic activity of 3DGF is largely enhanced after S-doping. The operating overpotentials at 10 mA/cm² current were measured to be 419 mV for 3DSG700, 376 mV for 3DSG800 and 435 mV for 3DSG900. The 3DSG grown at 800 °C shows the best catalytic activity. It is further confirmed by Tafel plots (Figure 4b) and the 3DSG800 shows the lowest Tafel slope of 96 mV/dec. It indicates that optimization of growth temperature is important to prepare S-doped graphene foam towered catalytic activity.

The HER kinetics of 3DGF and 3DSG were further investigated through electrochemical impedance spectroscopy (EIS). As shown in Figure 5, the charge transfer resistance ($R_{ct}$) of 3DSG800 is about 117 Ω cm², which is much lower than that of 3DSG700 (205 Ω cm²), 3DSG800 (471 Ω cm²) and 3DGF (1904 Ω cm²), suggesting the easier electron transfer at the 3DSG800/electrolyte interface [22].
4. Conclusions
In summary, we have successfully synthesized 3DSG by CVD and the effects of growth temperature on the electrocatalytic performance of 3DSG were also studied. The as prepared free-standing 3DSG possess high crystallinity and high porosity and it can be directly used as an electrocatalytic electrode for HER. The 3DSG exhibited significant improvement HER performance than 3DGF. Furthermore, we demonstrate that optimization of growth temperature is important to prepare 3DSG towered high electrocatalytic activity. These results suggest that rational design and prepare graphene combing with 3D porous structure and heteroatom doping is an effective way to develop highly active metal-free HER catalysts.

5. Acknowledgments
The research was supported by the National Natural Science Foundation of China (Grant No. 51372033), the National High Technology Research and Development Program of China (Grant No. 2015AA034202), and the 111 Project (Grant No. B13042).

6. References
[1]Fei H, Dong J, Arellano-Jimenez MJ, Ye G, Kim ND, Samuel ELG, et al., Atomic cobalt on nitrogen-doped graphene for hydrogen generation, Nat Commun, 6 (2015)
[2]Liu X, Dai L, Carbon-based metal-free catalysts, Nat Commun, 1 (2016) 16064
[3]Gong M, Wang D, Chen C, Hwang B, Dai H, A mini review on nickel-based electrocatalysts for alkaline hydrogen evolution reaction, Nano Res, 9 (2016) 28-46
[4]Shi Y, Zhang B, Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction, Chem Soc Rev, 45 (2016) 1529-41
[5]Jamesh MI, Recent progress on earth abundant hydrogen evolution reaction and oxygen evolution reaction bifunctional electrocatalyst for overall water splitting in alkaline media, J Power Sources, 333 (2016) 213-36
[6]Safizadeh F, Ghali E, Houlachi G, Electrocatalysis developments for hydrogen evolution reaction in alkaline solutions – A Review, Int J Hydrogen Energ, 40 (2015) 256-74
[7]Zeng M, Li Y, Recent advances in heterogeneous electrocatalysts for the hydrogen evolution reaction, J Mater Chem a, 3 (2015) 14942-62
[8]Hu C, Dai L, Carbon-Based Metal-Free Catalysts for Electrocatalysis beyond the ORR, Angew Chem Int Edit, 55 (2016) 11736-58
[9]Zhou W, Jia J, Lu J, Yang L, Hou D, Li G, et al., Recent developments of carbon-based electrocatalysts for hydrogen evolution reaction, Nano Energy, 28 (2016) 29-43
[10]Sathe BR, Zou X, Asefa T, Metal-free B-doped graphene with efficient electrocatalytic activity for hydrogen evolution reaction, Catalysis Science & Technology, (2014)
[11]Huang X, Zhao Y, Ao Z, Wang G, Micelle-Template Synthesis of Nitrogen-Doped Mesoporous Graphene as an Efficient Metal-Free Electro catalyst for Hydrogen Production, Sci Rep-Uk, 4 (2014)
[12] Jiang H, Zhu Y, Su Y, Yao Y, Liu Y, Yang X, et al., Highly dual-doped multilayer nanoporous graphene: efficient metal-free electrocatalysts for the hydrogen evolution reaction, J Mater Chem a, 3 (2015) 12642-5
[13] Zheng Y, Jiao Y, Li LH, Xing T, Chen Y, Jaroniec M, et al., Toward Design of Synergistically Active Carbon-Based Catalysts for Electrocatalytic Hydrogen Evolution, Acs Nano, 8 (2014) 5290-6
[14] He J, Chen Y, Lv W, Wen K, Li P, Qi F, et al., Highly-flexible 3D Li2S/graphene cathode for high-performance lithium sulfur batteries, J Power Sources, 327 (2016) 474-80
[15] Qi F, Li P, Chen Y, Zheng B, Liu J, Zhou J, et al., Three-dimensional structure of WS2/graphene/Ni as a binder-free electrocatalytic electrode for highly effective and stable hydrogen evolution reaction, Int J Hydrogen Energ, (2017)
[16] Ferrari AC, Basko DM, Raman spectroscopy as a versatile tool for studying the properties of graphene, Nat Nanotechnol, 8 (2013) 235-46
[17] Liu X, Zhou W, Yang L, Li L, Zhang Z, Ke Y, et al., Nitrogen and sulfur co-doped porous carbon derived from human hair as highly efficient metal-free electrocatalysts for hydrogen evolution reactions (vol 3 pg 8840, 2015), J Mater Chem a, 3 (2015) 10135
[18] Yu X, Zhang M, Chen J, Li Y, Shi G, Nitrogen and Sulfur Codoped Graphite Foam as a Self-Supported Metal-Free Electrocatalytic Electrode for Water Oxidation, Adv Energy Mater, 6 (2016)
[19] Jeon I, Zhang S, Zhang L, Choi H, Seo J, Xia Z, et al., Edge-Selectively Sulfurized Graphene Nanoplatelets as Efficient Metal-Free Electrocatalysts for Oxygen Reduction Reaction: The Electron Spin Effect, Adv Mater, 25 (2013) 6138-45
[20] Islam MM, Subramaniyam CM, Akhter T, Faisal SN, Minett AI, Liu HK, et al., Three dimensional cellular architecture of sulfur doped graphene: self-standing electrode for flexible supercapacitors, lithium ion and sodium ion batteries, J Mater Chem a, (2017)
[21] Lu Y, Chen J, Wang A, Bao N, Feng J, Wang W, et al., Facile synthesis of oxygen and sulfur co-doped graphitic carbon nitride fluorescent quantum dots and their application for mercury(II) detection and bioimaging, J Mater Chem C, 3 (2015) 73-8
[22] Ito Y, Cong W, Fujita T, Tang Z, Chen M, High Catalytic Activity of Nitrogen and Sulfur Co-Doped Nanoporous Graphene in the Hydrogen Evolution Reaction, Angew Chem Int Edit, 54 (2015) 2131-6