Journal of Colloid and Interface Science 509 (2018) 254–264

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

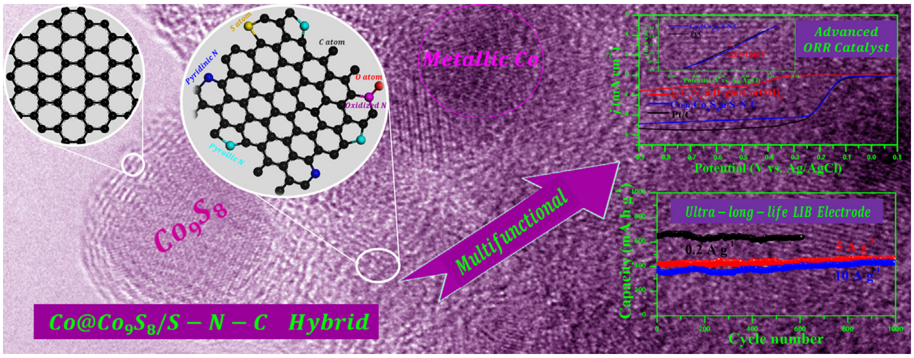
Regular Article

Sulphur and nitrogen dual-doped mesoporous carbon hybrid coupling with graphite coated cobalt and cobalt sulfide nanoparticles: Rational synthesis and advanced multifunctional electrochemical properties

Anquan Zhu, Pengfei Tan, Lulu Qiao, Yi Liu, Yongjin Ma, Jun Pan *

State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 June 2017
Revised 2 September 2017
Accepted 6 September 2017
Available online 08 September 2017

Keywords:
Sulphur
Nitrogen co-doped
Mesoporous carbon
Graphite coated Co and Co_9S_8
Oxygen reduction reaction
Li ion battery

ABSTRACT

Doping-type carbon matrixes not only play a vital role on their electrochemical properties, but also are capable of suppressing the crush and aggregation phenomenon in the electrode reaction process for pristine metallic compound. Herein, graphite coated cobalt and cobalt sulfide nanoparticles decorating on sulphur and nitrogen dual-doped mesoporous carbon ($Co@Co_9S_8$/S-*N*-C) was fabricated by a combined hydrothermal reaction with pyrolysis method. Benefited from g-C_3N_4 template and original synthetic route, as-obtained $Co@Co_9S_8$/S-*N*-C possessed high specific surface area (751.7 $m^2\ g^{-1}$), large pore volume (1.304 $cm^3\ g^{-1}$), S and N dual-doped component and relative integrated graphite skeleton, as results it was developed as decent oxygen reduction electro-catalyst and ultra-long-life Li-ion battery anode. Surprisingly, compared with commercial Pt/C, it displayed a higher half-wave potential (0.015 V positive) and lower Tafel slop (66 mV s^{-1}), indicating its superior ORR activities. Moreover, the ultra-long-life cyclic performances were revealed for lithium ion battery, exhibiting the retention capacities of 652.1 mAh g^{-1} after 610 cycles at 0.2 A g^{-1}, 432.1 and 405.7 mAh g^{-1} at 5 and 10 A g^{-1} after 1000 cycles, respectively. We propose that the synergistic effect of structure and chemical component superiorities should be responsible for the remarkable electrochemical behaviors of the $Co@Co_9S_8$/S-*N*-C.

1. Introduction

Energy conversion and storage systems, including regenerative fuel cells (FC) and rechargeable lithium ion battery (LIB) [1–6],

---

* Corresponding author.
E-mail address: jun.pan@csu.edu.cn (J. Pan).

http://dx.doi.org/10.1016/j.jcis.2017.09.012
0021-9797/© 2017 Elsevier Inc. All rights reserved.

are recognized as promising options to deal with the worldwide energy and environment crises issues resulting from the excessive consumption of traditional fossil fuels. Unfortunately, there are some bottlenecks, which appeal to us for exploring new-type nanostructures as satisfactory substitutes for LIB and FC [7,8]. For example, conventional graphite anode, with a theoretical capacity of 372 mAh g^{-1} [9], has achieved great success in commercialization during the past few decades, but it can't meet the satisfaction of next-generation high capacities and acceptable stabilities [10]. On the other hand, electrochemical oxygen reduction reaction (ORR) is a key process for FC [11]. In present state of art, Pt and Pt-based materials still represent the most effective ORR catalysts on account of their positive onset potential and large current density. Nevertheless, the large-scale commercialization is still limited by its natural scarcity and easy agglomeration in alkaline media [12–16]. On the basis of above problems, it absolutely challenges us to develop novel alternatives as ORR catalysts and LIB anode materials.

In recent years, transition metallic chalcogenides, especially Co_9S_8, have drawn great attention owing to its high lithium theoretical storage capacity and the similar electro-catalytic activities with Pt determined by the quantum chemistry calculations [12,13,17–20]. However, the intrinsic poor electrical conductivities and easy corrosion in alkaline electrolyte of pristine Co_9S_8 limit severely its practical application. To overcome these obstacles, a variety of efforts have been devoted [21,22]. Notably, coupling Co_9S_8 nanoparticles with other heteroatom-doped porous carbon matrixes walks in the forefront [23,24]. Recently, nitrogen and sulphur dual-doped porous carbon has been confirmed as an efficient oxygen electro-reduction catalyst because the introduction of heteroatoms into carbon skeletons would change the electron spin density and electronegativity of carbon matrixes [17,25–28], which is beneficial for the ORR electrode reactions. Like other carbonaceous materials, S and N co-doped carbon could improve the conductivity and mitigate the volume variation in electrode reaction processes, therefore, it is expected to be a promising conductive supporting material for LIB as well [10,28–30]. As we know, there were some attempts to synthesize Co_9S_8 nanoparticles immobilized on S and N doped graphite for enhanced ORR overall performances [12,17,31–33], but few reports about such materials used as LIB anodes. Moreover, as pointed out by Liming Dai et al. [34] investigation on synthesis-structure-activity correlations is of great significance. Hence, it is critical and meaningful to fabricate novel structural materials for outstanding electrochemical performances, such as heteroatom-doped carbon accompanied with metal chalcogenide compound. In our design concept, graphitic carbon wrapped metallic Co and Co_9S_8 nanoparticles immobilized on S, N co-doped carbon matrixes could effectively improve the durability of as-prepared $Co@Co_9S_8$/S-*N*-C. The synergistic effect of Co, Co_9S_8 and porous S, N co-doped carbon would be favorable to its outstanding ORR performances [1,12,31].

At the present work, utilizing porous g-C_3N_4 as template and *N*-source, we synthesized successfully mesoporous S and N co-doped carbon matrix coupling with $Co@Co_9S_8$ nanoparticles. The morphology, microstructure and chemical component of the $Co@Co_9S_8$/S-*N*-C were conducted by scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) and Raman spectrometer. Furthermore, the electrochemical properties towards ORR and LIB of the $Co@Co_9S_8$/S-*N*-C were investigated particularly.

2. Experimental

2.1. Materials preparation

2.1.1. Materials

Urea (AR, 99%) was bought from Aladdin Industrial Corporation (Shanghai, China). d-glucose (AR) was purchased from Xilong Chemical Co. Ltd. (Guangzhou, China). Cobalt acetate tetrahydrate ($C_4H_6CoO_4{\cdot}4H_2O$ 99% metals basis) and sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$, AR, $\geq$98%) were obtained from Aladdin Industrial Corporation. Pt/C catalyst was received from Alfa Aesar. Deionized water with specific resistance 18.25 MΩ/cm was available by a water purification system. All other reagents used in this study were analytically pure grade and without further purification.

2.1.2. Preparation of porous g-C_3N_4

Urea (10 g) was poured into a porcelain crucible (50 mL) with a lid covered, then maintained 100 °C for 2 h. After that, the crucible was heated from room temperature to 550 °C at a heating rate of 5 °C/min and kept this temperature for 4 h in a muffle furnace [35–37]. When the crucible was cooled down to room temperature, porous g-C_3N_4 was obtained.

2.1.3. Preparation of g-C_3N_4@d-glu/$Co(OH)_2$

First, 0.3 g porous g-C_3N_4 and 1.5 g d-glucose were dispersed into 30 mL deionized water and stirred for 1 h. The mixed solution was maintained at 120 °C for 10 h. When it was reduced to room temperature, the carbonized d-glucose covering g-C_3N_4 (g-C_3N_4@d-glu) was available after filtration with ethanol and deionized water. Second, the g-C_3N_4@d-glu was re-dispersed into 30 mL deionized water (named A), followed by added 0.025 g cobalt acetate tetrahydrate into solution A and stirred for 3 h to achieve the adsorption of Co^{2+} onto g-C_3N_4 surface (named B). When it was accomplished, the pH value of solution B should be adjusted to 8 using ammonium hydroxide solution, then stirred continuously for 24 h. In order to obtain the g-C_3N_4@d-glu/$Co(OH)_2$, the freeze dry need to be accomplished prematurely.

2.1.4. Preparation of the $Co@Co_9S_8$/S-N-C

As-prepared g-C_3N_4@d-glu/$Co(OH)_2$ was re-dispersed into 30 mL 0.0035 M sodium sulfide nonahydrate aqueous solution (named solution C) under sonication for 6 h. Solution C was freeze dried to obtain hybrid D. In order to prepare the $Co@Co_9S_8$/S-*N*-C, the hybrid D should be heated at 900 °C for 1 h (heating rate: 5 °C/min). After cooling down to room temperature, the black powders ($Co@Co_9S_8$/S-*N*-C) were collected by centrifugation with ethanol and deionized water for several times, and dried in a vacuum oven at 60 °C for 8 h.

2.2. Characterization

The morphologies and structures of as-prepared materials were explored using a field emission scanning electron microscope (Nova Nano SEM 230, FEI Co. Ltd.) with an acceleration voltage of 10 kV and transmission electron microscopy (TEM, JEM-2100F JEOL Ltd. Japan) with an acceleration voltage of 200 kV. X-ray powder diffraction patterns were recorded on an X-ray diffractometer (XRD; D/max 2550, Rigaku Corporation) with Cu Kα radiation (λ = 0.15405 nm). The surface chemical states were analyzed by X-ray photoelectron spectroscopy (ESCALAB 250Xi, ThermoFisher-VG Scientific), and the binding energies of all elements were calibrated through the C 1s peak (BE = 284.8 eV) as standard. Brunauer-Emmett-Teller (Quadrasorb SI-3MP) was