INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–12

Available online at www.sciencedirect.com

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Enhanced hydrogen storage performance of three-dimensional hierarchical porous graphene with nickel nanoparticles

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ARTICLE INFO

Article history:
Received 15 March 2018
Received in revised form
24 April 2018
Accepted 27 April 2018
Available online xxx

Keywords:
Graphene-based nanocomposites
Ni nanoparticles
Hierarchical porous structure
Hydrogen storage
Hydrogen spillover effect

ABSTRACT

Three-dimensional hierarchical porous graphene with nickel nanoparticles (3DHPG-Ni) was synthesized through electrostatic assembly method with the assistance of poly (methyl methacrylate) (PMMA) template and subsequent removal of PMMA template by calcination. The morphology, microstructure and hydrogen adsorption properties of 3DHPG-Ni nanocomposites were examined in detail. The obtained 3DHPG-Ni nanocomposite exhibited hierarchical porous structure composed of macro-, meso- and micropores, high specific surface area (925 m^2 g^{-1}), large pore volume (0.58 cm^3 g^{-1}) and excellent hydrogen storage capacity. Under the pressure of 5 bar, 3DHPG-Ni nanocomposite showed a maximum hydrogen capacity of 4.22 wt% and 1.95 wt% at 77 K and 298 K, respectively, demonstrating that the as-prepared 3DHPG-Ni nanocomposite was supposed to be a promising material with outstanding properties for practical applications in the field of hydrogen storage. The three-dimensional hierarchical porous structure, evenly distributed Ni nanoparticles and hydrogen spillover effect were responsible for the enhanced hydrogen storage capacities.

Introduction

Recently, the world's demand for a solution to the worldwide energy crisis and environmental pollution has inspired intensive research to develop clean and sustainable energy sources that can replace fossil fuels [1]. Among all kinds of energy sources, hydrogen is one of the most ideal energy carriers and alternative fuel sources because of its significant advantages including high efficiency, non-pollution, renewability, abundance and high gravimetric density. To develop a sustainable hydrogen economy, the main challenge remaining is the exploration of safe, efficient, renewable, light and affordable solid materials for hydrogen storage. Therefore, it is of great importance to develop the materials which can store hydrogen safely and efficiently. The activity of materials on hydrogen storage is primarily determined by the microstructure and specific surface area of materials. Thus, nanostructured carbon materials (such as activated carbon [2,3], carbon nanotubes [4] and graphene

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https://doi.org/10.1016/j.ijhydene.2018.04.202
0360-3199/

[5–7]) have received continuous interests as potential hydrogen storage media for their lightweight, high specific surface area, relatively low cost, excellent stability and fast kinetics. The main disadvantage is relatively low hydrogen storage capacity which is usually below 1 wt% at ambient temperatures. Hence, it is highly desirable to develop novel carbon materials that can be tailored to provide microstructure and composition meeting the specific demands of practical hydrogen storage system.

As the newest member in carbon materials, graphene is composed of a monolayer of carbon atoms packed into a dense honeycomb crystal structure [8]. This structure makes it possible to possess unique properties such as lightweight, large specific surface area, high thermal and electrical conductivity, mechanical strength, and chemical stability [9]. As a result, graphene has attracted a great deal of interests as a promising hydrogen storage medium [10–21]. Theoretical calculations predict that regular or irregular combinations of sp^3-bonded carbon atoms and graphene nanosheets are advantageous for hydrogen storage [22–31]. However, two-dimensional graphene nanosheets prefer restacking or aggregating into non-porous nanostructures during preparation, leading to dramatic decrease of surface area and pore volume [32,33]. As a consequence, the hydrogen adsorption capacities of graphene-based adsorbents are far below expectations. Three-dimensional graphene possesses a relatively high specific surface area and large pore volume, together with a multiple lattice-layered graphitic structure, making it quite promising as a hydrogen storage medium [34–39]. However, there are still few works about synthesis of three-dimensional graphene-based adsorbents for hydrogen storage applications [40,41].

Another effective way to improve the hydrogen adsorption property of graphene-based adsorbents is by hydrogen spillover [42–49]. Hydrogen spillover is defined as the dissociative chemisorption of hydrogen on metal nanoparticles, and subsequent transport of hydrogen atoms onto the surface of support followed by surface diffusion [50–52]. Therefore, graphene-based nanocomposites such as decoration of graphene nanosheets with metal nanoparticles have been developed in recent years to increase the hydrogen storage capacity of graphene materials [53–64]. Although encouraging progress has been achieved, the issue of structural stability and poor reversibility in transition metal dispersion has been a major concern because the transition metal atoms tend to aggregate easily for the strong metal cohesion forces [65,66]. Therefore, more studies are required to further improve the hydrogen storage performance of graphene-based adsorbents.

In the present study, three-dimensional hierarchically porous graphene with nickel nanoparticles (3DHPG-Ni) has been rationally designed and facilely fabricated through electrostatic assembly with the assistance of poly (methyl methacrylate) (PMMA) template and subsequent removal of PMMA template by calcination. The morphology, microstructure and hydrogen adsorption properties of 3DHPG-Ni nanocomposites are examined in detail. The results show that 3DHPG-Ni nanocomposites have enhanced hydrogen storage capacity due to the three-dimensional hierarchical porous structure, evenly distributed Ni nanoparticles and hydrogen spillover effect. This study, to the best of our knowledge, is the first of its kind to take advantage of hierarchical porous structure and hydrogen spillover effect simultaneously to improve the hydrogen storage performance of graphene materials.

Experimental

Materials

Carboxylic graphene oxide (GO-COOH) aqueous solution was purchased from Nanjing XFNANO Materials Tech Co., Ltd, China. Nickel chloride ($NiCl_2 \cdot 6H_2O$), Pyromellitic dinahydride anhydride (PMDA), 4, 40-diamino diphenyl ether (ODA, AR) and 1-methyl-2-pyrrolidone (NMP) of analytical grade were purchased from Sinopharm Chemical Reagent (Shanghai, China). PMDA and ODA were recrystallized from acetic anhydride and ethanol before use, respectively. NMP was distilled over phosphorus pentoxide before use. Ultrapure water was used throughout the experiment.

Preparation of 3DHPG-Ni nanocomposite

The monodispersed PMMA microspheres were synthesized by surfactant-free emulsion polymerization using a cationic free radical initiator, as described in a previous report [67]. The synthesized PMMA microspheres were positively charged in aqueous solutions. 3DHPG-Ni nanocomposite was fabricated through electrostatic assembly and high temperature calcination process. 20 ml of GO-COOH dispersion (1 mg/ml) was added dropwise into the aqueous suspension of PMMA microspheres (1 wt%) under vigorous stirring at room temperature. The negatively charged GO-COOH nanosheets were self-assembled on the surface of positively charged PMMA particles owing to the electrostactic interactions. After stirring for 2 h, a certain amount of $NiCl_2 \cdot 6H_2O$ aqueous solution was added dropwise into the mixture followed by magnetic stirring for 14 h. The resulting composite was collected and dried in vacuum at 60 °C for 24 h. Finally, the product was transferred into tube furnace and calcined at 600 °C for 3 h under nitrogen atmosphere to remove PMMA template. The obtained product was denoted as "3DHPG-Ni-x", wherein x represented the percentage of Ni nanoparticles in the 3DHPG-Ni nanocomposite. As a comparison, we synthesized three-dimensional hierarchically porous graphene without nickel nanoparticles by similar approach, denoted as 3DHPG material.

The formation mechanism of 3DHPG-Ni nanocomposite was illustrated in Fig. 1. The procedure was divided into three stages. In the first stage, negatively charged GO-COOH nanosheets were coated onto the surface of positively charged PMMA microspheres through electrostactic self-assembly. In the second stage, the positive Ni^{2+} ions were loaded onto negative GO-COOH by strong electrostatic interactions, thus forming $PMMA^+/GO\text{-}COO^-/Ni^{2+}$ comoposite microspheres. Finally, 3DHPG-Ni nanocomposite was produced by thermal annealing of above $PMMA^+/GO\text{-}COO^-/Ni^{2+}$ comoposite microspheres in nitrogen atmosphere. After high temperature calcination, the PMMA template was pyrolyzed and liberated as gaseous products from the composites. Therefore, the

Please cite this article in press as: Liu Y, et al., Enhanced hydrogen storage performance of three-dimensional hierarchical porous graphene with nickel nanoparticles, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.04.202