



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Ball-milling preparation of titanium/graphene composites and its enhanced hydrogen storage ability

Wei Ye*, Qianqian Chi, Han Zhou, Peng Gao**

College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou, Zhejiang, 311121, PR China

ARTICLE INFO

Article history:

Received 9 July 2018

Received in revised form

22 August 2018

Accepted 24 August 2018

Available online xxx

Keywords:

Kubas-type interaction

Ball-milling

Composites

Hydrogen storage

ABSTRACT

Mass pure Ti/graphene (GE) composites have been synthesized by direct ball-milling Ti powders and GE nanosheets. Through adjusting the reaction conditions, Ti–C bonding in Ti/GE composites was constructed on the interface between Ti nanoparticles and GE nanosheets, which was also confirmed by the following Raman and XPS measurements. Pressure-composition-isotherm (PCT) curves showed that the Ti/GE composites exhibited a higher hydrogen storage capacity (4.3 wt% for H₂ at 300 °C, 0.08 bar) and lower equilibrium pressure compared with that of simply physically mixed sample. In addition, the hydrogen adsorption process and the mechanism for the Ti/GE composites have also been investigated, in which a Kubas-enhanced adsorption process was found in the composites. In this Kubas-type adsorption process, hydrogen was adsorbed firstly by Ti atoms with a formation of Ti–H bonding and then the bonded hydrogen was spilled over to graphene, forming a C–H interaction.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

With the twin dilemmas of global warming and the growing shortage of easily obtainable fossil fuels, it is an urgent task to restructure our energy mix in depth. Hydrogen has been regarded as an attractive clean fuel in recent years as its combustion product is only water as well as high-energy density [1,2]. However, the major impediment for extensive usage of hydrogen energy is the demand for highly efficient storage for hydrogen molecules, where there is still lack of suitable solid mediums to store hydrogen effectively and safely [3,4]. In recent years, various nanomaterials have been

explored for reversible high-capacity hydrogen storage, but the hydrogen storage in most materials needs high temperature and high pressure [5–9]. The US Department of Energy (DOE) has set a target to achieve 5.50 wt% gravimetric density for hydrogen storage in light-duty vehicles by 2020 [10]. In order to address the above problems and achieve DOE target, new nanomaterials design and concepts for effective hydrogen storage are urgently needed.

It is worth noted that the Kubas-type interaction in transition metal, which results from a hybridization of *d* orbitals of transition metal with σ and σ^* orbitals of H₂ molecules (*d*-H₂), can greatly enhance the binding energy of hydrogen molecules [11,12]. This has boosted highly efficient hydrogen

* Corresponding author.

** Corresponding author.

E-mail addresses: yewei@hznu.edu.cn (W. Ye), gaopeng@hrbeu.edu.cn (P. Gao).<https://doi.org/10.1016/j.ijhydene.2018.08.166>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

storage materials design based on Kubas enhanced hydrogen storage mechanism, such as Sc-decorated fullerenes, Ti/carbon nanotubes (CNTs) composites, Ti-ethylene complexes, Ti-decorated polymers, and other transition-base nanomaterials [13–20]. These hybrid nanomaterials adsorb H_2 molecules with enhanced binding energy, and their hydrogen storage capacities are expected to meet the gravimetric goal of DOE target. Additionally, recent theory studies suggest that a single Ti atom anchored on single-walled carbon nanotube or at a central or lateral hole site on zigzag graphene nanoribbons, can strongly bind up with four hydrogen molecules, and the optimal H_2 storage capacity can reach to 8 wt% or 6 wt % with high Ti coverage, respectively [14,21]. The ultrahigh H_2 storage capacity is generated by the formation of hybridization bonding between $H_2-\sigma^*$ antibonding orbitals, Ti-*d* orbitals, and C-*p* orbitals with no energy barrier. Although theoretical calculations have indicated that Ti atoms decorated on carbon matrix could greatly enhance the hydrogen storage capacity, there are few experimental results achieving high H_2 storage capacity based on Ti–C hybrid nanomaterials. What's more, the cost for H_2 storage solid mediums should be drastically reduced for practical hydrogen energy utilization, which demands a simplified and low-cost nanomaterials synthesis protocol.

Herein, we have successfully prepared Ti nanoparticles/graphene composites through a simple ball-milling method, as an experimental proof of the Kubas-type interaction for enhanced hydrogen storage in transition metal cases. Ball-milling method can simplify and achieve macroscopic preparation as well as reduce the whole cost, especially suitable for the preparation of hydrogen storage materials [22,23]. By careful analysis of SEM and HRTEM images, it is concluded that Ti nanoparticles wrapped in GE matrix composites are formed in the ball-milling system. Furthermore, the Raman and XPS results indicate that Ti–C bonding in Ti/GE composites is formed at high ball-milling speed (600 rpm). The formation of Ti–C bonding on the interface of Ti nanoparticles and GE can not only strengthen the interaction of Ti nanoparticles and graphene substrates to enhance the structure stability, but also provide additional active sites for H_2 storage. Benefiting from highly dispersed Ti nanoparticles and Kubas-type interaction, hydrogen storage capacity of Ti/GE composites reaches 4.3 wt% at 300 °C, 0.08 bar, which is better than individual Ti powders, and the hydrogen storage equilibrium pressure is obviously decreased after the formation of Ti–C bonding. This work provides a simplified and low-cost protocol for transition metal/graphene composites for enhanced hydrogen storage ability based on Kubas-type interaction.

Experimental

Graphene sample was prepared by the low-temperature pyrolysis of the solvothermal product of sodium and ethanol according to the reported literature [24]. Ti powders with a purity of 99.9% and the as-prepared GE were used as raw materials for the following ball-milling treatment to prepare Ti/GE composites. All the samples were ball-milled using a planetary ball mill (pulverisette 7 plus, FRITSCH) in a ZrO_2 vessel under an Ar atmosphere at a ball-milling speed of

600 rpm for 10 h. The ball-to-powder weight ratio was 15:1. The samples were obtained and dried in a vacuum. All the samples were characterized by X-ray diffraction measurement (XRD) (Rigaku D/max IIIA, Cu $K\alpha$). The scan rate of $0.05^\circ s^{-1}$ was used to record the spectra in the 2θ range of $10\text{--}70^\circ$. Raman spectra were obtained by using a micro-Raman system with an Ar ion laser 488 nm, and a probing laser $50 W cm^{-2}$ was guided during the illumination. Field-emission scanning electron microscopy (FESEM) images were acquired by a SU8000 cold emission field scanning electron microanalyser (Hitachi, Japan), where the obtained powders were mounted on a copper slice. Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) images were recorded on a JEOL-2010 TEM at an acceleration voltage of 200 KV. X-ray photoelectron spectroscopy (XPS) was performed by using a PHI 5700 ESCA System with a monochromatic Al $K\alpha$ (1486.6 eV) radiation source and a hemisphere detector. Hydrogen-storage properties of the obtained samples were measured by the determination of the pressure-composition isotherm (PCT) curves using the Sievert's type apparatus (PCTPro by Hy-Energy Scientific Instruments, SETARAM, France), with pressure between 0.001 and 50 MPa and hydrogenation temperature at 100, 200 and 300 °C, respectively.

Results and discussion

The overall phase structure and crystallinity of the samples were firstly examined by powder XRD measurements. As shown in Fig. 1a and b, GE is non-crystalline with two broad diffraction peaks located at about 23° and 43° which can be attributed to (002) and (101) plane diffraction peaks of graphitized carbon, respectively. The raw Ti powder is hexagonal phase (JCPDS card no. 44-1294) with high crystallinity. It is found that the Ti/GE composites after ball-milling treatment of graphene and Ti powders at a speed of 400 rpm for 10 h (Fig. 1c), show two sets of XRD diffraction peaks corresponding to graphene and metallic Ti, respectively. The diffraction peaks associated with metallic Ti in Fig. 1c are similar to the XRD spectrum of raw Ti precursor, implying that Ti nanoparticles are still highly crystalline and do not undergo a recrystallization process for the fine recombination. Interestingly, when the ball-milling speed was up to 600 rpm, the low signal to noise ratio indicates the low crystallinity of metallic Ti at a higher ball-milling speed (Fig. 1d). The low crystallinity of metallic Ti may be attributed to the cracking of Ti powders into nanoparticles at high energy ball-milling system. In addition, a much higher ball-milling speed of 700 rpm was also performed in this work, and the inorganic $TiC_{0.981}$ (JCPDS card no. 73-0472) was formed, as shown in Fig. S1. In order to investigate the effect of mole ratios (n_{Ti}/n_{GE}) on the final product structure, a variety of mole ratios of $n_{Ti}:n_{GE}$ (from 3:1 to 2:1, 1:1 and 0.5:1) were selected at the ball-milling speeds of 400 and 600 rpm, respectively. The XRD patterns in Fig. S2 of Ti/GE composites with varied ratios of n_{Ti}/n_{GE} both at speeds of 400 and 600 rpm are similar with that in Fig. 1c and d.

In order to further examine the morphologies and microstructures of Ti/GE composites, SEM and TEM images of the

Download English Version:

<https://daneshyari.com/en/article/11011661>

Download Persian Version:

<https://daneshyari.com/article/11011661>

[Daneshyari.com](https://daneshyari.com)