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Green production of hydrogen by hydrolysis of graphene-modified aluminum through infrared light irradiation

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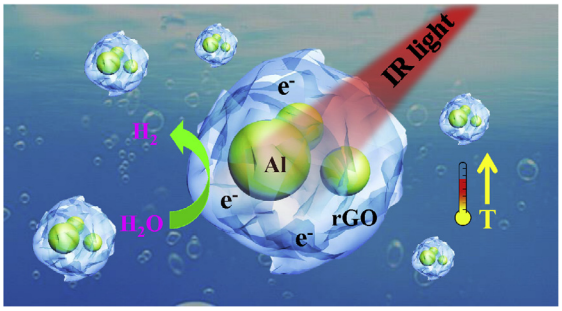
HIGHLIGHTS

- Producing hydrogen through infrared light irradiation by Al@rGO.
- Preventing passivation of Al and accelerating Al-water reaction by graphene coating.
- Infrared light absorption of graphene enhances water temperature.
- Byproduct is nature friendly and is recyclable for toxic absorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Promoting the Al-water reaction in a neutral condition without adding any sacrificial agents and generating no poisonous byproduct is always the aim of green production of hydrogen. In this study, we fabricated the reduced graphene oxide wrapped aluminum nanoparticles (Al@rGO) through an ultrasonic atomization process. And a high-efficiency hydrogen production is realized in pure water under the infrared light irradiation. Firstly, the graphene wrapping keeps the activity of aluminum nanoparticles by preventing the formation of dense passivation films on the surface of Al and accelerating the ions migration between Al and water. Secondly, the water temperature is enhanced due to the infrared light absorption of graphene, which contributes to the improved hydrogen generation as well. Moreover, the residual byproduct is nature-friendly and recyclable for toxic ion absorption applications. Our results provide an important technique towards the large scale green production of hydrogen by Al@rGO.

1. Introduction

Hydrogen possesses a high mass energy density and does not emit any pollution gas when being used as a fuel, which has attracted much attention due to its regenerative and environmental friendly properties [1]. However, the storage and transportation of hydrogen is always a difficult task due to its low boiling point and poor compressibility [2]. Developing in situ hydrogen generation techniques may be able to avoid these problems and promote the application of hydrogen energy [3]. As an advanced way of hydrogen production, the reaction of metal Al with water is considered to be a facile way to generate hydrogen with low cost and high efficiency [4]. Additionally, there is almost no by-product in this reaction, and the generated hydrogen possesses a high purity,

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which can be directly used for the portable emergency power supply for military, medical and civilian utilization [3]. However, a natural grown dense passive oxide layer is formed on the surface of Al when exposed in the air, greatly inhibiting the hydrogen generation efficiency [4].

Various methods have been applied to eliminate this passive oxide film and activate the reaction between the Al and water, including the addition of alkalis, salt as sacrificial agents, or mixing the aluminum and water vapor at high temperature and pressure. Although the hydrogen generation efficiency is improved, these methods obviously increase the production costs and safety requirement. Moreover, the solution with the addition of NaOH, $NiCl_2$ or Na_2SnO_3 sacrificial agents cannot be directly disposed because of its poisonous nature that pollutes environment [5]. In comparison with those reactions assisted by alkalis or elevated temperature, the Al-water reaction in a neutral condition is much safer and greener, but the surface passivation in neutral condition occurs much more easily and the metal activity is extremely low. To facilitate a continuous generation of hydrogen, increasing the fresh exposed Al surface is always applied through drilling, grinding, alloying or size reducing [6–8]. It is supposed that Al nanoparticles (NPs) could react with water without any activation additions but with a high reaction speed and conversion rate [9]. Bergthorson recommend to produce aluminum particles on-site directly before the hydrogen production takes place, which is also a promising way to prevent the formation of passivating layer [10]. However, due to its high chemical activity, the Al NPs must be kept under inert atmosphere, otherwise they may quickly become invalid or even explode.

The most challenging task for promoting Al NPs-water reaction is enhancing the efficiency of hydrogen generation and prolonging its storage time. However, conventional materials and techniques are difficult in meeting these requirements simultaneously [2]. Recently, it is found that the crumpled reduced graphene oxide wrapped nanoparticles or "nanosacks" may serve as a nanoreactor for accelerating a specific chemical reaction [11,12]. Although the nanoreactor concept has not been systematically developed for graphene-based structures, its development can be found in the significant recent literatures on crumpled graphene hybrids [13,14]. Extensive studies have confirmed that the crumpled graphene may serve as an efficient conductive additive, enhancing the particles dispensability and increasing the chemical reaction speed, which inspires the designing of reduced graphene oxide wrapped Al particles (Al@rGO) for promoting the Al-water reaction.

Here we fabricate a novel structure of Al@rGO nanoballs for hydrogen production through a facile ultrasonic atomization method. The graphene wrapping not only facilitates rapid small-molecule exchange and electron transfer interactions between Al and water, but also prevents the formation of a continuous compact passivation layer on the Al surface. It is interesting to find that the hydrogen can be quickly generated by using Al@rGO without addition of alkali and extra heating source, which demonstrates a high hydrogen generation rate and efficiency under a neutral water condition. Additionally, the byproduct of Al@rGO is a natural good adsorbent due to the synergistic effect of rGO and AlOOH, which displays an excellent performance for the toxic ions absorption. Compared with previous work, the structure of Al@rGO is novel, which greatly facilitates the hydrogen production. Although the preparation method is simple, a large amount of hydrogen can be achieved in a neutral environment, which may have a significant industrial application value. Moreover, the hydrogen generation in this study is controlled by the IR light instead of the external heat source, which achieves a totally green production and has seldom been reported in previous studies.

2. Methods

Graphene oxide was synthesized by a modified Hummers method [15] and purified several time before application. Most of the GO sheets own a size of $1 \sim 2$ μm, and the Al NP size is $50 \sim 500$ nm (commercial Al NPs from Dekedaojin Corp.). Al nano particle-filled graphene nano sacks were prepared by an aerosol method. Briefly, an ultrasonic nebulizer was used to create a suspended mist from an aqueous suspension of GO (0.5 mg/ml) and the target nanoparticle cargo, and carried by nitrogen gas flow through a heated horizontal furnace. The resulting hybrid materials were captured on a PTFE membrane filter (PTU024750, Sterlitech Co.).

The suspensions prepared for the ultrasonic atomization were mixed by Al nanoparticle and GO (mass ratio: 1/1) in DI water. The concentration of Al/GO has been optimized to 0.5 mg/ml to prevent sintering of nanoparticles.

2.1. Sample characterization

The structure of the sample was characterized by using a Bede D1 X-ray diffraction (XRD) system with a Cu Kα radiation ($\lambda = 0.15406$ nm). Surface morphology of the sample and its element contents were studied by using a FEI Quanta 200F scanning electron microscope (SEM) operated at a voltage of 20 kV equipped with energy-dispersive X-ray spectroscopy (EDX). The X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha American with an Al Kα X-ray source) was also applied to measure the elemental composition of samples. Specific surface area of the sample was obtained from the results of N_2 adsorption-desorption isotherms at 77 K (Micromeritics ASAP 3020) by using Brunauer-Emmet-Teller (BET). The structure of the sample is identified by using a FEI Tecnai G2 F20 transmission electron microscopy (TEM) equipped with selected area electron diffraction (SAED) patterns and the scanning transmission electron microscopy (STEM), which is operated at 200 kV. The microscopic Raman spectroscopy was recorded by using a micro-Raman spectrometer (InVia Reflex, Renishaw, UK) with excitation wavelength of 532 nm, and the laser power was kept below 0.85 mW to avoid laser induced heating effect on the sample. All peaks in the Raman spectra were fitted with Lorentzians. A 100× objective lens with a numerical aperture (NA) of 0.95 was used in the Raman experiments, and the spot size was estimated to be about 500 nm. Thermogravimetric analysis (TGA, SDT Q600) was carried out under air atmosphere at 10 °C/min with a temperature range of $10 \sim 900$ °C.

2.2. Hydrogen generation and temperature characterization

The hydrolysis reaction of composites with Al/rGO was performed in a self built reactor. The released hydrogen gas was passed through a condenser and was then measured in an inverted burette by water displacement. 10 mg composite powder and 10 ml distilled water were used for each test. No magnetic or mechanical stirring was employed during the whole hydrolysis process. The hydrogen generation conversion yield was calculated from the volume of squeezed water.

The hydrogen formed in the Al-water reaction drove out water from a second glass cylinder into a cup placed on an electronic balance. Since hydrogen has a low solubility in water, the volume of hydrogen evolved in the Al-water reaction could be measured by the mass flow meter. To study the temperature variation during the Al water reaction, a thermocouple was placed in the water.