Materials Science in Semiconductor Processing 84 (2018) 36–41

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Enhanced photocatalytic performance of visible-light active graphene-WO_3 nanostructures for hydrogen production

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ARTICLE INFO

Keywords:
Hydrogen evolution
Photocatalytic activity
Tungsten oxide

ABSTRACT

In this article, visible light driven graphene-WO_3 (WG) photocatalysts have been synthesized through facile hydrothermal process for H_2 evolution through water splitting under visible light illumination. For comparison, neodymium-WO_3 nanostructure was also prepared. The as-synthesized composites were characterized by XRD, SEM, BET, EDX, XPS, UV–vis absorption spectra and Photoluminescence (PL) emission spectroscopy. Experimental results showed that WG-7 composite (7% graphene content into WO_3) had excellent photocatalytic performance (rate of H_2 evolution 288/μmol h^{-1} g^{-1}) towards hydrogen production when compared to pristine WO_3. It was also confirmed by optical analysis that incorporation of graphene into WO_3 and Nd-WO_3 photocatalysts prevented the electron-hole recombination and boosts the reduction reactions for H_2 evolution. PL emission spectra confirmed the effective charge-separation in graphene incorporated WO_3 composite. It was demonstrated that photocatalytic activity for hydrogen production increases with increasing doping content of graphene upto 7 at%. However, further increase in incorporated content above optimal level has decreased the photocatalytic performance of the composite. The enhanced photocatalytic activity of WG composites could be attributed to extended visible light absorption, high surface area and efficient charge-separation due to synergistic effects between graphene and WO_3. This study gives a new perspective on the fabrication of novel photocatalyst for environmental and energy applications.

1. Introduction

Green energy production through water splitting has become crucial and challenging matter for scientific community and researchers to address major concerns regarding global energy and environmental applications [1]. Hydrogen evolution is a positive way for generating cost competitive, clean, and preferable H_2 fuels [2,3]. Therefore, executing research for the production of green energy has become the passion for global researchers, which could offer eco-friendly, cost effective means with excellent photocatalytic efficiency [4]. Significant work has been done on the production of energy, but have various drawbacks comprising high operating cost, low efficiency and need high-temperature along-with pH control [5,6,40,41]. Subsequently, it is indispensable to develop visible light driven photocatalytic materials to resolve many of precarious difficulties regarding energy production [7,8]. Up to now, numerous semiconductor based photocatalytic materials in the form of silicides, (oxy) sulfides, (oxy)carbides, (oxy)nitrides and others have used to demonstrate better photocatalytic activity towards H_2 production under visible-light illumination [9,10]. However, low response towards visible light, low reduction potential and fast charge carriers recombination rate limits the widespread use of semiconductor materials for photocatalytic performance [11,12]. Therefore, the design and fabrication of photocatalytic material that is responsive to visible-light was thrilling need of modern age to resolve the issues regarding energy and environment pollution. Among the numerous transition metal oxides, nanostructured tungsten trioxide is an n-type, indirect band gap (~ 2.4–2.8 eV) semiconductor metal-oxide with versatile properties and practical useful for gas sensing applications, water splitting, air cleaning, environment cleaning, heavy metal remediation and photocatalytic dyes degradation [13,14]. WO_3 has fascinated significant interest in photocatalysis applications owing to its resilient absorption within the visible region solar spectrum (< 400 nm), stable physic-chemical characteristics as well as photocorrosion resilience. Unfortunately, rapid charge-carriers recombination owing to low band gap and trouble in oxygen reduction owing to low-potential make pristine WO_3 photocatalytic material less efficient with extremely poor photocatalytic performance under visible-light, which indeed bounds its practical applications [15]. These are the prime hurdles encumbering the development of tungsten trioxide as applied photocatalyst. Recently, efforts have been made to enhance the

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https://doi.org/10.1016/j.mssp.2018.05.006
Received 6 January 2018; Received in revised form 15 April 2018; Accepted 4 May 2018

photocatalytic performance of WO_3 by increasing the efficiency of charge-carriers separation, doping, coupling with low band gap semiconductor material, hybridization, morphology control, and composites [16,17]. Loading surface of catalytic material with co-catalysts, mainly rare earth and noble metals and oxides including Eu, Nd, Pd, Pt, Rh_2O_3, CdO, etc, were usually employed to enhance the photocatalytic performance and stability of material [18,19]. The reason is that co-catalyst may accelerate the electron-hole pairs separation and decrease the activation-potential for H_2 production at meantime. However, cost and scarcity of the most active co-catalysts especially noble metals make it harder to use for the essential obligation of commercial-development. Therefore, it is dominant consequence to acquire a more cost competitive co-catalyst/composite to replace Pd, Pt, etc for commercial utilization and practical applications under solar energy as well. Owing to availability and cost-effectiveness, carbonaceous-materials have versatile properties with exceptional structure and high surface area that may add striking features to semiconductor based nanostructures [20,42]. Carbon material is utmost smart and well considered materials in modern age of technology and scientific-community owing to its astonishing range and versatility in mishmash with cost effective, availability and wide-ranging properties [21]. It has been well observed that physio-chemical, electrical and optical properties of C-materials can vary conferring to its different allotropic forms and also significantly depend on morphology, surface composition, surface area and its structure. High surface-area carbon-material have been broadly used for numerous applications including sensing, sorption, photovoltaic, storage, catalysis and H_2 evolution applications. Graphene, as a novel single layer and two dimensional materials with high chemical stability, large surface-area and thermal stability and high intrinsic electron mobility, is a very promising candidate for solar cells, electrochemistry, nano-electronics, photocatalysis etc. [22,23]. Due to its unique atom-thick 2d structure and remarkably physic-chemical properties, graphene based materials have been making a profound impact in photoelectrochemical and photocatalytic degradation applications especially WO_3/graphene system. It is worth mentioning that large surface area, optical transmittance, and high electrical-conductivity of graphene are appreciated in promoting electron-transfer in different applications especially photocatalytic performance [24,25,43]. Few metal-oxides, sulfides and nanoparticles with graphene based composites have been studied for photocatalytic H_2 production and [26–28]. However, little consideration has been focused on graphene modified WO_3 composites for H_2 fuels production. In present work, novel graphene-WO_3 and Nd-WO_3/graphene composites were prepared by hydrothermal method for the characterization of various properties. The as-synthesized composites showed excellent photocatalytic performance for hydrogen production under visible light irradiation.

2. Materials and methods

2.1. Materials and synthesis

Sodium-tungstate dehydrate ($Na_2WO_4{\cdot}2H_2O$), neodymium(III) acetate-hydrate ($(CH_3CO_2)_3$ $Nd{\cdot}3H_2O$), graphite, sodium chloride (NaCl), sulphuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), phosphoric acid (H_3PO_4), ethanol, distilled water and hydrochloric acid (HCl) were used for current work without any further purification. WO_3 nanostructure using $Na_2WO_4{\cdot}2H_2O$, and NaCl was prepared through facile hydrothermal method as reported in our previous work [29,30]. Nd-WO_3 composites were synthesized by dissolving 0.2 M solution of $Na_2WO_4{\cdot}2H_2O$ in 100 water. Then particular content of $(CH_3CO_2)_3$ $Nd{\cdot}3H_2O$ was added into above solution with constant stirring. Desired content of HCl and hydrochloric acid were, then, added in solution to control structure of material and pH. The solution, after 30 min stirring, was poured into 100 ml autoclave for heating at 180 °C for 24 h. The acquired solution was centrifuged, washed twice and dried at 70 °C. Moreover, graphene nanostructures were prepared from graphite-powder using hummer's scheme. 0.225 g powder of graphite is dissolved in 9:3 ratio solutions of H_2SO_4 and H_3PO_4 and stirrer continuously. 1.32 g of $KMnO_4$ was added into the solution with continuous stirring for 6 h until it become dark green. Then 10 ml of HCl and 30 ml of deionized water are added in the above solution. Centrifuge the prepared solution and then washed several times with distilled water and place it in oven for drying at 90 °C for 24 h. The 50 mg prepared powder of WO_3 was added in 40 ml ethanol in a glass beaker. Particular contents of graphene (1%, 4%, 7% and 10%) were added in WO_3 solution and then placed it for ultrasonic treatment for 1.5 h. Furthermore, the solution was transferred into 100 ml stainless steel autoclave and treated it in an oven for 23 h at 180 °C. The prepared precipitates were washed many-times by ethanol and de-ionized water. Then dried in a heating oven at 80 °C for 24 h and powdered material is formed.

2.2. Characterizations of prepared samples

Scanning Electron Microscope (SEM, HITACHI-S4800) was employed to explore the morphological properties of as-prepared composites. The X-Rays diffractometer with a source CuKa of wavelength 1.5418 Å (XRD, X′pert PRO-MPD Netherlands) was used to scrutinize the structural properties at operating-conditions (20–40 kV, 2.5–30 mA). Brunauer–Emmett–Teller (BET) (NOVA2200e-Quantachrome, USA) was used for the determination of pore distribution, pore volume, and specific surface area. EDX with SEM (JSM5910, INCA200 Oxford instruments) has been used for confirmation of material purity and elemental composition of synthesized nanostructures. XPS (ESCALAB 250 XPS System) with Al Kα, $h\nu = 1486.6$ eV used to investigate the chemical and electronic states of the existing composition of the prepared samples. UV–visible spectrophotometer (VARIAN, Cary 5000, USA) was used to study the absorbance of composites with solution of $BaSO_4$. The photoluminescence (PL) spectra was measured at room temperature with PL-spectrophotometer (HITACHI F-4500).

2.3. Photocatalytic activity measurement

The photocatalytic performance for production of green energy in the form of H_2 was determined inside closed quartz-reactor system under the metal-halide lamp with visible light illumination using cut-off filter ($\lambda \geq 400$ nm). In order to perform experiment, 30 mg photocatalyst (W, WG-1, WG-4, WG-7, WG-10 and Nd-WO_3) has been suspended in 100 ml solution comprising 0.1 M Na_2S and 0.04 M Na_2SO_3 inside photocatalytic reactor. The whole mixed solution was first placed in ultrasonic bath for 7 min and then the obtained solution was treated under N_2-gas for 30 min to confirm that catalytic reactor system was in anaerobic state, before exposure of visible light. The produced H_2 gas was intermittently examined with gas-chromatograph equipped with TCD detector, MS 5 A column, and carrier gas (N_2).

3. Results and discussion

The XRD patterns of photocatalysis including 1% graphene-WO_3 (WG-1), 4% graphene-WO_3 (WG-4), 7% graphene-WO_3 (WG-7), and 10% graphene-WO_3 (WG-10) nanostructure are presented in Fig. 1. XRD measurements were employed to determine the average crystal-size, and phase structure of hydrothermally synthesized photocatalytic material samples. These peaks are well-matched with WO_3 nanostructure that indexed through JCPDS No. 89-4476 and JCPDS No. 43-1035 for correspondingly representing monoclinic and hexagonal phase, demonstrating the high-crystallinity of photocatalytic material. No sharp peak regarding graphene was found, in WG-1 and WG-4, due to low doping content or shielded by main WO_3 peaks or restacking of graphene sheet. In WG-7 composite, diffraction peak owing to layer structure of graphene was observed at an angle of 26.62°, and 54.67°. XRD pattern of WO_3 nanostructure-graphene exhibited three main peaks at 23.14°, 28.27° and 33.26°, which was confirmed from the