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Charge transfer and intrinsic electronic properties of rGO-WO_3 nanostructures for efficient photoelectrochemical and photocatalytic applications

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ABSTRACT

The synthesis of WO_3 plate-like and rGO-WO_3 nanostructured catalysts by a new and simple wet chemistry followed by thermal decomposition method is reported. The prepared catalysts were characterized by X-ray diffraction, Fourier transformed infrared spectroscopy, Raman spectroscopy, UV–vis diffuse reflectance spectroscopy, photoluminescence spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscopy, scanning transmission electron microscopy techniques and Brunauer-Emmett-Teller surface area measurement. The photoelectrochemical properties and photocatalytic degradation of methylene blue by WO_3 and rGO-WO_3 nanostructured catalysts under simulated solar light, and visible light respectively was investigated. The incorporation of rGO in WO_3 decreased the band gap energy from 2.54 to 2.45 eV which also hindered the recombination rate of photogenerated electron-hole pairs and improved the electron transport properties. The plate-like structure of WO_3 and rGO-WO_3 nanostructured catalysts was observed from FESEM and TEM techniques. 5.3 and 4.2 folds higher photon-to-hydrogen conversion efficiency by rGO-WO_3 photoanode at 0.08 and 0.30 V respectively than WO_3 photoanode was demonstrated. The photocatalytic activity of WO_3 for the degradation of MB was also improved by forming a composite with rGO. The mechanism of the photoelectrochemical and photocatalytic process was discussed. This study provides a simple and scalable pathway to produce highly efficient rGO-WO_3 nanostructured photocatalyst for harvesting solar energy efficiently.

1. Introduction

The semiconductor photocatalysis is an excellent technique intended for solar energy conversion and environmental remediation [1]. To achieve clean and renewable energy, the direct conversion of solar energy to chemical energy by water splitting using photocatalysis is one of the best ways. The water splitting by solar energy in the presence of a semiconductor catalyst is an artificial photosynthesis process which converts the solar energy into hydrogen (H_2) and oxygen (O_2). The photoelectrochemical (PEC) cell is one of the best and widely used water splitting devices which involves solar energy collection with water electrolysis [2–4]. The PEC water splitting is a challenging technique, but it has the convenience of easy adoption and in-situ storage facilities. The TiO_2 has been broadly used as semiconductor photocatalyst for decontamination of organic pollutants and water splitting applications [2]. However, the demerits such as fast recombination of electron-hole (e^--h^+) pairs and lack of visible light absorption of TiO_2 limit on its efficient utilization [5].

The tungsten oxide (WO_3) is an n-type semiconductor material and has attracted much attention as visible-light-driven photocatalyst because of merits, such as narrow band gap energy (2.4–2.8 eV), deeper valence band (+ 3.1 eV) and superior physicochemical and thermal stability [6–8]. The efficiency of the pure WO_3 for the photocatalytic applications can be improved by inhibiting the recombination of e^--h^+ pairs. The enhancement of the photocatalytic activity of WO_3 has been achieved by adopting several methods which include, morphology control [9], semiconductor coupling [10], noble metal deposition [11], metal ion doping [12] and, formation of composites with graphene and/or reduced graphene oxide (rGO) [13]. Among these methods, the formation of composites with graphene and rGO has attracted tremendous interest because of the special properties such as high surface area, high electrical conductivity (10^6 S cm^{-1}), high carrier mobility (200,000 cm^2 V^{-1} S^{-1}) and, efficient electron (e^-) collection and transportation [14–16]. The composites formed with graphene such as TiO_2-graphene, CdS-graphene, ZnO-graphene, $Sr_2Ta_2O_7$-graphene and BiOBr-graphene oxide have been reported for photocatalytic

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applications [17–23]. But, there are few reports available on graphene and rGO-WO_3 composites for PEC application [24–26] and photocatalytic decontamination of environmental pollutants [13,27–29] and the composites have some drawbacks like the weak interaction with rGO and involve tedious synthesis procedure. Hence it is very urgent to develop a simple and scalable method for producing rGO-WO_3 composites for efficient utilization of solar energy for various applications.

To the best of our knowledge, for the first time, we developed a new and simple wet chemistry followed by thermal decomposition method for the synthesis of WO_3 plate-like and rGO-WO_3 nanostructured catalysts. The prepared catalysts were characterized by various techniques such as X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), Raman spectroscopy, UV–vis diffuse reflectance spectroscopy (UV–vis–DRS), photoluminescence (PL) spectroscopy, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and Brunauer-Emmett-Teller (BET) surface area measurement. The efficiency of the synthesized catalysts was investigated for photoelectrochemical and photocatalytic degradation of methylene blue (MB) under simulated solar light and visible light respectively. The reduction in the band gap from 2.54 to 2.45 eV was achieved by incorporation of rGO in WO_3 which also hindered the recombination of photogenerated e^--h^+ pairs and improved the electron transport properties. The photon-to-hydrogen conversion efficiency by rGO-WO_3 photoanode was improved to 5.3 fold higher than WO_3 photoanode. The photocatalytic activity for the degradation of MB was also improved by forming a composite with rGO and WO_3. The mechanism of the photoelectrochemical and photocatalytic process was discussed. We demonstrate a simple and scalable pathway to fabricate highly efficient rGO-WO_3 nanostructured photocatalyst for efficient conversion of solar energy.

2. Experimental

2.1. Materials

Graphite flake, natural (10 mesh) was procured from Alfa Aser, USA. Sodium nitrate ($NaNO_3$), sodium sulphate (Na_2SO_4), sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl), Methylene blue (MB) and isopropyl alcohol (IPA) were procured from Merck Ltd., India. Tungstic acid (H_2WO_4) was procured from Loba, India. ITO glass substrates ($< 10\ \Omega$, 1.1 mm thickness, $> 90\%$ transmittance) were procured from Shilpa Enterprises, India. All chemicals and reagents were of analytical grade and were used as such without further purification, and double distilled water was used throughout this work.

2.2. Synthesis of rGO-WO_3 nanostructures

The graphene oxide (GO) was prepared by Hummers method with some modifications [30], and it was reported elsewhere [20]. The GO dispersion in water (1 mg mL^{-1}) was prepared by sonication for 1 h. In a typical procedure, appropriate amount of the GO dispersion was added with 50 mL of water and 0.5 g of H_2WO_4. The mixture was sonicated for 2 min and stirred for 4 h at 30 °C (± 1 °C). Then, the solid product obtained was centrifuged and dried at 70 °C under vacuum. The product was calcinated at 300 °C for 1 h which resulted in rGO-WO_3 nanostructures. Without using any special atmosphere or chemical reagents, the GO could be reduced to rGO by heating it at 300 °C for 1 h [31]. The amount of GO dispersion was varied as 0.46, 2.31 and 4.60 mL to get 0.1, 0.5 and 1.0 wt% with respect to 2 mmol of WO_3 (equal to ~ 0.46 g) and the resulted rGO-WO_3 nanostructures are named as 0.1 GW, 0.5 GW and 1.0 GW respectively. The pure WO_3 was prepared by following the above procedure without adding GO dispersion.

2.3. Characterization

XRD spectra were recorded in the 2θ range of 5° to 80° with a step size of 0.05° and a scan speed of 1° min^{-1} using Cu Kα radiation (Rigaku Ultima III X-ray diffractometer 40 kV, 30 mA). Raman spectral analysis was carried out using High Resolution "LabRAM Hr800" Raman-LTPL Spectrometer with Ar Laser wavelength of 632.8 nm. FTIR spectra were recorded by "Thermo Scientific (Nicolet iS5)" spectrometer. The FESEM images were captured using "JSM-6700F, JEOL" instrument. The TEM images were captured using "ALOS F200X" instrument with an acceleration voltage of 200 kV. The elements present were mapped using STEM technique. XPS analysis was carried out using "PHI 5000 Versa Probe II" instrument, UV–vis–DRS spectrum was recorded by "Shimadzu UV-2600" UV–visible spectrophotometer equipped with an integrated sphere assembly and $BaSO_4$ as the reflectance reference. The photoluminescence (PL) spectra were recorded using "HORIBA Fluoromax 4CP-TCSPC" spectrophotometer with an excitation wavelength of 325 nm. The specific surface area of the catalysts was calculated using the Brunauer-Emmett-Teller (BET) model by measuring the N_2 adsorption-desorption isotherms with "Autosorb-iQ (Quantachrome Instruments, Boynton Beach, Florida, USA)" at 77 K. Before measurement, the samples were activated at 120 °C for 12 h. The Zeta potential of the samples was measured as a function of pH using "Zetasizer Nano ZSP, Malvern". The pH of the solution was adjusted with diluted HCl solution and the pH measurement was carried out by digital micro controller pH meter (Roy instruments).

2.4. Photoelectrochemical activity evaluation

A homemade three-electrode electrochemical cell (Fig. S1) was used to investigate the photoelectrochemical activity of the catalysts. The catalysts coated on ITO substrates, Ag/AgCl electrode and a platinum wire were used as working electrode, reference electrode and counter electrode respectively. The fabrication of working electrode involves, 5 mg of catalysts (WO_3 and rGO-WO_3) dispersed in 0.5 mL of IPA under sonication for 5 min 50 µl of the dispersion was dropped on ITO substrate in 1 cm^2 area and then air-dried. The coating process was repeated once again. The coated substrates were vacuum dried at 65 °C for 6 h. The electrochemical and photoelectrochemical measurements were carried out in 0.1 M Na_2SO_4 supporting electrolyte solution. The "Oriel® LCS-100™" solar simulator (Newport Corporation, USA, AM 1.5G, 100 mW cm^{-2}) was used as the irradiation source. Electrochemical and photoelectrochemical studies were performed using "CHI608B" electrochemical analyzer.

2.5. Photocatalytic activity evaluation

The photocatalytic activity of the catalysts was investigated for the photocatalytic degradation of MB under visible light irradiation in "Heber Annular Type photo reactor" (Fig. S2). A 500 W tungsten halogen lamp was held in borosilicate immersion jacketed tube, the IR radiation from the light source was cancelled by water circulation in outer jacket of the immersion tube. Highly polished and anodized aluminium reflector was fitted in the inner surface of the reactor hood. In a typical experiment, 15 mg of the catalyst was suspended in 50 mL of 10 mg L^{-1} MB solution. The suspension was first aerated in the dark for 30 min to reach adsorption-desorption equilibrium and then irradiated under aeration for thorough mixing. At regular time interval of 15 min on irradiation, 3.5 mL of the suspension was collected and then the catalyst was removed by centrifugation. The degradation of MB in the solution was analyzed by measuring the absorbance at 665 nm wavelength with "Aventes UV–vis spectrometer". Total organic carbon (TOC) content of the MB solution before and after the photocatalytic reaction was measured using "TOC-TN (SHIMADZU CORP., India)" analyzer. For the TOC analysis, 1 mL of the MB solution was diluted to 20 mL with double distilled water.