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Photoelectrochemical and photocatalytic activity of TiO_2-WO_3 heterostructures boosted by mutual interaction

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ABSTRACT

The TiO_2-WO_3 heterostructures with superior interfacial interactions were synthesized by simple solvothermal method followed by calcination. The electrical property of the heterostructures was tuned by varying the amount of TiO_2 and WO_3 to achieve higher photoelectrochemical activity. The prepared samples were characterized by X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscopy, scanning transmission electron microscopy and UV–vis diffuse reflectance spectroscopy. The strong interaction in the interface of TiO_2-WO_3 heterostructures and the solar spectral response of TiO_2 and WO_3 reduce the electron-hole pair recombination rate and enhance the photoelectrochemical activity. The TiO_2-WO_3 heterostructures show 17 times higher photon-to-hydrogen conversion efficiency than pure TiO_2 and WO_3 under solar light and almost complete removal of organic pollutant in 60 min under visible light. The TiO_2-WO_3 heterostructures also show good adsorption capacity for organic pollutants. The present study demonstrates that the prepared TiO_2-WO_3 heterostructures are promising materials for efficient water splitting as well as adsorption and photocatalytic removal of organic pollutants.

1. Introduction

Semiconductor photocatalysis is an extensively used technique for water splitting [1,2], photoelectrochemical cells [3,4] and decontamination of organic pollutants in air as well as water [5–7]. Because of the convenience of easy adoption and in-situ storage facilities, the photoelectrochemical cell is widely used in water splitting devices which involves water electrolysis using solar energy [8–10]. Photocatalysis is used to remove pollutants by conversion of optical energy into the electrochemical energy required for photo-oxidation in the presence of a catalyst [11]. In order to effectively utilize the solar energy, an intense focus is required for development of photocatalyst which could produce hydrogen and oxygen, and degrade pollutants under sunlight irradiation. Noticeably, TiO_2 has proven to be a suitable candidate for photoelectrochemical and photocatalytic applications [1,8,12]. However, there are some disadvantages such as wide band gap of about 3.2 eV, fast recombination of electron(e^-)-hole(h^+) pairs, and low electrical conductivity ($\sim 1 \times 10^{-12}$ to $\sim 1 \times 10^{-7}$ S cm^{-1}) making it not fit for efficient utilization [13]. Many approaches have been adopted to improve the photocatalytic property of TiO_2 such as doping with metal or metal oxides [14], noble metal deposition [15] and anion doping [16] etc.

The TiO_2 coupled with metal oxides shows better photocatalytic activity which is attributed to the separation of charges [17]. The tungsten oxide (WO_3), having low band gap values in the range of 2.4–2.8 eV, deeper valence band of + 3.1 eV, 15 times more acidity than TiO_2 and good thermal stability, is suitable to couple with TiO_2 [18–20]. The lower conduction band (CB) position of WO_3 than that of TiO_2 facilitates the electron transfer from TiO_2 to WO_3 and the holes transfer in opposite direction. Hence better charge separation may be achieved. Previous studies show that the enhanced photocatalytic activity of TiO_2/WO_3 is ascribed to their high surface acidity, high surface area and reduction in the rate of recombination of e^--h^+ pairs at the interface [21]. Designing of TiO_2/WO_3 heterostructures with high interaction at their interface can obviously target the above tasks [17,22]. TiO_2/WO_3 heterostructure prepared by hydrothermal method using preformed nanoparticles shown good photocatalytic degradation ability [23]. Qamar et al. reported the preparation of WO_3 surface modified TiO_2 thin film using plasma-assisted sputtering method and achieved enhanced PEC activity but this involves expensive equipment and tedious conditions [24]. Higashimoto et al. reported the preparation of WO_3/TiO_2 by impregnation of tungstate precursor solution with commercial TiO_2 and also physical mixing of c-WO_3 with TiO_2. There were spreaded on ITO substrate with triethyleneglycol as binder and then

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calcinated which shows enhanced photocurrent under UV light irradiation [25]. The TiO_2-WO_3 heterostructured system for photoelectrochemical application was also reported in which the fabrication involves complex electrodeposition procedure [26]. Electrodeposition of WO_3 on TiO_2 nanotube photoanode for solar water splitting with simultaneous wastewater treatment was reported. In which the fabrication of photoanode again involves tedious and time taking process [17]. There are several reports are available on synthesis of TiO_2/WO_3 photocatalyst by dip coats, anodization, sputtering and electrodeposition [27–32]. However, the use of TiO_2/WO_3 photocatalyst in commercial devices is still limited because of the low quantum yield due to low absorption of light, complex synthetic method and unexplored nature of heterostructures. Hence, it is high time to develop an easy method to optimize the targeted optical properties in TiO_2-WO_3 heterostructures with high interfacial interaction aiming for use in solar energy conversion devices.

In this work, TiO_2-WO_3 heterostructures were fabricated using solvothermal method and subsequent calcination process. The working electrode preparation to evaluate the photoelectrochemical activity involves simple drop-casting method. The prepared TiO_2-WO_3 heterostructures have superior interfacial interactions with tunable electrical property by varying the amount of TiO_2 and WO_3 and show better photoelectrochemical and photocatalytic activity. The prepared samples were characterized by various techniques such as X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and UV–vis diffuse reflectance (UV–Vis–DRS) spectroscopy. The enhanced photoelectrochemical and photocatalytic activity are attributed to the reduction in e^--h^+ pair recombination, solar light response of TiO_2 and WO_3 and strong interaction in the interface of TiO_2-WO_3 heterostructures. The TiO_2-WO_3 heterostructures also show good adsorption capacity towards the organic pollutant, methylene blue (MB). The efficient water splitting, as well as adsorption and photocatalytic removal of organic pollutants by the TiO_2-WO_3 heterostructures, have been demonstrated in the present study. Considering the literature on TiO_2-WO_3 as photocatalysts, the present work has several advantages. The fabrication methods of TiO_2-WO_3 heterostructures and the photoelectrodes involve mild reaction condition, inexpensive equipments, simple and well-controlled procedure which can be used for large scale production.

2. Experimental

2.1. Materials

Titanium isopropoxide (TTIP) was purchased from Aldrich, India. Tungstic acid (H_2WO_4) was purchased from Loba, India. Hydrochloric acid (HCl) and isopropyl alcohol (IPA) were purchased from Merck Ltd., India. Indium doped tin oxide (ITO)-coated glass substrates ($< 10\,\Omega$, 1.1 mm thickness, > 90% transmittance) were purchased 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 TiO_2-WO_3 heterostructures

The appropriate amount of TTIP and H_2WO_4 were stirred in 60 ml of ethanol for 10 min, and then 15 ml of HCl (1 M) was added dropwise and stirred for 15 min. The reaction mixture was maintained at 150 °C for 6 h in teflon-lined autoclave. The obtained product was centrifuged, washed using water and ethanol several times and then dried under vacuum. TiO_2-WO_3 heterostructures of different compositions were prepared by varying the amount of TTIP and H_2WO_4, and the corresponding products were named as given in Table 1. For comparison, the pure TiO_2 was prepared by following the above procedure without adding H_2WO_4 [33]. The pure WO_3 was prepared as follows: 5 mmol of H_2WO_4 was refluxed in 50 ml of ethanol for 4 h, and then ethanol was removed by distillation. The resulting product was calcinated at 300 °C for 1 h.

2.3. Characterization

The crystalline phase of the samples was characterized by XRD study using Rigaku Ultima III X-ray diffractometer (Cu Kα radiation, $\lambda = 1.5406$ Å) operating at 40 kV and 30 mA. The Raman spectroscopy was performed using high resolution “LabRAM Hr800″ Raman-LTPL spectrometer with Ar Laser wavelength of 632.8 nm. The “Thermo Scientific (Nicolet iS5)” spectrometer was used to record FTIR spectrum of the samples. The microstructure of the samples was investigated by TEM analysis using “ALOS F200X” instrument with 200 kV accelerating voltage. The elements present in the microstructure were mapped using STEM technique. The “PHI 5000 Versa Probe II” instrument was used to perform XPS analysis, and the binding energies were measured using the C 1 s peak at 284 eV as an internal reference. The optical property of the samples was studied by UV–Vis–DRS spectrum by “Shimadzu UV-2600” UV–visible spectrophotometer equipped with an integrated sphere assembly, and $BaSO_4$ was used as the reflectance reference.

2.4. Photoelectrochemical activity

The photoelectrochemical property of the samples under simulated solar light was investigated using “CHI608B” electrochemical analyzer in a three-electrode electrochemical cell (Fig. S1). 5 mg of the sample was dispersed in 0.5 ml of IPA under sonication, and 50 µl of the dispersion was drop-casted over 1 cm^2 area of ITO coated glass substrate, and air-dried. The coating procedure was repeated one more time, and then the substrate was vacuum dried. The sample coated ITO substrate, Ag/AgCl and a platinum wire were used as working, reference and counter electrode respectively, and 0.1 M Na_2SO_4 was used as the supporting electrolyte. The electrochemical cell was an open system and was in equilibrium with the atmosphere. The irradiation source was “Oriel® LCS-100™” solar simulator (Newport Corporation, USA, AM 1.5 G, 100 mW cm^{-2}).

2.5. Photocatalytic activity

The photocatalytic activity of the samples was evaluated by studying the photocatalytic degradation of MB under visible light irradiation in the “Heber Annular Type Photo-reactor” (Fig. S2). A 500 W tungsten halogen lamp (9000 lm) was used as the visible light source. The IR radiation from the light source was cancelled by water circulation in the outer jacket of the immersion jacketed borosilicate tube. The inner surface of the reactor hood was fitted with highly polished and anodized aluminium reflector. In a typical experiment, 15 mg of the sample was added to 50 ml of MB solution containing 10 mg L^{-1}. The mixture was aerated throughout the photocatalytic experiment for thorough mixing. The mixture was first kept in the dark for 30 min to reach adsorption-desorption equilibrium and then irradiated. During irradiation, 3.5 ml of the mixture was collected at an interval of 15 min and then the catalyst was removed by centrifugation. The absorbance of the solution at 665 nm wavelength was measured using “Aventes UV-Vis spectrometer” to evaluate the % degradation of MB.

3. Results and discussion

3.1. Characterization

Fig. 1(a) displays the XRD patterns of the prepared samples. The XRD patterns of TiO_2 and WO_3 are well matched with the standard JCPDS card no. 21–1272 and 89–4476 respectively. The anatase TiO_2 planes of (101), (103), (004), (112), (200), (105), (211), (213) and (204) are perfectly observed in the XRD patterns of TiO_2 at 25.2°, 36.6 °,