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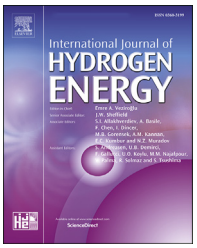

Mesoporous Ta_2O_5 nanoparticles as an anode material for lithium ion battery and an efficient photocatalyst for hydrogen evolution

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ABSTRACT

Mesoporous Ta_2O_5 nanoparticles (NPs) with high surface area were prepared using an 1-methyl 3-(2-bromoethyl) imidazolium bromide ionic liquid (IL) as structure directing and porous inducing agent. We have characterized the Ta_2O_5 nanoparticles (NPs) by XRD, BET analysis, TEM, SEM, DRS, FTIR, Raman spectroscopy and TG-DTA. From BET analysis a large surface area of asprepared Ta_2O_5 NPs was found to be 236.1 $m^2\ g^{-1}$. More importantly, Ta_2O_5 nanoparticles are less explored anode material for lithium ion battery as well as an effective photocatalyst for hydrogen generation. The significant reversible capacity of 150 mAh g^{-1} has been observed in Ta_2O_5 NPs even after 50 cycles at C/10 current rate. In addition to this, asprepared Ta_2O_5 NPs synthesized using IL exhibited remarkable hydrogen generation of 563.5 $\mu molg^{-1}\ h^{-1}$ compared to other Ta_2O_5 samples which are due to high surface area, small pore wall thickness and presence of surface hydroxyl groups on the photocatalyst.

Introduction

Increasing demand for energy in the current world and alarming environmental concerns urges contemporary researchers to develop innovative, efficient, low cost and environmentally benign electrochemical energy storage devices. In order to fulfill the above-mentioned perspectives, rechargeable lithium ion battery (LIB) is being considered as promising electrochemical energy storage device because of its outstanding features like high voltage, high volumetric and gravimetric energy density, low self-discharge rate, no memory effect, quick charge acceptance, excellent cycle life and wide temperature range of operation [1]. Nevertheless, LIB's power density, energy efficiency and rate performance have to be improved prior to their widespread usage [2]. However, to achieve the future demands of hybrid electric vehicles and clean energy storage, we need to enhance charge/discharge performances by more than one/two order of magnitude. Literature survey shows that designing the electrode material having nanosize could be more advantageous [3]. Rechargeable LIB has been used enormously to power the myriad portable electronic devices like cell phones, personal digital assistant (PDA), laptops, digital cameras and hybrid

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electric vehicles which favour environment by minimizing CO_2 gas emissions emanating from the rapid rise in transportation [4]. Currently, commercial anode materials mainly comprised of graphite, which diminishes the lithium storage performance in terms of energy and power density due to the low theoretical capacity (LiC_6, 372 mA h g^{-1}) and low Li-ion transport rate [5]. Moreover, attempts have been made to introduce new anode material for LIB instead of carbonaceous and the graphite electrode, due to their higher theoretical capacity and high packing densities, which induce high volumetric energy densities in energy devices and to avoid the formation of metallic lithium on the electrode during charging which gives rise to the safety problem [6,7]. Another alternative and promising energy generation systems is the photocatalytic water splitting reaction. Photocatalytic water splitting process is an economical approach to convert solar energy into renewable and storable hydrogen and oxygen since, both sunlight and water abundant on earth [8]. H_2 is a superb energy carrier, no environmentally harmful gases are produced during the combustion process of H_2 and hydrogen possess highest energy density per unit weight (120 MJ/kg) [9], and is the cleanest source of energy so it could be the ultimate fuel for posterity. Various nanostructured transition metal oxides have been employed as an anode material for LIB and catalyst for photocatalytic hydrogen generation [10–20]. Amongst transition metal oxides, tantalum pentoxide (Ta_2O_5) is one of the most significant transition metal oxides due to its salient features like wide band gap (E_g ~4.0 eV), extraordinary physical and chemical properties, high dielectric and refractive coefficients, excellent photoelectric performance and chemical stability [20–24]. To the best of our knowledge, there are some reports available on the synthesis of Ta_2O_5 nanomaterials for the H_2 generation [25–29]. Recently, mesoporous nanomaterials have been employed as electrode materials for LIB and photocatalytic hydrogen generation [30–34]. Interestingly, ionic liquids could be employed as promising reaction media to synthesise inorganic nanomaterials having mesoporous structure, beneficial morphologies and better surface area which plays vital role for diverse applications [35–45]. To the best of our knowledge, only a few reports are available on the synthesis of mesoporous Ta_2O_5 nanomaterials for the H_2 generation [46–51]. It has been anticipated that highly crystalline nanomaterials are promising candidates for efficient photocatalytic activity. But, to synthesize highly crystalline nanomaterials requires high-temperature supply which in turn increase the particle size and decrease the surface area [52]. So to combat the above mentioned issues, researchers have investigated and reported amorphous nanomaterials as better photocatalyst compared to crystalline nanomaterials. In fact, amorphous nanomaterials possess more negative conduction band potential, large surface area, higher active sites and shorter diffusion path for charge carriers. There are some reported works on amorphous nanomaterials to replace crystalline nanomaterials for photocatalytic applications [53–55]. Zhang et al. [56] reported that nanosized amorphous tantalum oxide acts as an efficient photocatalyst for hydrogen generation. Wang et al. [57] investigated and reported the crystalline-to-amorphous transformation of tantalum-containing oxides for photocatalytic hydrogen generation. Up to now, only a few reports are available with respect to Ta_2O_5 employing as anode material for lithium ion battery. Qin et al. [58,59] fabricated amorphous Ta_2O_5 thin films by reactive pulsed laser deposition and used as an anode material for LIB exhibiting a reversible discharge capacity of 400 mAh g^{-1}, explored the lithium insertion and transport behavior in a Ta_2O_5 film. Dang et al. [60] also reported lithium insertion/deinsertion characteristics of nanostructured amorphous Ta_2O_5 thin films.

Herein, we have reported the ionic liquid assisted hydrothermal synthesis of mesoporous Ta_2O_5 NPs having amorphous phase and crystalline phase obtained by calcining at higher temperature. And also, we have carefully characterized series of mesoporous Ta_2O_5 NPs for photocatalytic hydrogen generation and LIB applications. Furthermore, we have attempted to reveal how amorphous Ta_2O_5 NPs could be employed as better photocatalyst for water splitting reactions and crystalline Ta_2O_5 NPs could be employed as anode material for lithium ion battery.

Experimental section

Ionic liquid assisted hydrothermal synthesis of Ta_2O_5 nanoparticles

1.3 mmol of $TaCl_5$ was dispersed in 20 mL absolute ethanol and stirred for 1 h. Then 0.5 g of 1-methyl 3-(2-bromoethyl) imidazolium bromide ionic liquid was added to the above solution mixture followed by addition of 1 mL H_2O and stirred for 30 min. The obtained solution was transferred into the Teflon-lined autoclave (capacity 40 mL) and heated at 200 °C for 48 h. The white gel-like product was subjected to washing twice with distilled water followed by methanol several times and dried at 60 °C for 12 h. The dried product was ground and calcined at 400 °C and 800 °C for 3 h. The samples were named as Ta_2O_5-400 and Ta_2O_5-800 in which number indicates calcination temperature in °C. Synthetic preparation has been depicted in Scheme 1.

Material characterization

X-ray diffractograms were collected on RigakuSmartLab X-ray diffractometer with mono-chromatized Cu Kα radiation source (λ = 1.541 Å). UV–Vis diffuse reflectance spectra were recorded using Lambda-35 (Perkin Elmer) spectrophotometer in the wavelength range 200–1200 nm. The FTIR spectra were collected using Bruker Alpha-P spectrometer. Raman spectra were recorded at different spots in backscattering geometry using 514.5 nm Ar^+ laser in HORIBA LabRam HR800. The rate of recombination of charge carriers were studied by using Agilent Cary Eclipse Fluorescence spectrometer using Xe lamp with an excitation wavelength of 310 nm. Particle sizes and morphologies were characterized by JEOL-JSM-6390LV scanning electron microscopy, and JEOL/JEM 2100 high-resolution transmission electron microscopy. The chemical composition of the Ta_2O_5 NPs was determined by energy-dispersive X-ray spectroscopy (EDX) attached with FESEM (Quanta 3D FEG). Surface area and pore characteristics were analysed at liquid nitrogen temperature by Quanta Chrome Nova-1000 surface analyser instrument. Adsorption desorption isotherm measurements were carried out for the evolution of porosity and

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