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Nitrogen doped anatase-rutile heterostructured nanotubes for enhanced photocatalytic hydrogen production: Promising structure for sustainable fuel production

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ABSTRACT

Nitrogen doped anatase-rutile heterostructure nanotubes were prepared by controlled ammonia annealing of TiO₂ nanotubes synthesized by rapid break down anodization technique. The presence of anatase and rutile phases in a single nano-tube is confirmed by HRTEM. X-ray photoelectron spectroscopy confirmed the presence of oxygen vacancy and N-doping. The band gap studies revealed visible light absorption of the N-doped samples and Mott–Schottky analysis showed cathodic shift in flat band potential for the N doped samples indicating an increase in n-type conductivity. The photoelectrochemical studies revealed higher photocurrent and photon to current conversion efficiency for N-doped samples supporting the Mott Schottky results. The photo-catalysts were prepared by loading Pt on to the pristine and N-doped nanotubes by NaBH₄ reduction. The synergistic role of non-stoichiometry and Pt loading towards photocatalytic activity is demonstrated from the H₂ generation studies by water splitting. The enhanced photocatalytic performance of the Pt loaded N–TiO₂ nanotubes is ascertained from the H₂ generation rate of ~30 mmol h⁻¹ g⁻¹, which is one of the highest observed rate under simulated solar radiation of 1.5 AM as well as visible light. The significance of surface area, mesoporous structure and visible light absorption in enhancing H₂ generation is ascertained by BET and band gap studies. The present strategy of preparing high surface area Pt loaded N doped anatase-rutile TiO₂ heterostructure nanotubes is a promising method for the synthesis of highly efficient composite photocatalysts for solar light harvesting.

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Introduction

Hydrogen as a fuel from renewable energy resources has drawn immense attention in the research community due to the dramatic increase in energy need, depletion of natural nonrenewable energy resources like coal and petroleum, and environmental pollution. Among the various methods of H₂ production, light assisted water splitting using Pt loaded TiO₂ photocatalyst is of high interest due to the abundant availability of water, sunlight, clean way of H₂ production, stability of TiO₂ towards photochemical corrosion and abundance in earth crust [1,2]. However, TiO₂ absorbs only the UV part of sunlight. Among the various modifications adopted to make TiO₂ visible light absorbing, anion doping especially nitrogen doping is found to be the most effective [3–6]. Asahi et al. reported enhancement of visible light absorption in TiO₂ upto 550 nm on N-doping, which was attributed to the formation of inter band states on top of TiO₂ valence band by mixing of N 2p and O 2p states [7]. Subsequently many studies reported band gap narrowing by N doping in TiO₂ [8–10]. Some studies stated negligible band gap narrowing and ascribed the observed visible light activity to localized N 2p states within the band gap [11,12]. Effect on N-doping on different phases of TiO₂ has also been reported [10,13]. However, studies combining N-doping with Pt loading witnessed enhanced hydrogen evolution rate by sun light water splitting [14–17].

It has been reported that compared to zero dimensional structures, mesoporous one dimensional TiO₂ nanostructures exhibit higher photocatalytic activity with minimal Pt loading because of better charge mobility, low electron–hole recombination rate and large surface area [18,19]. In addition, catalysts based on anatase/rutile heterostructures were found to exhibit higher photocatalytic activity compared to those based on anatase or rutile alone because of the efficient charge separation at the phase junction, where the electron transfer is much faster than the recombination process [20–25]. Although there are reports on H₂ generation using Pt loaded anatase-rutile as well as Pt loaded mesoporous/one dimensional N–TiO₂ catalysts we have not come across any studies on H₂ generation by water photolysis using catalysts having all these properties. Hence studies pertaining to synthesis of Pt loaded mesoporous, N-doped anatase/rutile TiO₂ heterostructure nanotubes and hydrogen generation by solar/visible light water splitting using them were carried out expecting enhanced H₂ production. The present study opens a pathway for the synthesis of mesoporous quasi-one dimensional TiO₂ heterostructures and their band gap engineering for efficient solar hydrogen production.

Experimental

Synthesis of Pt–N–TiO₂ nanotube powders

Anatase TiO₂ nanotube powders were synthesized by, previously reported, potentiostatic rapid breakdown anodization technique using Ti and Pt foils as the working and counter electrodes respectively in 0.1 M perchloric acid electrolyte [26]. A constant potential of 10 V was applied across the electrodes,

kept 15 mm apart, using a programmable DC power supply (Agilent N6700series). The anodization process was continued till the foil transformed completely into TiO₂ powder. The TiO₂ powder obtained was washed several times with de-ionized water, centrifuged and dried for 12 h at 100 °C. The nitrogen doped TiO₂ nanopowders were prepared by annealing the as prepared TiO₂ nanotube powders under 50 sccm NH₃ flow at 450 and 550 °C for 2 h followed by furnace cooling. The N-doped TiO₂ nanotube powders prepared at temperatures of 450 and 550 °C are designated as N-TiO₂-450 and N-TiO₂-550 respectively.

The platinum loading of TiO₂ photocatalyst was carried out, as reported previously [16]. Since highest H₂ generation was observed for 2 wt% platinum loading in our previous study, the present TiO₂ samples are loaded with 2 wt% Pt. This is achieved by adding excess amount of sodium borohydride (NaBH₄) to a colloidal suspension of 50 mg TiO₂ nanotube powder in about 5 ml of aqueous chloroplatinic acid (H₂PtCl₆) solution containing 50 ppm Pt, under stirring. After the chemical reduction, the Pt loaded suspension was centrifuged and washed repeatedly with ethanol and distilled water followed by drying at 50 °C for 6 h. The photocatalysts prepared were designated as Pt-TiO₂, Pt-N-TiO₂-450 and Pt-N-TiO₂-550 respectively.

Materials characterization

The morphological analysis of the samples was done by Field Emission Scanning Electron Microscope (FESEM), (JEOL 6360) and Transmission Electron Microscope (TEM) (JEOL 2010). The samples for TEM studies were prepared by placing a drop of sample suspension in methanol on a carbon coated copper grid and allowing it to dry. The crystal structure of the nanotube powders was analyzed by selected area electron diffraction (SAED). The phase identifications of the pristine and doped samples were carried out using X-Ray Diffractometer (D8, Bruker). The Brunauer Emmett Teller (BET) surface area of the samples was measured using a surface area analyzer (ASAP Tri-star II 3020, US). Nitrogen gas was used as the adsorbate and the surface area was obtained from the N₂ adsorption–desorption isotherm. An UV Vis spectrometer (PerkinElmer, Lambda 750S) equipped with a 60 mm diameter integrated sphere in reflectance mode was used for band gap measurements. Photoluminescence studies were recorded using a Photoluminescence spectrometer (Renishaw, UK), equipped with a confocal microscope with an “argon ion laser” operating at 514.5 nm at a power level of 200 mW. The chemical state of pristine and doped samples was analyzed using an X-ray photoelectron spectrometer (XPS) (SPECs, Germany) equipped with Ar ion source for sputter-etch cleaning of specimens. Al K α X-ray at 1486.74 eV was used as the incident radiation. The photoelectron energy spectra were collected using the PHOIBOS 150 MCD-9 analyzer with a resolution of 0.67 eV for 656 kcps at a pass energy of 12 eV. The spectrometer was calibrated using a standard silver sample. Data were processed by SpecsLab2 software. The binding energy of C 1s electron from contaminated C at 284.6 eV was used as the reference to account for any charging of the sample and the peak positions were compared to standard

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