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Visible and direct sunlight induced H_2 production from water by plasmonic Ag-TiO_2 nanorods hybrid interface

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ABSTRACT

This report signifies the synthesis of TiO_2 nanorods (TNR ~79 nm) and nanospheres (TNS ~19 nm) and their Ag loaded counterparts AgTNR and AgTNS for the photocatalytic hydrogen production from water under monochromatic visible and direct sunlight. The Ag-TNR nanohybrid junction was sensitized at a matching monochromatic wavelength of 457 nm and sunlight to produce ~90 μmol and 105 μmol of gas, respectively, increase in the efficiency is explained due to the surface plasmon (SPR) effect of Ag nanoparticles and is also correlated to fluorescence quenching (due to better charge distribution along larger nano-interface), crystal structure and surface area (146 $m^2 g^{-1}$) of fabricated AgTNR nanocomposite. The elongated morphology of AgTNR led to the effective distribution of charge along larger interface resulting in the increase of photocurrent density (0.01 mA/cm^2) which boosts the reaction rate. Plasmonic metal (Ag) activated with matching wavelength to SPR produces an electric field and the TiO_2 present in the proximity encounters these effects results in the formation of Schottky barrier, the SPR effect is also more towards Ag-TiO_2 interface which results in the ejection of electron towards the conduction band of TNR.

This study demonstrated that Ag nanoparticles loaded lengthy TiO_2 nanorods (~79 nm) exhibited highly improved H_2 production (90 μmol) from water relative to TiO_2 nanospheres (~19 nm) due to the plasmonic effect at 457 nm light irradiation that also exhibited better H_2 production (105 μmol) rate under direct sun light (8 h) exposure.

1. Introduction

Titanium dioxide (TiO_2) based semiconductor nanostructures are both theoretically and technologically relevant for hydrogen production from water due to its stability, efficiency, availability and brilliant optical and electrical properties [1–3]. TiO_2 is a multifunctional material widely used for energy conversion processes such as photovoltaics, photocatalysis, and photoelectrocatalysis [4–7]. Several advanced and modified TiO_2 based electrodes have been reported since the discovery of photovoltaic cell by O'Regan and Grätzel in1991 [8]. Federico Bella et al. have reported [9–11] several polymer based flexible and vertically aligned TiO_2 nanotubes as the effective electrodes to avoid recombination, the quasi-1D TiO_2 showed superior charge transport and effective photoconversion efficiency, similarly Masoud Faraji et al. [12] have developed a Binder-free PANi-g-MWCNT/TiO_2NTs/Ti electrode material for the potential application in supercapacitors.

The photocatalytic performance of TiO_2 is strongly dependent on morphology and dimensionality; previous reports suggest that 1D nanostructures like nanotubes, nanorods etc, can be more useful [13–16] as the solar conversion efficiency is usually determined by the competition of electron transport towards the reaction site and recombination of electrons with holes, and these 1D structures provide larger interface for better charge distribution. Still the deficiencies like the optical absorption of TiO_2 [17] which is in UV region due to its larger energy gap (E_g ~3.2 eV) limits its efficiency, to overcome this drawback, doping and synthesis of nanodiodes with plasmonic metals like Ag and Au is used to sensitize it in visible light [18–21]. Reports reveal that doping of metals like Ag and Au leads to the formation of Schottky barrier which is further coined as Schottky nanodiodes [22,23]. These Schottky nanodiodes convert photon energy into electrical energy [24] and can be effective for photolysis of water. The metal doping of TiO_2 with Ag and Au is effective in two ways, by helping to sensitize it in visible light region due to the surface plasmon resonance (SPR) effect [25–27] and are also helpful in generating the high kinetic energy hot electrons under photon irradiation because of low electron heat capacity of metals permitting easy and nonadiabatic energy transfer [28]. These hot electrons emitted by the deposited

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metal are prompted towards metal-semiconductor interface and when the energy of the electron is high enough to cross over the Schottky barrier they are easily transferred to semiconductor conduction band (CB) [29] and are redistributed along the elongated interface of nanorods, nanotubes etc. Previous reports investigated the use of modified TiO_2 surface with Ag and Au for optimum photocatalytic activity for H_2 production [30,31]. These two modification related to TiO_2, i.e, loading with noble metals Ag /Au and transformation into 1D morphology has also been effective in several other photocatalytic processes like sensors, photovoltaics and environmental cleaning [32–37]. As shown in Fig. ESI-1 (electronic supporting information), certainly in the case of bulk material, it is difficult for the electrons to reach the reaction site due to fast recombination of charge carriers. Similarly, in the case of spherical nanoparticles they have to cross a number of grain boundaries which again led to their recombination but in the case of 1D nanostructures, the effective distribution of the electrons can help them to easily reach the respective reduction site.

So, the present study has been performed to study the role of the morphology of TiO_2 and Ag loading for H_2 production from the water using different monochromatic and sunlight illumination sources. Herein it was found that single monochromatic beam and sunlight with λ_{max} same as plasmonic absorption band of Ag-TiO_2 nanorod hybrid junction was responsible for enhanced photocatalytic hydrogen production from water.

2. Experimental

2.1. Chemicals and reagents

Analytic grade chemicals titanium butoxide ($Ti(OBu)_4$, 97%, Sigma-Aldrich), silver nitrate ($AgNO_3$, 99% Loba Chemie Ltd), sodium hydroxide (NaOH, 99%, SD Fine Ltd), sodium sulphide (Na_2S, 98% SD fine Ltd), nitric acid (HNO_3, 99%, Spectrochem Ltd), ethylene glycol (MW=4000, Loba Chemie), acetone (99%, Sigma-Aldrich) were used as received. All solutions were made using DI water obtained from Milli-Q (Millipore) an ultrafiltration system (35 mho cm^{-1} at 25 °C).

2.2. Synthesis of TiO_2 nanorods (TNR), nanospheres (TNS) and photodeposition of silver (Ag)

The hydrothermal synthetic approach was adopted for the synthesis of TNR. Commercially available TiO_2 (P25, Degussa Germany) was used as a precursor for the synthesis of TNR, which is a mixture of rutile and anatase polymorph (30% and 70%, respectively). In a typical experiment, a mixture of 2.5 g of TiO_2 (P25) was mixed with 35 mL NaOH (10 mol/L), and heated at 130 °C in a Teflon-lined autoclave for 20 h. The filtered mixture was washed several times with HNO_3 (0.1 mol/L) to adjust the pH at 7. The 50 mL of this suspension (pH=7) was treated hydrothermally in an autoclave at 150 °C for 48 h. The resulting slurry was then washed several times with DI water and dried at 100 °C to harvest the TNR.

TNS were synthesized by template synthesis approach reported elsewhere [38]. A mixture of $Ti(OBu)_4$ (1 mL) and ethylene glycol (22.2 mL) was stirred vigorously for 8 h. The mixture was poured quickly in 100 mL acetone containing 1.5 mL DI water and acetic acid (0.4 mL), and was further stirred at room temperature for 3 h to form titanium glycolate spheres. These spheres were stirred at 70 °C for 8 h to produce TNS and were washed several times with DI water and dried at 100 °C.

The metal (Ag) photodepositions [39] were carried out in the sealed reaction tubes (20 mL pyrex). In a typical procedure, 100 mg of respective TiO_2 powder TNS/TNR was suspended in the reaction mixture containing DI water and isopropyl alcohol (4 mL each), The respective amount of $AgNO_3$ (0.1 mol/L) corresponding to different wt % (1, 2, 3 and 5 wt%) was added to these suspension and purged with Ar for 20 min to create an inert atmosphere and was irradiated with UV (125 W, Hg arc) for 3 h under continuous stirring. The photocatalysts were washed several times with DI water under several cycles of centrifugation and then dried at of 40 °C. The Ag loaded samples were abbreviated as AgTNR (nanorods) and AgTNS (nanospheres).

2.3. Characterization and photocatalytic activity

The optical absorption properties of the photocatalysts were studied by UV–Visible (Analytic Jena, Specord 205, Germany) spectrophotometer using Hg and Xenon lamp as excitation sources. The crystal properties and unit cell structure were determined by X-ray diffraction (Pan analytic Xpert Pro, Almelo Netherlands) with Cu-Kα at 1.54 Å operating at 45 kV and diffraction angle between 20–80°. Morphology and particle distribution were studied by transmission electron microscopy and field emission imaging (TEM and FESEM, Hitachi 7500 and SU8180, Tokyo, Japan, respectively) operating at 120 kV and 30 kV. Elemental composition and ratio were determined by energy dispersive spectroscopy (SEM-EDS, JEOL, 7600) operated at 30 kV. Spectrofluorimeter (Perkin-Elmer LS55) was used for the analysis of photoluminescence (PL) spectral properties at room temperature, excited with xenon lamp (320 nm) in ethanol suspension. The procedure for potential voltage studies has been discussed in section ESI-2.

The photocatalytic activity of the as-prepared photocatalysts (TNR, AgTNR, TNS, and AgTNS) was carried in a reaction tube (20 cm^3, pyrex) containing 0.040 g photocatalyst and 5 mL water (Fig. ESI-3) 200 μL of Na_2S (0.1 M) was added to the reaction mixture to act as hole scavengers. Before irradiation, the reaction mixture was purged with Ar (20 min) to create an inert atmosphere for the reduction. The reaction samples was irradiated (Modu laser-Steller Pro-L, line frequency 50–60 Hz, USA) separately with several monochromatic wavelengths like 457 nm, 487 nm, 514 nm, the reaction was also carried out under multiline (457+487+514 nm), UV (266 nm, 125 W Hg arc lamp, Philips) and sunlight (9th May 2016, Patiala, India temperature 38 °C) irradiation for 8 h. The H_2 evolved during the reaction was quantified by the gas chromatograph with thermal conductivity detector (GC-TCD, Nucon Ltd, India) with molecular sieve (5X A column, Lab India Bombay), the column was programmed at room temperature while as injector and detector were set at 70 °C and 60 °C, respectively. The amount of H_2 evolved during the reaction was quantified against a standard (0.018%) H_2 gas (Sigma gasses India).

3. Result and discussion

3.1. Optical and morphological properties

Two different morphologies of TiO_2 nanorods (TNR) and nanospheres (TNS) were subjected to Ag photodeposition. The UV–Vis absorption spectra of all the photocatalysts are presented in Fig. 1, which shows a typical absorption edge in between 360 and 400 nm due to the geometry of TiO_2, after the Ag loading the rise of surface plasmon resonance (SPR) band (457 nm both for AgTNR and AgTNS, respectively) is observed due to coherent oscillation of Ag nanoparticles with identical frequency.

The polymorphism and crystal properties of as-synthesized photocatalysts were determined by X- ray diffraction studies (Fig. 2). The diffraction pattern of TNR and TNS displayed a typical anatase phase properties with edge length (a=3.7, b=3.7 and c=9.4) showing the tetragonal crystal system and calculated density of 3.92 g/cm^3. The pattern of TNR displayed a relatively intense and narrow peak (101 plane, 25.4°) attributed to 1D growth direction, and 101 plane is also considered as the thermodynamically most stable facet of anatase polymorph. In the case of TNS after Ag loading the crystallinity is also modified and another peak was observed to rise at 45° corresponding to 200 plane of Ag. FESEM and TEM micrographs of the photocatalysts are shown in Fig. 3 and 4, respectively. The hydrothermally synthesized TNR consists of rice gain shaped elongated particles with an average