SYNTHESIS AND CHARACTERIZATION OF NIOBIUM(V) AND SILVER(0)-DOPED VISIBLE LIGHT RESPONSIVE TITANIA NANORODS

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ABSTRACT

Titania nanoparticles are used in versatile areas of photo-catalysis. TiO₂ is a wide band-gap semiconductor and thin films of TiO₂ have indirect band gaps in the range ~3.2-3.35 eV. As such, titania thin films absorb radiation of wavelength ≤ 380 nm in the ultraviolet (UV) range of the electromagnetic spectrum and this radiation accounts only for 5% of the total radiation incident on the Earth surface whereas the visible and infrared (IR) radiations account for 40-45% and 50-55%, respectively. As such, titania along is not a very successful photo-catalyst. In order to circumvent this problem, Grätzel and co-workers developed the first dye-sensitized solar cell (DSC), in 1991, which utilizes a mesoporous thin film of interconnected titania nanoparticles to serve as dye absorber and electron transport medium whereas a monolayer of dye molecules with very high molar absorption coefficient adsorbed on the surfaces of titania particles in the mesoporous layer to absorb visible radiation for electronic excitation followed by injection of electrons to the conduction band of titania nanoparticles for concomitant transport towards the conducting FTO layer. Innumerable research activities devoted on DSCs have resulted in photon to electricity conversion efficiency (η) of over 15%. Perovskites-sensitized, extremely thin absorber solar cells h give over 20% of efficiency though environmental instability of perovskites present as a practical challenge. Even then, light absorption relies on a part of 40-45% of visible radiation incident on the Earth surface. Although IR radiation accounts for the highest fraction, absorption of IR radiation by a molecule/thin film etc. results only in vibrational excitations. However, Photon Up-conversion is a way round where several IR photons can be added together to yield one visible or UV photon. By introducing a ladder of energy levels within the band gap of titania, with successive energy gaps corresponding to the vibrational energy levels of titania nanoparticles, it is possible to up-convert IR photons to visible photons. The surface plasmon resonance effect of silver nanoparticles can be utilized in the direct absorption of visible radiation. As such, we prepared Nb(V) and Ag(0)-doped TiO₂ [Nb(V)-Ag(0)-TiO₂] by the sol-gel synthesis of TiO₂ nanorods in the presence of Nb(V) and Ag⁺ and the latter reduced to Ag(0) simultaneously using a reducing agent such as citrate ion or ascorbic acid. XRF analysis clearly showed the presence of Ti, Nb and Ag while XRD revealed the presence of TiO₂ in anatase phase, Nb₂O₅ phase and the Ag phase in Nb(V)-Ag(0)-TiO₂.

SEM images clearly show the presence of 20-30 nm wide, 200 nm- 2 μm long nanorods of TiO₂ on which spherical islands of Ag nanoparticles are deposited. Light absorption of the composite has been significantly red-shifted with respect to that of bare TiO₂ nanoparticles, both in the thin film states, making the latter visible-responsive. The IR Up-conversion has been demonstrated by adding a small amount of the powder to distilled water, in the dark where water photo-splitting initiates instantaneously and remains for over an hour. More sophisticated measurements of IR Up-conversion by the composite will be done in future in collaboration with Western Norway University of Applied Sciences.

Keywords: TiO₂ nanorods; Silver Quantum Dots; Nb(V) Doping; Surface Plasmon Resonance; Photon Upconversion.

INTRODUCTION

Titania or titanium dioxide is perhaps the most studied semiconductor material for its heterogeneous photocatalytic studies in destroying water pollutants, water splitting to produce hydrogen and oxygen gases and for use in solar cells to convert photon energy to electricity. In many applications, nanoparticles (particles with at least one dimension in the nano-scale of 1 nm to 100 nm) are preferred over flat surfaces or large particles owing to the fact that nanoparticles have much higher catalytic efficiency than their bulk counterparts due to the very large surface area-to-volume ratio of nanoparticles compared to their bulk materials. Interconnected thin films of TiO₂ nanoparticles are usually used in most of these applications. Fusing of nanoparticles to produce interconnected nano-particulate thin films can be done at much lower temperatures than the melting point of the corresponding bulk material since in the nano-scale physical properties of materials are size- and shape-dependent and in particular melting point decreases drastically as the particle size is reduced towards the lower end of the nano-scale. These thin films can be prepared by the Spay Pyrolysis Deposition (SPD) Method where an aerosol spray of the nanoparticle suspension is directed towards the heated substrate surface for the deposition of the nanoparticles on the substrate forming a thin film containing interconnected nanoparticles. We have designed, developed and manufactured a novel and improved SPD method where we introduced an atomizer chamber between the precursor solution and the pyrolysis
chamber. The aerosol stream of nanoparticle suspension is allowed to incident on the Teflon sphere in the atomizer chamber for any aggregated particles to separate and the aerosol stream directed towards the pyrolysis chamber thus contains only discrete nanoparticles. As such, we were able to produce optically transparent thin films of many materials on many substrate surfaces (1-5). This method is particularly useful in making thin films of titania. Thin films of titania have indirect band gap in the energy range ~3.2-3.35 eV and hence titania absorb radiation of wavelength < 380 nm which are in the ultraviolet (UV) range of the electromagnetic spectrum. The UV radiation accounts for only less than 5% of the solar spectrum incident on the Earth surface. In order to utilize a wider range of solar spectrum, O'Regan and Grätzel invented the dye-sensitized solar cell (DSC) in which interconnected nano-particulate titania particles were covered with a monolayer of light absorbing dye molecules (6). These dye molecules absorb in the visible range and electrons in the highest occupied molecular orbitals (HOMOs) get excited to the lowest unoccupied molecular orbitals (LUMOs) from where they are injected to the conduction band (CB) of the titana nanoparticles in femtosecond time scale. Titania nanoparticles are capable of absorbing any radiation below λ < 380 nm. In this way, 5% of UV and some percentage of visible light are harvested for conversion to electricity. This has resulted in an enhancement of efficiency of radiation to electricity conversion from less than 1% to 7.1-7.9% in simulated solar light, in 1991. Grätzel and co-workers reported 10.6% efficiency in 1993 with N3 dye [cis-Bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato ruthenium(II)] (7) and 10.4% with N749 dye [the so called black dye, tris(isothiocyanato)terpyridyl-4,4',4''-tricarboxylato ruthenium(II) which was developed to increase the wavelength range of visible light absorption] in 2001 (8). In 2003, further enhancement to 11.8% was reported from the same research group where N3 has been modified to increase light absorption coefficient from 14,000 dm³ mol⁻¹ cm⁻¹ to 15,000 dm³ mol⁻¹ cm⁻³ at 535 nm to result in N719 dye [di-tetra butylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)] (9). Innumerable modifications done on basic DSC arrangement has now reached over 25% efficiency with the use of Cu(II) bipyridyl complex based dyes (10). Similarly, in photoelectrochemical water splitting experiments, solar-to-hydrogen conversion efficiency of 7.5% has been recently achieved (11).

Silver nanoparticles have strong light absorption in the visible range due to surface plasmon resonance (SPR) effect which is due to conduction electrons on the metal surface undergoing a collective oscillation when excited by light at specific wavelengths resulting in unusually strong scattering and absorption properties. The absorption onset is size dependent 60 nm silver nanoparticle appear blue in colour when illuminated with white light. This is due to SPR maximum at 400 nm (violet light). By changing the size of silver nanoparticles this absorption maximum can be tuned from 400 nm to 530 nm (green light) (12). Silver nanoparticles have molar absorption coefficients of over 40,000 dm³ mol⁻¹ cm⁻¹ which are nearly 3 times higher than those of typical dyes used in DSCs (13). As such, the use of silver nanoparticles harvest some of the visible light in DSCs is important in enhancing their efficiencies. The solar spectrum incident on the Earth surface contains 50-55% infrared (IR) radiation. The absorption of IR radiation does not contribute to electronic excitations since the energy of IR radiation is insufficient for electronic excitations. IR absorption results in bond vibrations and hence heating the solar cells. However, IR radiation can be up-converted to visible or UV radiation by introducing a ladder of energy levels within the band gap of the semiconductor such that electronic energy levels introduce match with corresponding vibrational levels of the semiconductor. As such, n number of hv IR photons can be added to b(nv) where b is a visible or UV photon. While there are several different types of photon up-converting materials we focus here titania based such materials. Usually rare earth ions. Güdel and co-workers (14) initiated the study of using transition metal ions as photon upconverting ions doped in suitable host lattices. They have studied Mn²⁺, Ni²⁺ (15), Mo⁴⁺ (16), Re⁴⁺ (17), and Os⁶⁺ (18) based photon up-conversion materials (19). Same researchers have reviewed the up-conversion behaviour of Ti²⁺, Re⁴⁺, and Os⁶⁺ doped materials (20). Wu et al., in 2002, reported Mo-doped TiO₂ which can up-convert 978 nm laser IR radiation to a broadband in the visible range from 475 nm to 700 nm (21). Enhancing solar cell efficiency using IR up-converting materials has been reviewed (22). There the studies on the use of lanthanide ions such as Er³⁺, Ho³⁺, Tm³⁺, Yb³⁺ and Pr³⁺ to up-convert IR radiation has been discussed.

Xu et al. described the water splitting photocatalytic activities of titania reduced by various metals such as K, Ca, Na, Mg, Al and Zn and shown that titania reduced by Mg has the highest efficiency for water photo-electrolysis. They have converted white P-25 TiO₂ nanoparticles to light blue, dark blue and black coloured doped titania core-shell structures (23). Gonell et al. integrated Er³⁺/Yb³⁺-co-doped yttrium oxide (Y₂O₃) submicrometric particles with outstanding up-conversion properties into mesoporous titanium oxide (TiO₂) structures sensitized with cadmium selenide (CdSe) for efficient solar hydrogen generation (24). Several recent publications appear in the literature on the use of Nb(V)-doped TiO₂ for photon-upconversion based water photosplitting by IR radiation (25). In this manuscript, preparation and characterization of Nb(V)-doped, Ag Quantum Dot-attached TiO₂ nanowires will be described. These composite nanowires have the capability to absorb in the UV radiation incident on the Earth surface, some parts of the visible range by the surface plasmon resonance effect of silver quantum dots and upconverting some IR radiation to visible radiation by the ladder of energy levels introduced by the doped Nb(V) ions. As such, this is an
excellent photocatalyst capable of harnessing a major fraction of the solar spectrum incident on the Earth surface. The material is also photocatalytic in the dark by using the upconverted IR radiation and is a good candidate for photosplitting of water to generate hydrogen fuel.

**EXPERIMENTAL**

Titanium(IV) tetraisopropoxide (TTIP) (98%, Aldrich), Silver nitrate (99.9%, Aldrich) and Niobium(V) ethoxide, (99.95%, Aldrich) were used as starting precursors and absolute ethanol as a solvent to prepare silver quantum dot attached TiO$_2$ nanorods doped with 20% niobium. This was done through a sol-gel method. First, TTIP (2 ml) was dissolved in ethanol (20 ml) mixed with silver nitrate (0.0384 g) and niobium(V) ethoxide (0.031 ml), by stirring the mixture, for 15 min, at room temperature, followed by adding droplets of 4.0 M NH$_3$ into the solution until pH of the solution reaches about 3-4. Finally, distilled water was slowly added to the solution while stirring for 30 min which resulted in the conversion of the sol to a gel. The resulting gel was dried at 50°C for 24 h. And then the dried product was refluxed in NaOH at 200°C, for 12 h. The refluxed powder was gathered by centrifuging at 4000 rpm for 4 min. The resulted powder was autoclaved at 140°C for 2 h and purified by washing with 0.10 M nitric acid and distilled water. The final product obtained was allowed to air-dry and the dried material was rounded to a powder.

The composite material thus obtained was characterized by X-ray Powder Diffractometry (XRD) (Siemens D5000 X-ray powder diffractometer, Cu Kα radiation of wavelength, $\lambda = 0.154$ nm and scanning rates of 1° and 2° min$^{-1}$), X-ray Fluorescence Spectroscopy (XRF, Fisher X-ray Fluorescence Spectrometer), Scanning Electron Microscopy (SEM, Hitachi SU6600 Scanning Electron Microscope (SEM) at the acceleration voltage of 10 kV and from Leo 1530 VP) and Energy Dispersive X-ray Spectroscopy (EDX) and UV-Visible Spectroscopy.

**RESULTS AND DISCUSSION**

The XRD shown in Figure 1 contains peaks at 20 values of 25.4° which corresponds to reflections of the rutile form of TiO$_2$. These are marked as TiO$_2$ in the diffractogramme. It is interesting to note that rutile form of TiO$_2$ has been preserved even after the Nb(V) substitution for some Ti(IV) sites. Substitution of Nb(V) for some Ti(IV) sites is facilitated by the similar ionic radii of 60 pm and 64 pm, respectively (26). Such favourable substitution does not alter the rutile crystal structure of TiO$_2$ as revealed by the XRD data. However, Nb(V) substitution for Ti(IV) sites mandatorily demand the uptake of oxide anions to counter balance excess positive charge. This introduces trapped electrons and hence the n-type semiconducting behavior of TiO$_2$ is increased by this substitution. The peaks at 20 values of 32.15° and 38.10° which are due to reflections respectively for Ag$_2$O and Ag.

Figure 1: X-Ray Diffractogramme of Nb(V) doped, Ag Quantum Dot attached TiO$_2$ nanowires.

SEM images shown in Figure 2 clearly show the presence of TiO$_2$ nanowires of dimensions of 20-30 nm width and 200 nm-2 μm lengths.

Figure 2: Scanning Electron Microscopic images of Nb(V)-doped, Ag Quantum Dot attached TiO$_2$ nanowires.

UV-visible Spectrum of Nb(V)-doped, Ag Quantum Dot attached TiO$_2$ nanowires is shown in Figure 3.
Figure 3: UV-visible Spectrum of Nb(V)-doped, Ag Quantum Dot attached TiO₂ nanowires.

The absorption in the entire visible range and extending towards near IR range in the absorption spectrum clearly shows that the composite material has the capability to absorb light in these regions. As such, the material is a radiation absorber in the near IR, entire visible and UV regions of the electromagnetic spectrum. We are now studying measure its ability to up-convert IR radiation absorbed by the material to visible range. Since we have no facility to measure anti-stokes luminescence in Sri Lanka this study will be done in Norway in collaboration with. As a demonstration, we added a small amount of our material into distilled water in a round bottom flask and kept under stray room light in a dim evening. Gas bubble evolution occurred immediately at a rate of 3 mL per min confirming that this is the fastest water photo-splitting catalyst developed so far and is capable of working with IR radiation by up-converting IR radiation to visible radiation.

CONCLUSION
A photocatalyst capable of absorbing in the UV and visible ranges and up-converting infrared radiation to visible radiation was developed and characterized. It comprises of Nb(V)-doped, Ag quantum dot attached TiO₂ nanowires. The Nb(V) ions introduce energy levels within the band gap of TiO₂ thus enabling IR photon up-conversion. Ag quantum dots contribute through surface Plasmon resonance absorption and scattering of visible radiation.

REFERENCES


Biography

R.B.S. Dilan Rajapakse (B.Sc.) is a Ph.D. student working on nanotechnology-based smart and intelligent textiles under the supervision of Professor R.M. Gamini Rajapakse of University of Peradeniya. He developed photon upconversion and surface plasmon resonance absorption-based photocatalyst for water splitting. He is a Visiting Demonstrator to Nanoscience & Nanotechnology and Analytical Chemistry M.Sc. Degree Programmes offered by the Postgraduate Institute of Science, University of Peradeniya. He has three journal publications, several communications and three pending patents to his credit.

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