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Multiphase titanium oxide nanomaterial for augmented vis–NIR photon absorption

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ABSTRACT

Nanomaterials based on titanium di-oxide (titania) are intensively being studied for their incorporation in the next generation photovoltaic devices due to titania's excellent photocatalytic properties. Inefficient utilisation of deeper visible and near infra-red region (NIR) photons has however limited the exploitation of such materials. In this paper, we report a unique titanium oxide nanomaterial that is sensitive to photons of wavelength even longer than 600 nm and is composed of not one but multiple phases of titanium oxide. It has exhibited enhanced absorption that is three times greater in visible region and six times greater in NIR than base titanium. Synthesised by a phenomenon created via the interaction of ultrashort pulses with a titanium substrate, this photoabsorptive nanomaterial is dopant free and is structurally formed as a dense three dimensional network. Further effective tuning of the optical properties of the synthesised multiphase titanium oxide nanomaterial can make it a potential absorber material in photovoltaic devices.

1. Introduction

Enhanced absorption of photons over a broad range of the solar spectrum is desirable in a diverse range of applications that include various photonic and optoelectronic devices. With the advent of nanomaterials, which are uniquely characterised by a large surface to volume ratio, the possibility of harvesting more number of photons has increased. Salient features like the ability to modify the band gap of the absorber material, by tailoring the shapes and sizes of nanostructures, as well as enhancing light trapping by generating nano sized patterns are now possible through such nanomaterials [1–3]. Photovoltaic devices possibly have the greatest need for such absorber materials that exhibit greater photon absorption. Nanomaterials based on numerous metals, metal oxides and semi-conductors like Si (both in crystalline and amorphous form), TiO_2, CdS, CdSe, CdTe, CIGS, ZnO and CuO have all been applied in photovoltaics [1,4,5]. Titanium di-oxide (or titania) in particular, gained a lot of interest after the reporting of its excellent photo-catalytic properties by Honda and Fujishima [6,7]. Widely used as a pigment due to its high refractive index and brightness since decades, TiO_2 has been considered for photovoltaic applications as it has low levels of toxicity, low cost and good resistance to corrosion [7]. This oxide of titanium naturally occurs in three different forms, *rutile, anatase and brookite*. It has been used in the form of nanoparticles, nanotubes, and nanorods, often synthesised via various physical and chemical methods that are quite cumbersome and difficult to reproduce on a large scale [8]. However, titanium di-oxide nanomaterials have also been plagued by the problem of weak absorption. The large band gap of TiO_2 causes only the photons present in the ultraviolet region to be efficiently absorbed, which accounts for a very small percentage of the incident solar spectrum. Various mechanisms have been proposed to shift the band gap of TiO_2 towards the visible region of the solar spectrum. Nanostructures of different morphologies based purely on single phases of TiO_2 (rutile or anatase) as well as doping of TiO_2 with various non-metals (like C, N and S) and transition metals (like V, Cr, Ni, Fe) have been reported with an effort to increase the absorption in the visible region [9–13]. However, the absorption spectrum obtained has been limited, with no significant absorption being reported at wavelengths beyond 600 nm in the deeper visible and near infra-red region (NIR) of the solar spectrum. As such, there is a need for a new titanium based nanomaterial with a broader and enhanced absorption spectrum that can effectively trap and absorb photons over the entire range of the solar spectrum. This serves as an important first step towards improving the prospect of such titanium based nanomaterials being implemented in photovoltaic devices that can ultimately lead to the superior performance characteristics of the devices.

In this work, we report on titanium oxide photoabsorptive nanomaterial with a widened absorption spectrum that has

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demonstrated greater sensitivity towards absorption of photons of wavelength even beyond 600 nm in the deeper visible and near infra-red region (NIR) of the solar spectrum. This was achieved by not limiting the composition of the nanomaterial to a single titanium oxide phase. On the contrary, a multiphase nanomaterial was synthesised free of any external dopants to make it more photoabsorptive and having an absorption capability that was independent of the wavelength of photons in the deeper visible and near infra-red region. This multiphase titanium oxide nanomaterial is structurally three dimensional in nature. It has been synthesised by the formation of an ionised plume and a unique phase transformation process brought about by the interaction of ultra-short pulses with a titanium metal substrate. The multiphase aspect of the titanium oxide nanomaterial has been exploited to expand the photon absorption range over a wider area of the vis–NIR of the solar spectrum by the effective tuning of its phases. Such a unique titanium oxide nanomaterial has, to the best of our knowledge, not been reported earlier.

2. Material and methods

The titanium oxide nanomaterial was synthesised on grade 2 pure Ti samples under conditions of standard ambient temperature and pressure (SATP), at a temperature of 298.15 K and an absolute pressure of 0.98 atm, by a single step femtosecond laser phase transformation process. First the Ti samples were cut to the following dimensions $10 \times 10 \times 2$ mm^2 using a diamond saw and a coolant. Any possibility of the presence of minor surface defects and contaminants was removed by ground finishing and polishing, followed by ultrasonic cleaning in distilled water. Thereafter, the generation of the three dimensional nanomaterial was initiated by scanning of the laser beam along parallel lines on the sample surface.

A direct diode pumped, Yb-doped fibre amplified laser system (Clark-MXR Inc. IM-PULSE series ultra-short pulse laser) was employed to get a femtosecond pulse laser beam of pulse repetition rate (frequency rate) ranging from 200 KHz to 26 MHz. The laser beam having a Gaussian shaped beam profile and a central wavelength of 1040 nm has a highly focused spot diameter of about 10 μm. A two axis computer controlled galvano scanner scanned the laser beam normally on the sample surface at the rate of 5 mm/s with an average power of 16 W. The titanium oxide nanomaterial was generated at laser fluence values of 5.14, 2.46 and 1.64 J/cm^2, each at three different pulse widths (durations): 214, 714, 1428 fs, with peak power ranging from 90 MW/pulse to 1885 MW/pulse.

Material and phase characterisation studies of the nanomaterial was done by using an energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy XPS X-ray diffractometer (XRD) and dispersive Raman microscope. Surface and structural morphology was studied by the high resolution scanning electron microscope (SEM) (Hitachi S 5200) and transmission electron microscope (TEM). The dimensions of the nanomaterial were measured by using NIH's ImageJ™ software on the obtained TEM images. X-ray diffraction (XRD) analysis was performed to identify the different titanium oxide phases of the nanomaterial. The source of the X-rays having of wavelength 1. 54184 Å was CuKα radiation. The XRD profile for each laser parameter was obtained for a 2θ range of 30–78°. The absorption properties of the laser irradiated areas covered with the synthesised nanomaterial were measured using a spectrophotometer (AvaSpec-2048 Fibre Optic Spectrometer) of the broadband spectrum range of 200–1100 nm. The Raman spectra was measured using a dispersive Raman spectroscope at multiple laser beam wavelengths of 532 and 785 nm.

3. Theory

The synthesis of the titanium oxide nanomaterial via ultra-short laser material interaction can occur either due to the initial ejection of target titanium atoms in a coalesced form or by the subsequent assembling and collisions occurring in the plume of ablated atoms. It is known that, due to the extremely brief nature of the interaction time between the ultra-short laser pulses (femtosecond (fs) duration) and the titanium target material, the bulk of the target lattice remains cold and only electron excitation takes place, causing the density of the target material to remain constant [14]. The multiple ultra-short laser pulses hitting the target with only a few nanoseconds of time separation between each consecutive pulse results in a large amount of energy being transferred to the target material (titanium) with not enough time for it to be dissipated. This leads to the formation of a plasma plume consisting mostly of ejected titanium target material atomic species which subsequently diffuse and collide with the air molecules. The collision of the target titanium species with the air molecules leads to their recombination and reduction in temperature. Vapour condensation then follows, leading to the nucleation and growth of the coalesced nanomaterial and the subsequent formation of a three dimensional network due to

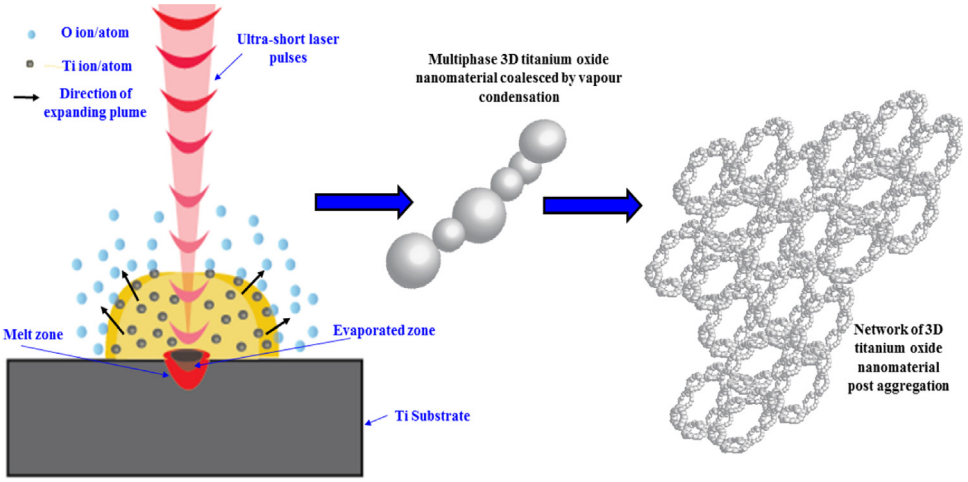

Fig. 1. Multiphase titanium oxide nanomaterial formed by ultra-short laser synthesis mechanism.