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Plasmon hybridisation of self-assembled 3d multiphase nano-titanium oxide towards broadband photon absorption

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ABSTRACT

Nanomaterials with a broadband photon absorption capability are essential for better performing solar cells. Plasmonic nanostructures and Quantum Dots, often fabricated via complex time intensive methods, have a narrow absorption spectrum. In this paper, we report a plasmon hybridised self-assembled 3D nano network of multiphase titanium oxide, which was synthesised via a single step bottoms-up method, and is structurally both multi-layered and three dimensional in nature. The surface plasmonic effect was induced on the self-assembled nanomaterial through its hybridisation with Au and Au/palladium alloy that resulted in the achievement of an enhanced and broadened absorption spectrum extending over the entire visible as well as the near infrared region of the solar spectrum. Further studies were also carried out to examine the impact of various factors like the size, composition and degree of hybridisation of the self-assembled 3D multiphase nano titanium oxide network on its photon absorption capability.

1. Introduction

Enhanced photon energy harvesting has become a critical component in the realisation of more efficient solar cells. Materials which exhibit superior optical properties by having an enhanced and broadened absorption bandwidth are thus most desirable [1–3]. Photoabsorptive nanomaterials in the form of single layered plasmonic nanostructures and quantum dots (QDs) are being employed to boost the absorption of light and improve the performance of the cell, by exploiting the plasmon resonance [2,4–6] and quantum confinement effect respectively [7–9]. In plasmonic metal nanomaterials, conduction electrons oscillate collectively at resonant frequency, which cause the incident light to be strongly scattered or absorbed [4]. This characteristic property is thus utilized in trapping of photons of different wavelengths, by correspondingly tuning the resonant frequency of the nanoparticles, that is a known function of the particle size, shape, material and the refractive index of surrounding medium [4,10–12]. Resonances in between the resonant frequencies of two individual metals can also be achieved by alloying of metal particles, which further provide an opportunity to broaden the absorption spectrum [13]. In semiconductor quantum dots, the confinement of electrons within the particle arises due to reduction of the particles size below the Bohr radius of the semiconductor material, which results in its size-tunable optical properties [7,14]. The absorption ability of such discrete energy level and narrow band gap quantum dots are also being manipulated by doping and change in their morphology [15–17]. The incorporation of such plasmonic nanostructures and quantum dots in solar cells has thus provided a number of avenues to enhance the photon absorption capability through band gap modification and augmented photon trapping. However, their applications has been limited due to expensive and complex fabrication processes, which also constrain the degree of their controllability and a very narrow absorption bandwidth that is strongly dependent and limited to their Plasmon resonant peaks, as in case of plasmonic nanostructures [13], or the band gap and amount of stacking, as in case of quantum dots [18,19]. As such there is a paucity of nanomaterials which can exhibit a broadened and enhanced absorption bandwidth that can be easily fabricated and do not require additional cost bearing steps like doping or multiple stacking.

In this work, we report a plasmon hybridised self-assembled 3D multiphase nano-titanium oxide that has demonstrated an enhanced photon absorption capability over a wide range of the solar spectrum, extending from visible to near infrared wavelengths (300–1000 nm). To serve as a template, an entirely self-assembled three dimensional nanomaterial network that is nanoporous, free of dopants and composed of multiple oxide phases of titanium was fabricated in our previous study, by a phase transformation process brought about by the interaction of ultra-short laser pulses with base titanium substrate

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[20]. This cross linked self-assembled network of nanomaterial fabricated on a base titanium substrate and having multiple resonant optical modes due to its complex structure, assisted in expanding the spectral response of titanium that was limited to ultraviolet region, and effectively displayed the ability to harvest photons over deeper visible and near infrared region of the solar spectrum (600–1000 nm). However, photons extending over the lower visible region of the solar spectrum (300–600 nm) were not effectively utilized. Considering that the visible region accounts for up to 44% of the solar irradiation on the ground level, it is vital to tap these wavelength photons and enhance the photon absorption capability of the self-assembled nanomaterial network [21]. Au monolayer nanoparticles which only exhibit a plasmon resonance peak in the visible region were thus exploited and amalgamated to induce localised surface plasmon resonance (LSPR) behaviour and sensitize the self-assembled nanomaterial to expand its absorption spectrum in the visible region. This induction of the LSPR effect in multiphase nanomaterial was done via the fabrication of a plasmon hybridised multiphase nanomaterial that is multilayered and three dimensional. To prevent undesirable effects arising out of Au nanoparticle aggregation, which could inhibit effective photon harvesting, Au/Pd alloy plasmon hybridised nanomaterial was also fabricated and studied. Assessment of the influence of Au and Au/Pd plasmon hybridisation on the nanomaterial was conducted by varying the degree of hybridisation to optimize the surface plasmon coupling at the interface of the metal nanoparticles and core nanomaterial. To incorporate further controllability and study the feasibility of tuning the optical properties of the hybridised nanomaterial towards broadband photon absorption, the effect of change in the phase composition and average size of the aggregated nanospheres constituting the nanomaterial network on the absorption spectrum was also studied. It was observed that plasmon hybridisation with Au lead to almost a forty percent increase in visible light absorption and a fourteen percent increase in NIR absorption of the core multiphase nanomaterial. Similarly, for plasmon hybridisation with Au/Pd., when compared to just the core multiphase nanomaterial, a substantial hundred and twenty percent gain in visible light absorption and eight percent gain in NIR absorption was achieved. This characteristic property of having a broadened and enahnced absorption spectrum, as well as providing a greater degree of tunability and controllability of its optical absorption properties, makes the plasmon hybridised multiphase nano network, which was uniquely fabricated by a simple, time/cost effective approach, a potential candidate for further investigation into achieving “full spectrum” black body state, that can eventually be integrated and utilized for solar cell applications.

2. Material and methods

A diode pumped, Yb-doped femtosecond laser system (Clark-MXR Inc. IM-PULSE Series Ultrashort Pulse laser) was employed to synthesise core self-assembled multiphase titanium oxide nanomaterial by scanning the ultrashort laser pulsed beam on grade 2 pure titanium sample along evenly spaced parallel lines under conditions of standard ambient temperature and pressure (SATP), at a temperature of 298.15 K and an absolute pressure of 0.98 atm. The titanium samples of dimensions 10×10×2 mm, were ground finished, polished and ultrasonically cleaned in distilled water prior to laser irradiation. Maintained at an average power of 16 W, the 1040 nm central wavelength, Gaussian shaped laser beam was scanned at a speed of 5 mm/s on the titanium samples at effective laser fluence values of 5.14 J, 2.46 J and 1.64 J per unit square centimeter. To incorporate an additional study variable, the duration of ultrashort laser pulses was varied, and the experiments were conducted at laser pulse width values of 214fs, 714 fs and 1428 fs. The multiphase titanium oxide nanomaterial fabricated at different lasing conditions was then hybridised via plasma assisted deposition process, by using a Sputter Coater (Quorum SC 7620) for various time durations using Au and Au/palladium alloy targets. Two sample sets of plasmon hybridised multiphase titanium oxide nanomaterial decorated with noble metal coatings of Au and Au/palladium alloy (Au:Pd::80:20) of varying atomic % concentrations were thus generated. The first set of core self-assembled nanomaterial samples, synthesised at all the previously stated laser parameter conditions, were coated with average Au atomic concentrations of 1.74% and 3.56%. The second set of core self-assembled nanomaterial samples, again synthesised at all the previously stated laser parameter conditions, were coated with Au palladium alloy having average Au atomic concentrations of 0.82%, 1.63% and the corresponding palladium atomic concentrations of 0.30%, 0.68% respectively.

Morphological study of the self-assembled multiphase titanium oxide nanomaterial was conducted using a Field Emission Scanning Electron Microscope (FE-SEM) (Hitachi SU8230). Structural and material composition study was conducted using a Transmission Electron Microscope (TEM) (Hitachi H 700 CTEM) and Energy Dispersive X-ray Spectroscopy (EDX). The Raman spectra at two laser beam wavelengths, 532 nm and 785 nm, was measured using a dispersive Raman Spectroscope. The absorption spectrum of both the plasmon hybridised as well as the non-hybridised core self-assembled multiphase nanomaterial was acquired in the broadband range of 200–1100 nm using a deuterium-halogen source spectrophotometer (AvaSpec-2048 Fibre Optic Spectrometer).

3. Results and discussion

The formation of self-assembled multiphase titanium oxide nanomaterial via ultrashort laser-material interaction process is governed by vapour condensation mechanism. The plasma plume consisting of atomic species from titanium target material ejected due to the incident laser beam, expands outwards into the ambient atmosphere resulting in collision with the air molecules [22]. The temperature subsequently reduces as a result of these collisions, causing vapour condensation to commence [22,23]. This is followed by the nucleation and growth of nanoscale structures which later aggregate to form a three-dimensional network of nanomaterial. A prior study done on the core synthesised multiphase titanium oxide nanomaterial with no sputter coated Au or Au/Pd layer revealed a self-assembled 3D network of spherical nanostructures aggregated to form circular pores [20]. The density of the network increased with the laser fluence condition at which they were synthesised. TEM analysis showed that the mean particle size of the individual spherical nanostructures which coalesced and agglomerated together to form the 3D network of nanomaterial, increased at higher laser fluence and shorter laser pulse durations [20]. Furthermore, a bimodal particle size distribution was seen at the highest laser fluence. EDS elemental line scan analysis had revealed that the nanostructures were composed of titanium and oxygen and this was further validated by an area scan analysis too, which clearly showed the oxygen and titanium distribution in the synthesised nanostructures [20]. Additional material characterization studies like XRD and XPS had revealed that the core nanomaterial was composed of multiple phases of titanium oxide, namely: rutile, anatase, Ti_3O and non-stoichiometric $(TiO_{.716})_{3.76}$ [20]. This multiphase titanium oxide nanomaterial exhibited the ability to effectively absorb photons in the deeper visible and Near Infrared region of the solar spectrum [20].

In the present study, the core nanomaterial composed of 3D aggregated titanium oxide nano spherical structures were initially synthesised by an ultrashort laser pulses, as seen in Fig. 1(A), and then hybridised with Au and Au/Pd alloy nanoparticles and nano islands, as seen in Figs. 1(B) and (C) respectively, to induce the phenomenon of localised surface plasmon resonance (LSPR). The study of the morphology of the Au and Au/Pd alloy plasmon hybridised nanomaterial revealed that the deposition of the above noble metals was non-uniform along the depth of the 3D nanomaterial network. The Au atoms deposited on the nanomaterial formed a thin layer of coalesced large islands, covering a large area of topmost layer of the