Structural and Optical Analysis of Ag Nanoparticles assisted Vertically Aligned TiO₂ Nanowires based photoanode for Dye-sensitized Solar Cells Application

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Structural and Optical Analysis of Ag Nanoparticles assisted Vertically Aligned TiO₂ Nanowires based photoanode for Dye-sensitized Solar Cells Application

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Abstract:

In this work, vertically aligned TiO₂-Nanowires (TiO₂-NWs) and Ag Nanoparticles assisted TiO₂ Nanowires (TAT-NWs) were deposited on glass and flexible PET substrates using the Glancing Angle Deposition (GLAD) technique. The morphology and structural analysis of the samples manifest the successful deposition of vertically aligned TiO₂-NWs and TAT-NWs. The HR-TEM image of TiO₂-NWs shows the polycrystalline nature. Further, the XRD result confirms the polycrystalline nature of both the TiO₂-NWs and TAT-NWs samples. Besides, the HR-TEM image confirms the presence of small crystal grains of Ag Nanoparticles (Ag-NPs) at the mid of the annealed TAT-NWs. It is evident from the Selective Area Electron Diffraction (SAED) analysis of the TiO₂-NWs and annealed TAT-NWs that the crystallinity of TiO₂ present in the annealed TAT-NWs improves after annealing. The absorption spectrum analysis of TAT-NWs deposited on glass substrate shows enhance absorption peak in the visible region with a maximum peak at ~463 nm wavelength compare to the TiO₂-NWs, which may be attributed to the Surface Plasmon Resonance (SPR) effect of Ag-NPs. Further, it is interesting to observe that the TAT-NWs deposited on PET substrate show further absorption enhancement in the UV and visible region. In addition, the Photoluminescence analysis reveals that the bandgap of the TiO₂-NWs is ~3.12 eV, which supports the bandgap extracted from the Tauc plot. Therefore, the proposed method of fabricating TAT-NWs on glass and flexible ITO coated PET substrate using the GLAD technique may be applicable for developing novel photoanode for Dye-sensitized Solar Cells (DSSCs) and other optoelectronic applications.

Keywords: Flexible, GLAD, Nanoparticle, Nanowires, Plasmonic, TiO₂

1. Introduction

Titanium dioxide (TiO₂) is one of the most extensively investigated materials for various applications like photo-catalysis, photo degradation, energy storage, photovoltaic devices and optoelectronic devices [1, 2]. In the last decade, one-dimensional (1D) TiO₂ nanostructures have been significantly studied because of their ability to enhance the light absorption due to scattering of lights inside the nanostructure, which facilitates the photocatalytic reactions and by providing the direct pathway for charge carrier [3]. Many researchers are trying to develop highly efficient photovoltaic devices based on 1D-TiO₂ nanostructure as photoanode. It may be noteworthy to mention that the market demand for clean renewable energy sources is increasing globally day-by-day. In this sector, Dye-sensitized solar cells (DSSCs) will play a major role in fulfilling this market demand because of their potential for low-cost production, ease of fabrication, environmentally friendly and the possibility to fabricate on a flexible substrate [4]. Many researchers are trying to improve the efficiency of DSSCs since their invention by O'Regan and Gratzel in 1991 [5]. The highest reported efficiency of DSSCs is ~12.8% [6], which is lower than that of solar cells like perovskite solar cells [7], thin-film solar cells [8], polymer solar cells [9] and crystalline silicon (Si) solar cells [10]. Nevertheless, the efficiency of DSSCs can be improved by enhancing the photon absorption and making electron transport easier in various layers namely photoanode, sensitizers, electrolyte and counter electrode. One of the most important layers of DSSCs is the photoanode, which plays an important role in the absorption of photon and electron transport to the external circuit of the cell to generate power. Among the metal-oxides, TiO₂ nanostructure is the most commonly used material as photoanode for DSSCs because of its unique properties like photocatalytic, less charge carrier recombination rate, non-toxic, environment-friendly and chemical stability [11]. However, the large bandgap of TiO₂ nanostructure hampers the absorption of light in the visible region, which affects its performance in wide applications. To overcome the issues many researchers are trying to modify TiO₂ nanostructure-based photoanode by putting metal nanoparticles (NPs), doping of material and by changing the morphology to boost the overall performance of DSSCs [12-14].

The main issue of this layer is the increase in the thickness of the photoanode while trying to improve the photon absorption and increase in the recombination of photo-excited electrons inside the cell, which is responsible for lowering the efficiency [15, 16]. In recent years, researchers are trying to address these issues by developing vertically oriented one-dimensional (1D) metal-oxide nanostructures decorated with metal nanoparticles (MNPs) [17, 18]. The metal NPs decorated metal-oxide nanostructures improve the efficiency by creating a short electron pathway through the 1D structure, at the same time, enhancing the photon absorption through localized surface plasmon resonance of MNPs. This effect of localized surface plasmon resonance depends on the shapes, sizes and types of metal used. Therefore, synthesizing the desired size of metal NPs to incorporate with metal-oxide needs a controlled growth mechanism. Further, Gold (Au) and Silver (Ag) are the most widely used novel metals due to their tuneable Surface Plasmon Resonance (SPR) effect in the visible region. However, Ag is relatively low cost compared to Au and the SPR effect can be tune in the visible region by changing the shape and sizes [14]. Again, controlling the size of NPs decorated on the metal-oxide is still challenging since the controlled growth technique need state-of-the-art fabrication technique [19]. Moreover, most of the recently reported techniques are not catalytic-free and employed more than one synthesis technique to develop photoanode for DSSCs [15, 20]. The glancing angle deposition technique (GLAD) is a cost-effective technique that can grow vertically oriented nanowires and metal NPs without using any catalyst [21, 22]. Therefore, it will be interesting to develop Ag-NPs embedded TiO₂-NWs based photoanode using the GLAD technique.

In this work, TiO₂-NWs and TiO₂-NWs/Ag-NPs/TiO₂-NWs (TAT-NWs) based photoanode was fabricated using the GLAD technique without using any catalyst on glass and flexible PET substrate. The morphology, structural and optical properties of the samples are discussed in this work. The morphology and structural properties were also characterized using Field Emission-Scanning Electron Microscopy (FE-SEM), High-resolution Transmission Electron Microscopy (HR-TEM) and X-ray diffraction (XRD). The optical properties of the samples were also analysed using UV-Vis spectroscopy and photoluminescence spectroscopy.

2. Experimental Details

Vertically oriented TiO₂ nanowire (TiO₂-NWs) and TiO₂-NWs/Ag-NPs/TiO₂-NWs (TAT-NWs) are deposited on glass and flexible PET substrates using Glancing Angle Deposition (GLAD) inside the E-beam evaporation system (Model No.: Smart Coat 3.0, HHV India). The TiO₂-NWs and Silver (Ag) nanoparticles were deposited using TiO₂ (99.999% pure, Tecnisco Advanced Materials Pte Ltd, Singapore) and Ag (99.999% pure, Tecnisco Advanced Materials Pte Ltd, Singapore) source material. A special GLAD system was integrated inside the E-beam chamber, which allowed changing of the desired angle through the axis of the GLAD system. The process of forming vertically oriented TiO₂-NWs on the substrate through the GLAD process has been discussed in our previous work [23]. Similarly, in this work, the GLAD technique was employed to grow unique TiO₂ nanostructures embedded with Ag-NPs without using any catalyst. The samples were rotated at speed of 30 rpm, which are kept at a distance of 20 cm from the evaporating source material during the deposition. The e-beam chamber was clean properly using acetone before making the chamber vacuum. The chamber pressure was initially maintained at $\sim 6 \times 10^{-6}$ mbar. It is observed that the chamber pressure gradually drops to $\sim 2 \times 10^{-5}$ mbar during the initial deposition process, which may be due to the release of oxygen gas from the evaporation material. In the first round of deposition, TiO₂-NWs (240 nm) samples were deposited on glass (1 cm x 1 cm) substrate using the GLAD technique. And, in the second round of deposition, TiO₂-NWs (120 nm) were first deposited on glass (1 cm x 1 cm) and ITO coated PET (1 cm x 1 cm) substrates, followed by Ag NPs (30 nm) deposition on the top to TiO₂-NWs (120 nm). Further, TiO₂-NWs (120 nm) were deposited above the Ag-NPs (30 nm)/TiO₂-NWs (120 nm). Finally, we achieved the staking of TiO₂-NWs (120 nm)/Ag-NPs (30 nm)/TiO₂-NWs (120 nm) (TAT-NWs) samples using the GLAD technique without using any catalyst. The deposition rate was maintained at ~ 0.6 Å/sec for 12 minutes for each deposition of TiO₂ (30 nm) and 7 minutes for the deposition of Ag (30 nm) at ~ 0.8 Å/sec. The morphology of the as-deposited TiO₂-NWs sample was analysed using Field Emission Scanning Electron Microscope (FE-SEM) (Sigma 300 Zeiss). Further, the structural properties of as-deposited TiO₂-NWs and annealed TAT samples were analysed by High-resolution Transmission Electron Microscopy (HR-TEM) (JEM-2100 JEOL). Finally, the as-deposited TiO₂-NWs and annealed TAT samples were also characterized by X-ray diffraction (XRD) using X-PertPro PanAnalytical with Cu K-alpha radiation ($\lambda = 1.54060$ Å) which is operated at 30 mA and 40 kV. The optical properties were analysed for TiO₂-NWs and TAT samples using UV-Vis spectrophotometer (AN-UV-6500N ANTech) under the wavelength range of 370 nm to 800 nm. The samples were also characterized using a Photoluminescence spectrophotometer (F-7000 Fluorescence Spectrophotometer HITACHI) under an excitation wavelength of 340 nm using a 370 nm filter.

3. Result and Discussion

3.1 Morphology and structural analysis

3.1.1 FE-SEM analysis

The top view FESEM image of the sample shown in Fig. 1 reveals the successful growth of vertically aligned TAT-NWs on glass substrate using GLAD techniques by e-beam evaporation technique. It is observed that the average diameter of TAT-NWs is ranging from ~20 nm to ~100 nm as seen from the inset of Fig. 1. The calculated average diameter of the TiO_2 NWs is 50 nm. The porous nature observed from the top view reveals the formation TAT-NWs. Similar morphology is observed from the top view image of GLAD deposited TiO_2 NWs [24]. Such nanostructure enhanced the photon absorption due to an increase in the surface-to-volume ratio. In addition, this unique nanostructure may help in designing flexible solar cells for trapping more incident photons [25]. It is also observed that larger diameter NWs are formed, which may be due to the cluster formation at the initial stage of nucleation [26].

Fig. 1 Top view FE-SEM image of as-deposited TAT-NWs sample and inset shows the magnified image showing the porous nature of the sample

3.1.2 TEM analysis

The TEM images of the as-deposited TiO_2 -NWs and annealed TAT-NWs are shown in Fig. 2. Fig. 2(a) shows typical TiO_2 -NWs having a diameter of ~20 nm at the top and a length of 240 nm. The arrow mark in Fig. 2 (a) indicates the growth direction of the TiO_2 -NWs during the growth process. This result also reveals that the vertically aligned NWs are successfully grown on the substrate by the GLAD technique, which supports the top view image of FE-SEM. The magnified HR-TEM image as shown in Fig. 2(b) reveals the presence of small grains of TiO_2 crystal, which indicates that the as-deposited TiO_2 -NWs are polycrystalline in nature. Also, the SAED analysis as shown in the inset of Fig. 2(b) manifest that the as-deposited TiO_2 -NWs are polycrystalline in nature. Further, the annealed TAT-NWs sample shown in Fig. 2(c) reveals that the Ag-NPs are successfully embedded at the middle of the TiO_2 -NWs. The size of the Ag-NPs deposited at the middle is ~30 nm indicated by the dotted circle in Fig 2 (c). Again, the SAED analysis of the annealed TAT-NWs sample showing the bright ring patterns indicated the polycrystalline nature of TiO_2 and Ag as shown in the inset of Fig. 2(c). It is also evident from the brighter ring pattern of the SAED result of annealed TAT-NW sample that the crystallinity of the TiO_2 is improved after annealing at 500 °C for one hr in ambient condition compared to the as-deposited TiO_2 -NWs sample. The total length of TAT-NWs is 270 nm and the diameter is ~50 nm. The larger diameter of the TAT-NWs may be due to the cluster formation during the initial nucleation process [26]. However, the length of the NWs is precisely controlled using this proposed GLAD technique. The lattice constant calculated from the ring of the SAED result of TAT are 3.70, 1.81, 1.73, 1.62 Å which corresponds to (101), (200), (202) and (211) of anatase TiO_2 crystals and 2.56, 2.15, 20.8 Å corresponds to (101), (111) and (210) of rutile TiO_2 crystals (JC-PDS No. 84-1286 and JC-

PDS No. 75-1753). Moreover, the lattice constant 1.92, 1.44 and 0.12 Å extracted from the SAED ring of the TAT-NWs sample corresponds to (200) Ag and (220) Ag crystals of Ag NPs. Further, the annealed TAT-NWs sample shows the presence of small crystal grains of Ag-NPs shown in Fig. 2(d), which supports the SAED result of TAT-NWs. The EDX analysis confirms the presence of Oxygen (O), Titanium (Ti) and Silver (Ag) as shown in Fig. 3. It may be mentioned that the e-beam deposited TiO₂ thin film are mostly amorphous [27]. However, Y. M. Abdulraheem et. al. reported that the TiO₂ thin film deposited at room temperature is polycrystalline. It is reported that the TiO₂ crystallinity can be improved by annealing at above 400 °C [28].

Fig. 2 (a) Shows a typical TEM image of as-deposited TiO₂-NWs, (b) shows the magnified image of top portion of TiO₂-NWs showing the presence of crystal grain and inset image shows the SEAD results of TiO₂-NWs, (c) Shows the TEM image of annealed TAT-NWs sample and SEAD result in inset shows polycrystalline nature, (d) The magnified TEM image of middle portion of TAT-NWs showing the presence of crystal grain of Ag-NPs.

3.1.2 XRD analysis

Fig. 4 shows the XRD results of TiO₂-NWs and TAT samples deposited on glass substrate using GLAD at 30 rpm. It is observed that the weak peaks at 25°, 47° and 55° are from the crystal lattice of (101), (200) and (211) of anatase TiO₂, respectively (JCPDS No. 84-1286). Moreover, the weak peaks at 36° and 41° are from the crystal lattice of (101) and (111) of rutile TiO₂, respectively (JCPDS No. 75-1753). The TAT-NWs samples also show similar weak peaks from anatase and rutile TiO₂ crystal grains. Further, it is very interesting to observe small peaks at 44°, 64.8° which are from Ag crystals (200) and (220) respectively (JCPDS No. 04-0783). The inset of Fig. 4 shows the magnified peak of Ag from (220) crystal at 64.8°. The XRD analysis of the as-deposited TiO₂-NWs and TAT-NWs samples manifests the presence of mixed phases of polycrystalline anatase and rutile TiO₂. Further, the XRD result also confirms the presence of Ag-NPs, which were embedded successfully inside the TAT-NWs. It is noteworthy to mention that the e-beam deposited TiO₂-NWs are mostly amorphous or mixed phases of amorphous and polycrystalline [27, 25]. Alberto Casu et. al. reported the deposition of TiO₂ nanostructure having mixed phases [29].

Fig. 3 EDX spectrum showing the elemental presence of TAT Sample

Fig. 4 Shows the XRD result of TAT and TiO₂ nanowires deposited at room temperature and the inset shows the magnified resolution-showing a peak from Ag

3.2 Optical Analysis

3.2.1 UV-Vis Spectroscopy

The optical absorption spectra were measured for the TiO₂-NWs and TAT-NWs samples, which are deposited on the Glass and PET substrates. These two samples were scanned from 340 nm to 800 nm wavelength ranges at room temperature to analyse the absorption spectra of the samples. The absorption intensity of the samples was recorded using UV-Vis Spectrophotometer (AN-UV-6500N, ANTech). Fig. 5 shows the absorption spectra for TiO₂-NWs, TAT-NWs deposited on the glass substrate and TAT-NWs deposited on PET substrate. TiO₂-NWs reveals a stronger absorption peak in the ultraviolet (UV) region, which is due to the transition of an excited electron from the valence band to the conduction band [30]. It is observing that TAT-NWs deposited on glass substrate shows enhance absorption in the visible region as compare to TiO₂-NWs [31]. This absorption

Fig. 5 UV-Vis absorption spectrum of as-deposited TiO₂-NWs and TAT samples deposited on the glass substrate and PET substrate and the inset shows the bandgap of TiO₂-NWs using Tauc Plot

enhancement in the visible region may be due to multiple scattering of a photon inside TiO₂-NWs and the Surface Plasmon Resonance effect (SPR) of Ag-NPs. It may be noteworthy to mention that the absorption enhancement from the TAT-NWs sample in the visible region around 400 to 600 nm with the absorption peak at ~463 nm may be due to the SPR effect that occurs at the interface between Ag-NPs and TiO₂-NWs. Similarly, Sung K. Lim et. al. reported that the absorption peak of Ag-NPs may be tuned from the resonance wavelength of 460 nm to 540 nm (± 40 nm) by altering the nanoparticle diameter [32]. It is also interesting to observe that TAT-NWs deposited on PET substrate manifest enhanced optical absorption in the UV and visible spectrum as compare to TiO₂-NWs and TAT-NWs on the glass substrate. This indicates that the TAT-NWs deposited on PET substrate may be applicable for developing flexible photoanode for Dye-Synthesis Solar cells (DSSCs) and other flexible optoelectronic devices. The inset of Fig. 5 shows the $(\alpha h\nu)^2$ versus $h\nu$ curve (Tauc Plot), where $h\nu$ is the photon of energy incident on the TiO₂-NWs and α is the absorption coefficient. From this Tauc plot, the bandgap of TiO₂-NWs is determined by extrapolating the linear portion of the curve to the X-axis of the $(\alpha h\nu)^2$ and energy curve. The bandgap of the as-deposited TiO₂-NWs sample from extrapolation is observed to be ~3.15 eV. The bandgap obtained from the extrapolation is in good agreement with the bandgap obtained by Kiran Gupta et. al. [33].

3.2.2 Photoluminescence Spectroscopy

The broadband PL intensity spectrum of as-deposited TiO₂-NWs and TAT-NWs samples are plotted in Fig. 6, which is excited at 340 nm wavelength at room temperature. It is observed that the as-deposited TiO₂-NWs and TAT-NWs sample shows broad emission with a maximum peak at ~398 nm and ~397 nm, respectively. The emission peak at ~398 nm (~3.12 eV) from TiO₂-NW may be due to the main bandgap emission of anatase TiO₂-NWs [34]. However, the TAT sample shows an emission peak at ~397 nm (~3.12 eV) with lower emission intensity, which may be due to the presence of unoccupied oxygen level created by Ag-NPs on the interface of TiO₂-NWs. However, the main bandgap of TiO₂ NWs obtained from the PL analysis supports the bandgap energy extracted from the Tauc plot. It is also observed that the photoluminescence property of TiO₂-NW decreases due to the reduction of recombination of electrons and holes after the incorporation of Ag-NPs, where the Ag-NPs acting as an electron sink [35].

Fig. 6 PL spectrum of as-deposited TiO_2 -NWs and TAT (TiO_2 -NWs/Ag metal NPs)

Fig. 7 Gaussian fitted PL peaks of annealed TAT sample

Further, to realize the defects present in TiO_2 metal oxide, the Gaussian function was fitted to the PL spectrum of TiO_2 -NWs as shown in Fig. 7. The samples appear maximum emission peak at ~ 397 nm (~ 3.12 eV) which is due to the emission of the main bandgap transition of electrons from the conduction band (CB) to the valence band (VB). On the other hand, the light emission at ~ 425 nm (~ 2.92 eV) may be due to self-trapped excitons transition from the oxygen defects [36]. Further, the emission peak at ~ 490 nm (~ 2.53 eV) is because of the oxygen vacancies at the mid-band gap of TiO_2 NWs [37]. Bandgap energy showing the emission of photons from the defects is illustrated in the inset of Fig. 7.

4. Conclusion

In this work, TiO₂-NWs and TiO₂-NWs/Ag-NPs/TiO₂-NWs samples were deposited successfully on Glass and ITO coated PET flexible substrate using the catalytic free GLAD technique. The morphology and structural characterization manifest successfully deposition of TiO₂-NWs/Ag-NPs/TiO₂-NWs on glass and PET substrate. The top view image of FESEM analysis shows the uniform deposition of TAT-NWs over the glass substrate. Further, the average top diameter of the nanowires is ranging from ~30 nm to 80 nm. The TEM image of as-deposited TiO₂-NWs shows the polycrystalline nature of the sample. Again, the HR-TEM image manifests that the Ag-NPs are successfully deposited in the middle of the NWs. Moreover, the XRD analysis confirms the polycrystalline nature of the TiO₂-NWs and the presence of Ag-NPs. It is interesting to observe that the TAT-NWs sample shows an enhanced absorption spectrum in the near UV and visible regions. However, TAT-NWs deposited on PET substrate shows enhance absorption in the UV and visible region showing potential candidate for flexible electronics application. The bandgap of TiO₂-NWs obtained from the extrapolation of the Tauc plot is ~3.15 eV. Moreover, the bandgap of TiO₂-NWs obtained from the PL measurement is ~3.12 eV, which is almost similar to the bandgap obtained from the Tauc plot. Therefore, the proposed technique of developing metal nanoparticle embedded TiO₂-NWs on glass and PET substrate using the catalytic free GLAD technique may be applicable for rigid and flexible optoelectronic applications.

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Figures

Figure 1

Top view FE-SEM image of as-deposited TAT-NWs sample and inset shows the magnified image showing the porous nature of the sample

Figure 2

(a) Shows a typical TEM image of as-deposited TiO₂-NWs, (b) shows the magnified image of top portion of TiO₂-NWs showing the presence of crystal grain and inset image shows the SEAD results of TiO₂-NWs, (c) Shows the TEM image of annealed TAT-NWs sample and SEAD result in inset shows polycrystalline nature, (d) The magnified TEM image of middle portion of TAT-NWs showing the presence of crystal grain of Ag-NPs.

Figure 3

EDX spectrum showing the elemental presence of TAT Sample

Figure 4

Shows the XRD result of TAT and TiO_2 nanowires deposited at room temperature and the inset shows the magnified resolution-showing a peak from Ag

Figure 5

UV-Vis absorption spectrum of as-deposited TiO_2 -NWs and TAT samples deposited on the glass substrate and PET substrate and the inset shows the bandgap of TiO_2 -NWs using Tauc Plot

Figure 6

PL spectrum of as-deposited TiO₂-NWs and TAT (TiO₂-NWs/Ag metal NPs)

Figure 7

Gaussian fitted PL peaks of annealed TAT sample