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Research Article

Visible Light Activity of Enhanced Screen-printed Titanium Dioxide

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Abstract

This research focused on investigating the effect of novel Alpirin as a natural light harvesting pigment for sol-gel derived titanium dioxide with silver plasmon. The absorbance, transmittance, refractive index, optical conductivity, band gap, the crystalline sizes and average dislocation density of TiO_2 were investigated. It was observed that these optical properties were improved as a result of doping with Alpirin. Further significant improvement was observed on the addition of AgNPs that was deposited through one successive ionic layer adsorption and reaction (SILAR) cycle. The average crystalline size of Alpirin doped titanium dioxide was with average dislocation density of and the band gap of 2.52 eV while that of alpirin +AgNPs doped TiO_2 was with average dislocation density of and the band gap of 2.00 eV as against the undoped TiO_2 with average crystalline size of and average dislocation density of and band gap of 3.65 eV. The synergy between alpirin + AgNPs show that the incorporation of metal nanoparticle is beneficial for enhanced photoactivity.

Keywords: Alpirin; Photoactivity; Silver; Titanium Dioxide

Introduction

Titanium dioxide is a promising photocatalyst for the degradation of organic pollutant [1]. Its specific properties like the optical, electronics, excellent chemical stability, non -toxicity to the environment and relatively cheap nature have given it a wider research interest [2,3]. Unique properties such as high transmittance, high refractive index, relatively high energy conversion efficiency and high stability make it a better prospect for optical applications [4]. When light of appropriate intensity shines on titanium (iv) oxide surface, pairs of electrons and wholes are generated inside its crystal lattice. Free electrons are usually produced in the conduction band and the holes at the valence band [5]. However, the major limitation associated with using titanium dioxide as a photoanode is the high electron whole recombination as a result of its wide band gap energy; which causes a small fraction of the solar light from the ultraviolet region to be utilized [67]. To maximize the photoactivity of TiO_2, it is necessary to reduce the wide band gap energy [1]. Many attempts have been made recently to enhance TiO_2 with metals and non metals such as nitrogen [8], silver [4], iron, gold [9], copper [10]. Recent research has indicated that the use of natural ruthenium dye [11], cynodon dactylon [6], sepia melianin [1] among other dyes which are cheap, abundant, renewable and ecofriendly have significantly modified the photoactivity of titanium dioxide. However, solar cells fabricated with co-doped TiO_2 proved to be more efficient. [10] doped TiO_2, with Fe, Cu and mix Fe-Cu and observed that mix Fe-Cu has more power conversion efficiency than doping with single metal. Deposition of Ag on doped TiO_2 showed enhanced photovoltaic properties due to the synergistic effect between Ag and doped TiO_2, the Ag-NPs has dual effect on the performance of TiO_2 including the enhancement of the absorption coefficient and optical absorption due to surface Plasmon resonance [12,13]. Incorporating a very small amount of metal into natural dye has not been fully explored. This research area still remains very economical due to the cheap source of the natural dye and its natural abundance and renewability. However the photocatalytic activity of TiO_2 also strongly depends on the preparation methods and on the post-treatment conditions. It has decisive influence on the chemical and physical properties [14,15]. There are different methods that has been used to synthesize TiO_2. These include gel method [16,17] and vapour deposition method [7], hydrolysis of inorganic salts [3,18] chemical spray pyrolysis, sol-gel technique, hydrothermal treatment, and arc discharge method [19,20]. Currently, sol–gel is one of the most successful techniques on how to prepare nanosized metallic oxides with high photocatalytic activity [3,20]. Screen printing deposition technique is one of the most reported methods of producing the nanostructured metal-oxide layer within DSSCs [21,22]. This deposition technique produces films in large quantity with the use of relatively cheap and simple designs with excellent scales of economy [23]. The aim of this research work is to investigate the doping influence by the novel alpirin natural dye as well as alpirin dye mixed with silver plasmon on the optical and structural properties of sol gel derived titanium iv oxide. Alpirin is a dye extract from *Alpinia purpurata* commonly called red ginger flower and it is not an edible plant.

Materials and Methods

Materials

The sol-gel derived TiO_2 was purchased from Solaronix Renewable Energy. *Alpinia purpurata* flower samples were collected from a flower garden in a residential compound in Abia State. Silver nitrate ($AgNO_3$), tin (ii) chloride, methanol and soda lime substrate glass were purchased from Allan's Resources. All the other materials used in this research work were supplied by Sheda Science and Technology Complex (SHETCO) Abuja.

Deposition of TiO_2

The substrate glass was cleaned with deionized water and ultrasonicated in isopropanol for about 10 minutes. TiO_2 nanoparticles were gradually screen printed unto soda lime substrate glass with the help of squeegee at annealing temperature of 500°C for seventy minutes. The films were allowed to cool down to room temperature. That was a necessary condition to remove thermal stresses and avoid cracking of the glass or peeling off the TiO_2 film [24].

Deposition of silver nanoparticles

The substrate glass was cleaned using cotton wool soaked with sodium lauryl sulphate and rinsed with de-ionized water. Later dipped into a mixture of H_2SO_4 and chromic acid to make the surface hydrophilic and was thereafter rinsed with distilled water. It was then immersed in 0.1 M tin (ii) chloride ($SnCl_2$) for 20 mins then rinsed with distilled water for 20 mins and immersed in 0.01M silver nitrate ($AgNO_3$) and rinsed with a mixture of distilled water and hydrochloric acid (HCl). This process gave the structure glass/TiO_2/AgNPs with one complete SILAR cycle. SILAR method is relatively simple, cheap, and time-saving and can be carried out at room temperature. It offers an easy control to the thickness of the film or nanoparticle.

Dye extraction

The flowers of *Alpinia purpurata* were air dried under room temperature for about thirty (30) days until they became invariant in weight and were well blended to very fine particles. 1g of the flower sample was measured using electronic chemical balance and soaked in methanol and HCl mixed in the ratio of 99:1 to form acidified methanol. The solution was vibrated on a magnetic Stirrer Hotplate78-1(PEC medicals USA) for twenty (20) mins at uniform acidity (pH of 3). Dye extract at the pH of 3 displays broad absorption peak in the 480-560nm range resulting from π - π^* transitions due to the mixed contributions of the yellow–orange betaxanthins (480 nm) and of the red–purple betacyanin (540 nm) [25; 26]. It was filtered to separate the solid residue from the clear dye solution.

Doping process

The samples with structures; glass/TiO_2 and glass/TiO_2/AgNPs were doped with *alpirin* for 48 hours. As reference, another sample with structure of glass/TiO_2 was left undoped.

Characterization and measurement

The thicknesses of both doped and undoped samples were measured using a Veeco Dektak 150 profilometer. Each sample went through the optical study using the UV/Vis/NIR spectrophotometer (6.2.0.1588 spectrophotometer). The scanning for each sample was done thrice in the wavelength interval of 0 nm to 1000 nm and the various averaged curves were taken in order to obtain the absorbance, transmittance, reflectance, refractive index and optical conductivity. The reflectance was obtained using Equation (1)

$A + T + R = 1$ ------------- (1)

Where A is the absorbance, T is the transmittance, R is the reflectance. From Equation (1) the reflectance values were obtained as shown in Equation (2) given by [27].

$1 - (A + T) = R$ ------------ (2)

The refractive index (determines the extent of permeability at which light rays can travel through a medium.

Refractive index values of the samples were obtained from equation (3) as given by [4,28].

$\eta = \frac{(1+\sqrt{R})}{(1-\sqrt{R})}$ ----------- (3)

Extinction coefficient (k) for the samples were calculated using equation (4) given by [29].

$k = \frac{\alpha \lambda}{4\pi}$ --------------- (4)

Where α is the absorption coefficient, is the wavelength and π is equal to 3.142.

The X-ray diffraction pattern was recorded on a Rigaku Ultima IV X-ray diffractometer.

Results and Discussions

Optical analysis

The thickness of the samples shows that they are all thin films with the thickness of about 75 nm. Figure 1 shows the UV-Vis absorption spectra of undoped and doped TiO_2 samples within the wavelength range 0 – 1000 nm. It is obvious that the absorption edge was shifted to the visible region due to doping. However the shift went higher as a result of the Ag nanoparticles. The optical absorption enhancement is attributed to the intensified near-field surface plasmon resonance (SPR) of metallic AgNPs, which interacted with the dye molecule thereby enhancing dye absorption. This result is in agreement with those obtained by [2,13,28]. Figure 2 shows the variation of transmittance with wavelength for undoped and doped TiO_2 samples. High transmittance for all the samples was observed. We also observed a slight drop with TiO_2 doped with apirin, the transmittance dropped further for sample doped with alpirin + silver nanoparticles within the visible spectrum. This shows that the film can be used as optical windows in solar cell. This result agrees with those obtained by [2].

Figure 1: Uv-vis spectra of undoped and doped TiO_2 samples.

Figure 2: Variation of transmittance with wavelength for undoped and doped TiO_2 samples.

From the results obtained in figure 3 we observed high reflectance in the visible region for the sample doped with alpirin. The reflectance increased further on doping with AgNPs + alpirin as compared to the undoped sample. This result is in agreement with [28].

The results obtained in figure 4indicate high refractive index within the visible region for the doped samples. It is observed that the refractive index increased for sample doped with alpirin and increased further on doping with AgNPs + alpirin. This shows that the medium is highly permeable for light rays and very good for solar cell applications.

Figure 5 show the variation in extinction coefficient with wavelength for undoped and doped TiO_2. We observed that the extinction coefficient increased on doping with alpirin with peak at

400 nm and also increased further on doping with AgNPs + alpirin a peak at 447 nm.

Figure 3: Reflectance for undoped and doped TiO_2 samples.

Figure 4: Variation of Refractive Index for undoped and doped TiO_2.

Figure 5: Variation of Extinction Coefficient with wavelength for undoped and dope TiO_2.

Figure 6: Direct band gap for (a) undoped TiO_2 (b) TiO_2 doped with alpirin (c) doped with AgNPs and alpirin.

The direct energy band gap of the films was evaluated at the intercept of zero y-axis of linear extrapolation of the plot. Figure 6 gives the direct band gap of (a) 3.65 eV for undoped TiO_2, (b) 2.45 eV for Alpirin/TiO_2 and 2.10 eV for Alpirin/$AgNO_3$/TiO_2. From these results, it is obvious that optical band gap energy of pure undoped TiO_2 decreased on doping with Alpirin which allows delay in recombination of ion and increases photoactivities of TiO_2.

The X-ray diffraction

Figure 7: XRD pattern for (a) undoped TiO_2 (b) TiO_2 doped with alpirin (c) doped with AgNPs and alpirin.

The XRD pattern for the undoped TiO_2 with peaks at 2θ =25°, 38°, 48°, 54°, 55°, 63° and 75° which correspond to miller indices [101], [004], [200], [105], [211], [204], [116], and [215] is shown in Figure 7(a). The patterns of deposited sample are attributed to reflections of anatase phase with tetragonal crystal structure. The results correspond to those obtained by [20;4]. In Figure 7(b), there was phase transformation from amorphous to anatase and to rutile. It was also observed that the anatase phase with the tetragonal crystal structure has more peaks than the rutile phase. It is considered widely that this is as a result of improved charged carrier separation, possibly through the trapping of electrons in rutile and the consequent reduction in electron-hole recombination. This result corresponds to those obtained by [30]. There are three additional peaks at, and as shown in figure 7(c). The x–ray diffraction patterns is also attributed to reflections of anatase phase with tetragonal crystal structure, there is also the presence of Silver chlorargyrite AgCl. Using Debye-Scherer Equation.

The average crystalline sizes were for undoped TiO_2, for TiO_2 doped with alpirin and for TiO_2 doped with Ag + alpirin. The average dislocation densities were; for undoped TiO_2, for TiO_2 doped with alpirin and TiO_2 doped with Ag + alpirin. The XRD of the synthesized nanoparticles are very broad which indicates large crystallite sizes. Anatase TiO_2 is seen as the main polymorph present in the samples. The diffraction angles indicate a body centered tetragonal crystalline structure of TiO_2. The peaks of the doped samples were shifted to the higher diffraction angles as compared to that of the undoped TiO_2 sample. The results show that average crystallite size of TiO_2 slightly increases when it was doped with alpirin and decreases when it was doped with Ag + alpirin.

Conclusion

The impact of alpirin and Ag + alpirin on the optical and structural properties of TiO_2 nanoparticles synthesized of TiO_2. The UV-vis spectroscopy showed the shifting of absorption edge of doped TiO_2 to the visible spectrum as compared with the undoped TiO_2. The transmittance for the TiO_2 samples was high which lends good application as optical window solar cells. The refractive index increases for TiO_2 doped with alpirin and went higher on doping with Ag + alpirin. The average dislocationdensities increase with decreasing particle size. These properties show high permeability as required in optical windows.

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