Optical studies of titanium dioxide/silver/gold (TiO$_2$/Ag/Au) nanocomposites as photo anode in dye sensitized solar cells

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Abstract
In dye-sensitized solar cells (DSSCs), the performances of the photo anodes depend on the bandgap of semiconducting nanomaterials. Titanium dioxide (TiO$_2$) is usually used in preparation of photo anode but it absorbs only the ultraviolet light, owing to its large bandgap of about 3.2 eV, and another drawback is that TiO$_2$ has low electron mobility. In this study, optical studies of (TiO$_2$/Ag/Au) nanocomposites as photo anode were carried out in order to test the possibility of improving the efficiency of the DSSCs. Dye molecule was extracted from the leave of sensitive plant (*Mimosa pudica*) using ethanol as solvent. TiO$_2$/Ag/Au were deposited on a glass substrate using doctor blade method; the deposited thin films were annealed in a furnace at 450 $^\circ$C for 1 h after which the annealed thin films were dye loaded for 12 h with *Mimosa pudica* extract. The dye loaded thin films of TiO$_2$/Ag/Au were then characterized with a UV-vis spectroscopy to get the transmittance. The absorbance and the optical bandgap were calculated. The optical absorption spectra and optical bandgap spectra of TiO$_2$/Ag/Au thin films were examined. The maximum absorption was observed within the range of the visible region when the position of TiO$_2$/Ag/Au is of volume ratio 1:1:0.8 and optical bandgap of 3.75eV. Anticipatedly, the performance characterization with further review on TiO$_2$ with Ag/Au nanocomposites using *M. pudica* extract, as a sensitizer will enhance the development of an authentic and competitive dye sensitized solar cell.

Keywords: Dye sensitized solar cells (DSSCs), thin films, *Mimosa pudica*, Photo-anode
1 Introduction

Fossil fuels are the main source of energy consumed worldwide. It is a non-renewable source of energy. Energy is generated from fossil fuel, and so improves the life condition of mankind [1]. The critical fact is that fossil fuels emit greenhouse gas (carbon dioxide) when it burns which are the major causes of global warming [2] due the long term rise in earth's average surface temperature. As man’s population increases, the demand for energy increases, and the more the usage, the more the environmental hazards. Therefore, a viable and renewable energy sources to replace diminishing fossil fuels are required. Various forms of renewable energy sources have been identified including wind, hydro, biomass, biofuel, geothermal and solar energy. Of all the energy sources, solar energy receives the attention of researchers because it was recognised to serve as the primary energy sources for other types of energy [3]. Solar energy provides a clean, cheap and renewable energy for human race, the quest for conversion of solar energy to electricity led to the invention of solar cells.

Solar cells are categorized into three different generations; first generation, second generation and third generation solar cell [4]. The first generation consists of crystalline semiconductor wafers with a thickness of 200-300 nm. The second generation are based on thin film technology having thickness usually in the range 1-2 nm [5]. The third generation technology is mainly focused on the material e.g. wide band gap metal oxide semiconductors that include titanium dioxide (TiO$_2$), ZnO among others. Dye sensitized solar cells (DSSCs) is an example of third generation technology [6-10].

DSSCs are devices that convert solar to electric energy by light sensitization established on wide energy band semiconductor [11]. It is currently attracting widespread scientific and technological interest because of its minimal production cost, environmental friendliness, simple method of fabrication, lower toxicity manufacturing process, straightforward scale, low weight and potential use in flexible panel as compared to conventional p-n junction devices [12].

A modern DSSC is composed of photo-anode, photosensitizer, electrolyte and a counter electrode. Nanostructure semiconductor metal oxide e.g. TiO$_2$ are usually deposited over a transparent conducting glass substrate to prepare photo-anode [2, 3, 11].
The performance of the photo-anodes depends on the band gap, morphology, and composition of metal oxides and thickness of metal oxides. In recent times, a new method has evolved for increasing the light absorption of photo-anode in DSSC; the use of nanoparticles with size ranging between 1-100 nm [13, 14]. Nanostructured metal oxide have emerged as strong candidates for wide range of application on account of its unique physical, chemical, optical, electrical and thermal properties [15-18]. With respect to its unique properties, silver nanoparticles (AgNPs) are being incorporated into photovoltaic application [19-20]. The effects of annealing temperature on the optical properties of AgNPs thin films deposited on glass substrate by spin coating technique has been investigated [5]. The result revealed that light absorption spectral range and thermal stability could be enhanced using silver nanoparticles [5].

The use of inorganic dye has been predominant for the production of the DSSCs [22-26]. The most efficient inorganic dye i.e. ruthenium complexes employ as photosensitizers in DSSCs have exhibited high power conversion efficiencies up to 11-13% [27, 28]. The disadvantage of these complexes is high cost and sophisticated preparation techniques. Investigation of low cost, readily available dye as efficient sensitized for DSSCs have been studied. Natural dyes extracted from fruit, leaves, roots and flowers have been proven to be efficient dye as a sensitizer in DSSCs [2, 3, 6].

In this work, natural pigment was extracted from the leaves of *Mimosa pudica*, an organic plant locally known as “sensitive plant or touch me not plant”. The optical spectral study of the extracted pigment of *M. pudica* using ethanol as solvent was primarily characterized by UV-vis spectrophotometer. Titanium dioxide incorporated with silver and gold nanoparticles (TiO$_2$:AgNPs:AuNPs) as photo-anode material using doctor blade technique was characterized using a UV-vis spectrophotometer.

2 Materials and Methods

2.1 Materials

The materials utilized for this study included: titanium (iv) oxide nanopowder (< 0.35 nm) of 97% purity supplied by Sigma Aldrich, 100 µg/ml cocoa pod extract-mediated silver nanoparticles (AgNPs) [29] and 340 µg/ml kola pod extract-mediated gold nanoparticles (AuNPs) obtained from the Laboratory of Industrial Microbiology and Nanobiotechnology LAUTECH Ogbomoso.
2.2 Preparation of natural photo-sensitizers

*Mimosa pudica* was obtained from a nearby local farm in Ogbomoso, Nigeria. The leaves from the plant were taken and washed severally with distilled water, followed by air-drying. The dried leaves were ground into powder. Two gram of the powder was weighed and poured into a bottle. The photosensitizer was extracted by dissolving 2 g of the fine powder into 50 ml of ethanol; the solution was left undisturbed for 24 h at room temperature. The residue was the filtered out, the resulting dye solution was optically characterized and utilized as natural photosensitizers without any further purifications. To ensure stability before use, the filtrate was kept in a separate clean bottle and protected from direct sunlight.

2.3 Substrate preparation

Microscopic glass slides (25.4 mm × 76.2 mm × 1.0 mm) were used as substrates. The rectangular glass slide was first cleaned in a detergent solution using an ultrasonic bath for 15 min. They were washed with detergent solution for 10-15 min in ultrasonic sonicator and rinsed in distilled water for 15 min at 30 °C. The substrate was cleaned with isopropanol alcohol (IPA) in ultrasonic bath for 15 min at 30 °C and dried in a stream of nitrogen gas (N$_2$).

2.3.1 Preparation Titanium dioxide (TiO$_2$) paste

About 30 ml of ethanol was measured and added to 3 g of TiO$_2$ powder in a beaker. The solution was placed on a magnetic stirrer for 1 h until homogenous mixture is formed.

2.3.2 Preparation of (TiO$_2$:AgNPs:AuNPs)

The blend solution of (TiO$_2$: AgNPs: AuNPs) was done by mixing TiO$_2$ solution with AgNPs and AuNPs solution at different volume ratio (1:1:0.2, 1:1:0.4, 1:1:0.6, 1:1:0.8, 1:1:1) ml and stirred with plastic spatula to obtain homogenous mixture.

2.3.3 Preparation of photo anode (TiO$_2$:AgNPs:AuNPs)

Blend pastes were deposited on a cleaned glass substrate at different volume ratio using doctor blading technique. The thin film were dried at 100 °C and later annealed at 450 °C in a furnace for 2 h. The temperatures of the films were cooled down to 80
before being immersed in to natural dye solution kept at room temperature for 12 h for complete sensitization.

2.3.4 Characterization and measurement
The UV-vis absorption characteristics of natural pigment were analysed using Jenway UV-vis spectrophotometer. It was observed that the natural pigment of *Mimosa pudica* has absorption which wavelength falls within the visible region of the spectrum. The optical absorption spectra of the photo anode were measured using UV-vis spectrophotometer (Avantes, Avalight – DH – 5bal). The absorbance of the samples was determined from transmittance value obtained from the spectrophotometer by using the relation in Eq. (1).

\[
A = \log \left( \frac{1}{T} \right)
\]  

(1)

Where A is the absorbance, T = I / I₀, I is the transmitted light and I₀ is the incident light.

The energy band gap of the thin film sample was calculated with the help of the \((\alpha \cdot \hbar \nu)^2\) versus energy band gap value. The theory of the interband absorption shows that at the optical absorption edge, the absorption coefficient \(\alpha\) varies with the photon energy \(\hbar \nu\) according to Eq. (2)

\[
\alpha(\hbar \nu) = A (\hbar \nu - E_g)^{1/2}
\]  

(2)

where A is a constant and \(E_g\) is the optical bandgap. Thus a plot of \((\alpha \cdot \hbar \nu)^2\) versus \(\hbar \nu\) is a curve line whose intercept on the energy axis gives the energy gap. The band gap energy of the films have been determined by the extrapolation of the linear regions on the energy axis \(\hbar \nu\). The absorption coefficient \(\alpha\) associated with the strong absorption region of the film was calculated from absorbance \(A\) and the film thickness \(t\) using the relation.

\[
\alpha = 2.303A/t
\]  

(3)

The thickness of thin films was determined using:

\[
t = \frac{m}{2AD}
\]  

(4)
Where $m = m_2 - m_1$ and $m_1 = \text{mass of substrate before deposition}$, $m_2 = \text{mass of substrate after deposition}$, $A = \text{Area covered by the films}$, $D = \text{density of TiO}_2$.

3 Results and Discussion

The UV-vis optical absorption spectra of *Mimosa pudica* using ethanol as solvent are revealed in Figure 1(a). It is observed that the natural pigment showed maximum absorption in the region around at 325, 347 and 430 nm. The absorption of the light falls within the visible region of the electromagnetic spectrum. Figure 1(b) shows the optical transmittance spectra of TiO$_2$:AgNPs:AuNPs at different volume ratio. The transmittance is generally high between wavelengths of 200-800 nm with a gradual fall near the fundamental absorption region. The sample with the 1:1:0.6 has the highest average transmittance value of about 49.8% and the lowest transmittance of 17% when the volume ratio was 1:1:1. In Figure 1(c), the absorbance spectra of TiO$_2$:AgNPs:AuNPs at different volume ratio is presented. The spectra revealed that the deposited films have high absorbance in the UV region, whereas the absorbance is low in the visible region. In general, the absorbance of the films decreases with increasing wavelength and decreasing photon energy. For each sample, there is an absorbance level that differs from the other. Peak absorbance was observed at volume ratio 1:1:0.8. In Figure 1(d), the energy gap spectra of TiO$_2$:AgNPs:AuNPs was presented. It was observed that the energy gap of the prepared TiO$_2$:AgNPs:AuNPs was 3.75eV compared to as prepared TiO$_2$ which was 3.57eV. The inclusion of silver and gold nanoparticles with TiO$_2$ makes the energy gap to be shifted in positive direction. The shift of conduction band in the positive direction decreases the efficiency of electron–hole separation at the interface and thus increases the electron/electrolyte recombination rate resulting in reduction in photo-current. The increase in the recombination rate also result lower $V_{OC}$ which is not essential for making an efficient DSSC [30].
Figure 1. (a) UV-Vis absorption spectrum for light harvesters obtained from leaves of sensitive plant, (b) Transmittance spectra for TiO$_2$:AgNPs:AuNPs at different volume ratio, (c) Absorbance versus wavelength of TiO$_2$:AgNPs:AuNPs films blend at different volume ratio, (d) Absorption spectra for TiO$_2$:AgNPs:AuNPs films blend at different volume ratio

4 Conclusion
The natural photosensitizer from *Mimosa pudica* leaves was successfully appraised as natural photosensitizer in photo-anode of DSSCs. The absorption peak of the extracted pigment falls within the UV-vis region. The optical study using UV-vis spectrophotometry for TiO$_2$:AgNPs:AuNPs photo-anode at different volume ratio have been investigated. Based on the results, the TiO$_2$:AgNPs:AuNPs thin film has a
good absorbance at doping concentration of 1:1:0.8 in the visible region. The band gap of the as prepared TiO$_2$ is 3.57eV. With the inclusion of silver and gold nanocomposites, the band gap increases to 3.75eV. On account of its large band gap, it is not advisable to use TiO$_2$:AgNPs:AuNPs nanocomposites as photo-anode in DSSCs.

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