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Synthesis and Characterizations of TiO_2/Ag Photoanodes for used Indigo Carmine Sensitizer Based Solar Cells

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Abstract

In this work we have prepared Ag doped TiO_2 composite semiconductor by microwave hydrothermal methods. The prepared TiO_2/Ag photoanode was characterized via XRD, FE-SEM and DRS spectroscopy techniques. Then this composite was used as a photoanode material for dye sensitized solar cells. The TiO_2/Ag photoanode was prepared by spin coating technique. The sensitizer of this solar cell is indigo carmine and it was prepared in different pH solution in ACN. The higher solar cell efficiency values were achieved up to 1.91% with TiO2/Ag photoanode and in pH 5.3 indigo carmine dye solution. As a result, in this study, it was observed that the addition of Ag nanoparticles was increased the efficiency of solar cell by 20-45%.

Keywords: Dye sensitized solar cells, indigo carmine, TiO_2/Ag.

1. Introduction

Dye sensitized solar cells (DSSCs) has been regarded as a third generation solar cell [1], they paid attention to important class of photovoltaic cells [2]. Nowadays, DSSCs have been the subject of many studies related to solar cells due to their low cost, facile fabrication, and environmental friendly behavior. Typically, DSSCs have four main components as following; large band gap semiconductor coated photoanode, light sensitive sensitizers, redox couple electrolyte, and counter electrode. In recent decade due to the harmful effects of dyes and solvents used in DSSCs, reports have been enormously used the environmental friendly materials in DSSCs [3]. For this reason, the use of environmentally friendly natural dyes, which do not contain noble metals, are increasing day by day. These dyes are examined in three main categories as following; i) metal complexes dyes, ii) organic dyes and iii) natural dyes [4, 5] Different natural dyes have been used as sensitizers in DSSCs, for example chlorophyll, carotene, anthocyanin, and tannin [6, 7].

Indigo carmine (disodium;(2E)-3-oxo-2-(3-oxo-5-sulfonato-1H-indol-2-ylidene)-1H-indole-5-sulfonate) is an organic salt, purple solid and soluble in water. It is also natural organic dye and widely used in many industrial applications like textiles, printing, dying and food. Indigo carmine is derived from indigo dye. Indigo is one of the important dye groups for textile industry because blue dyes were found seldomly in the past. [8, 9]. The indigo carmine structure is shown in Fig 1.

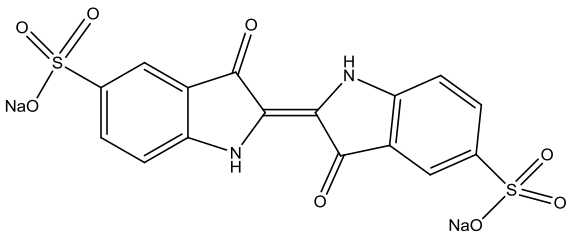

Figure 1. Indigocarmine structure.

TiO_2 is an encouraging material and mainly used photoanode material in DSSCs. It has unique properties in DSSCs such as low toxicity, excellent electron transport and good chemical stability. Also, it has several potential applications for gas sensor, lithium ion batteries and photocatalysis [10–12]. In DSSCs, several semiconductors (ZnO,

SnO_2, etc.) have been used as an alternative for the TiO_2. TiO_2 consist in three crystalline forms; rutile, anatase and brookite. The anatase form of TiO_2 is the most suitable polymorphs because of their unique charge transport property. The rutile is the most stable thermodynamic polymorph of TiO_2 at all temperatures. Therefore, anatase TiO_2 crystallization depends on preparation conditions and temperature [13,14]. TiO_2 is widely used as photoanode materials for DSSC applications. The potential advantages of TiO_2 are the chemical stability, high electron mobility and environmentally friendliness etc. The Ag nanoparticles have several application as catalysis, enzyme immobilizations, solar cells etc. The Ag nanoparticles have accelerated electron mobility.

In this study, we have prepared TiO_2/Ag nanocomposite semiconductor electrode and it can be used dye sensitized solar cells. The TiO_2/Ag nanocomposite were prepared microwave assisted hydrothermal procedure. Then these composites were characterized X-ray diffractometry (XRD), field emission-scanning electron microscopy (FE-SEM), energy dispersive X-ray analysis (EDS) and diffused reflectance spectroscopy (DRS) spectra. The indigo carmine dyes were used as the solar cells. The indigo carmine solution with different pH values were prepared in water and characterized by cyclic voltammetry (CV) and UV-Vis techniques. As investigated solar cells were prepared using this dye and TiO_2/Ag photoanode, traditional Pt counter electrode and iodide/triiodide electrolyte. The current density voltage curves were performed via electrochemical workstation (CHI 660C) under the solar simulator (Oriel LCS-100).

2. Materials and Methods

2.1 Materials

Indigo carmine ($C_{16}H_8N_2Na_2O_8S_2$), titanium isopropoxide ($C_{12}H_{28}O_4Ti$), silver nitrate ($AgNO_3$), potassium hydroxide (KOH), ethyl cellulose, 2-propanol, fluorinated tin oxide glass (FTO glass, 7 Ω/sq.), 4-tert butylpyridine were purchased from Sigma Aldrich. Iodine (I_2) was attained from Riedel de Haen. Dihydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6.6H_2O$) was obtained from Alfa Aesar. All materials were analytical grade and used as received without further treatment.

2.2 TiO_2/Ag nanocomposite synthesis

TiO_2/Ag nanocomposite were synthesized via microwave hydrothermal synthesis methods. The 5 mL titanium isopropoxide (17 mmol) and 0.17 g $AgNO_3$ (1mmol) were dissolved 60 mL deionized water and transferred Teflon lined microwave hydrothermal cup. This solution was vigorously stirred under magnetic stirrer at 30 min. Then the 1.3 g KOH was added this solution and stirred with a magnetic stirrer at 30 min. The microwave radiation, temperature and time are settled 380W, 100°C and 1h, respectively. The grey product was centrifuged and washed with ultrapure water and ethanol three times. Then, the TiO_2/Ag nanocomposite was dried 60°C for 12h. To compare all samples, TiO_2 nanoparticles were synthesis using similar procedure.

2.3. Different pH of indigo carmine solution preparation

10mM indigo carmine solution was prepared in 50 mL ultrapure water. The pH of this solution was selected as 5.3. For the comparison, the pH values 11.5 and 14 indigo carmine solutions were performed using 0.1M KOH. Indigo carmine is redox indicator and its solution is blue at the pH range of 0-11, but its color is changed to yellow at pH range of 11-14. Therefore, in this study indigo carmine solutions were prepared in three different pH values for solar cell applications.

2.4. Solar cell fabrication

The photoanode films were coated on the fluoride doped tin oxide (FTO) conductive glass by spin coating technique. The viscous paste, which includes TiO_2 or TiO_2/Ag nanocomposite and ethyl cellulose were elaborated and coated on FTO glass and sintered at 450°C at 30 min. The TiO_2 or TiO_2/Ag photoanodes were immersed in a 10 mM dye sensitizer solution for 24 h in the dark. The performed counter electrode was used as; a one drop 5 mM $H_2PtCl_6.6H_2O$ solution spreading on FTO glass. The counter electrode was sintered at 450°C for 30 min. The electrolyte solution was prepared using of 0.1 M LiI, 0.05 M I_2 and 0.5 M 4-tert-butylpyridine in acetonitrile. The solar cells assembly were sandwiched and clipped together with photoanode and counter electrodes. The electrolyte solution was injected into the internal space of the cells.

3. Results and Discussion

3.1 TiO_2/Ag nanocomposite

The XRD spectra of the TiO_2 and TiO_2/Ag nanocomposite were shown in Fig 2. The small amount of the Ag nanoparticles was added to the TiO_2 anatase structure does not deformation. The calculated values of TiO_2 and TiO_2/Ag samples are given in Table 1. The lattice strain and crystallite size were performed from using X'Pert High Score Plus software;

$$D = \frac{0.89\,\lambda}{\beta\,cos\theta} \qquad \beta = \beta_{obs} - \beta_{std} \tag{1}$$

$$\varepsilon = \frac{\beta}{4\tan\theta} \qquad \beta = \sqrt{(\beta_{obs}^2 - \beta_{std}^2)} \tag{2}$$

Where ε is the lattice strain, λ is the X-ray wavelength angular line, D is crystalline size, β is full width at half maximum (FWHM) and θ is the Bragg's angle. The achieved crystalline size of TiO_2 and TiO_2/Ag are 25.4 and 65.7 nm, respectively. The achieved strain of TiO_2 and TiO_2/Ag are 0.64 and 0.46 %, respectively. The differences between both crystalline size and strain values of prepared TiO_2 and

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TiO_2/Ag samples can be explained that, when the Ag is asserted in the system, the TiO_2 anatase lattice can be expanded and this expansion mechanism can be raises the crystalline size.

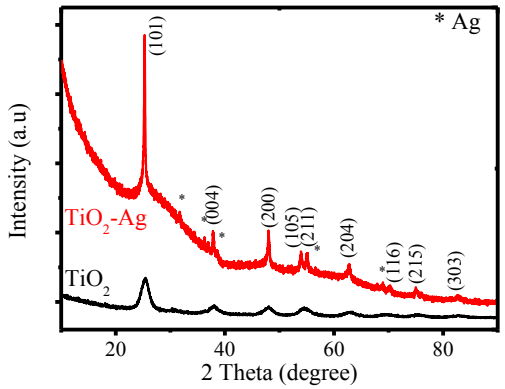

Figure 2. XRD patterns of TiO_2 and TiO_2/Ag.

Table 1. Crystalline properties for TiO_2 and TiO_2/Ag

Photoanode	Lattice Parameters		Volume	Cyrstalline size	Micro Strain
	a (Å)	c (Å)	$(Å)^3$	(nm)	(%)
TiO_2	3.804	9.391	135.89	25.4	0.64
TiO_2/Ag	3.814	9.415	135.94	65.7	0.46

The FE-SEM images and EDS spectra of TiO_2/Ag nanocomposite are shown in Fig 3. As seen in Fig. 3, the small Ag nanoparticles for doped TiO_2 surface for uniform distribution. The EDS spectra demonstrated that the TiO2 structure were doped with Ag ions, and Ag nanoparticles has deposited on TiO_2. Also, the weight percent and atomic percent of the Ag nanoparticles were found to be 0.10 and 0.02%, respectively. This small Ag nanoparticles were accelerated electron mobility and could be improved the solar cells efficiency. In this study, the DRS spectra of the both TiO_2 and TiO_2/Ag nanocomposite were taken and the band gap values of these samples were compared. The DRS results shown that the TiO_2/Ag nanocomposite absorbed more light in all region of UV-Vis compared to TiO_2. This is probably due to the Ag nanoparticles, because the color of TiO_2/Ag nanocomposite is grey. It was also decreased the light reflection. The band gap values of the TiO_2/Ag nanocomposite and TiO_2 were calculated using Kubelka-Munk equation and the detailed calculation can be seen in the previous study [15]. According to this study the band gap values of the TiO2 are 3.17 and 3.22 eV, respectively. The band gap values of anatase TiO_2 is 3.2 eV. The band gap values of both TiO_2 and TiO_2/Ag nanocomposite are suitable for the dye sensitized solar cell applications.

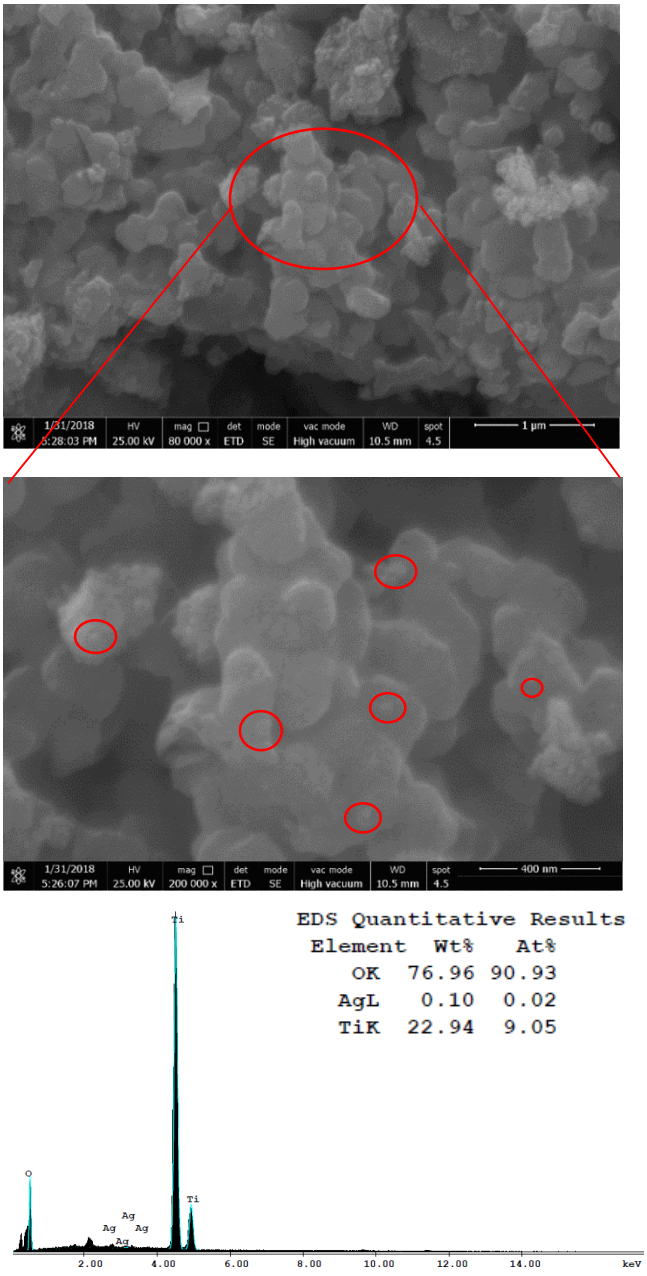

Figure 3. FE-SEM images and EDS spectra of TiO_2/Ag samples.

3.2. Indigo carmine

The 10 mM indigo carmine redox indicator solution were prepared at different pH values (5.3, 11 and 14) using ultrapure water. These pH values were selected, due to the color of indigo carmine changes at these pHs value. These dyes were characterized by cyclic voltammetry and UV-Vis techniques. The UV-Vis absorption spectra of these dyes were shown in Fig 5. It is seen that, the absorbance of these

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solutions were decreased, while the pH values of dye solutions were increased. The both UV and Vis region light absorption of indigo carmine is higher at natural pH (5.3) than basic pH values. The light absorption of indigo carmine occurs at both 200-375 and 500-700 nm regions.

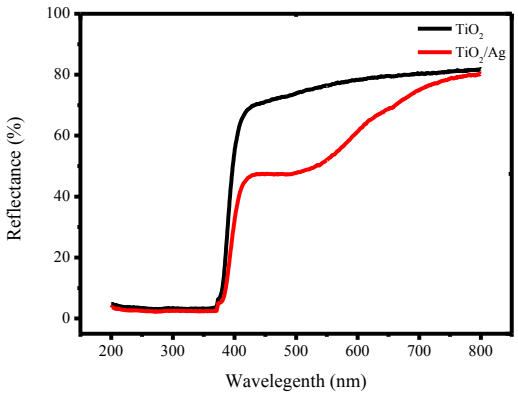

Figure 4. DRS spectra of TiO_2 and TiO_2/Ag samples.

The cyclic voltammetry curves of indigo carmine at different pH values are shown in Fig. 6. The HOMO and LUMO molecular orbital levels can be calculated in following equations [9,16];

$$E_{HOMO} = -e(E_{ox} + 4.40)\ eV \quad (3)$$

$$E_{LUMO} = -e(E_{red} + 4.40)\ eV \quad (4)$$

$$E_g = E_{LUMO} - E_{HOMO} \quad (5)$$

where E_{HOMO} is the HOMO orbital energy, E_{LUMO} is the LUMO orbital energy, E_{ox} is the first oxidation potential, E_{red} is the first reduction potential and E_g is the band gap energy. The Ferrocene/Ferrocenium is used as an internal standard for CV measurement. The estimated LUMO and HOMO levels of indigo carmine at different pH values (5.3, 11 and 14) are -5.08/-3.97, -5.12/-3.84 and -5.26/-3.71 eV, respectively. The HOMO, LUMO and E_g values of different pH conditions indigo carmine dye is summarized in Table 2. Additionally, the CV curves show that, the first oxidation peak is slightly decreased when the pH values are increased. The all dyes which have different pH values were suitable for the DSSCs applications. The LUMO molecular orbital level is so important in the dye sensitized solar cell study, due to the electron injection of the semiconductor conduction band. The conduction band of the TiO_2 is -4.00 eV. When the LUMO band of dyes are very close the TiO_2 conduction band, the more electron can be moved the conduction band. The LUMO band gap value of indigo carmine solution at pH 5.3 is close to the conduction band of TiO_2 and we predicted that this dye has higher solar cell performance. The UV-Vis absorption spectrum of this dye is also support this prediction.

Table 2. Electrochemical parameters of different pH solutions of indigo carmine

pH	Eox (NHE)	Ered (NHE)	HOMO (eV)	LUMO (eV)	Eg
5.3	0.68	-0.43	-3.97	-5.08	1.11
11	0.72	-0.56	-3.84	-5.12	1.28
14	0.86	-0.69	-3.71	-5.26	1.55

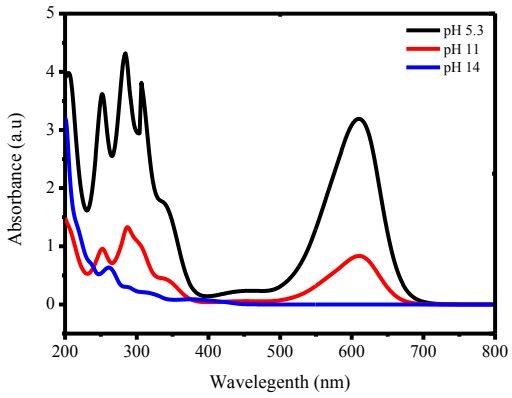

Figure 5. The UV-Vis absorbance spectra of indigo carmine at different pH values.

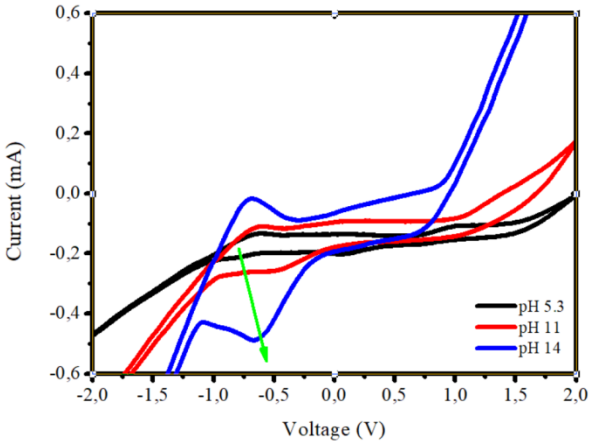

Figure 6. Cyclic voltammetry curves of indigo carmine at different pH values.

3.3. Solar Cells

To investigate the effect of Ag nanoparticles on indigo carmine based dye sensitized solar cells, series devices were prepared with both TiO_2 and TiO_2/Ag photoanodes. All parameters of fabricated DSSCs can be calculated using following equations;

$$FF = \frac{Jm \times Vm}{Jsc \times Voc} \quad (6)$$

$$\eta = \frac{Jsc \times Voc \times FF}{Pin} \quad (7)$$

where η is the solar cell efficiency, V_{oc} is the open circuit potential, J_{sc} is the short current density, J_m and V_m are the maximum current and voltage, respectively. P_{in} is the power of light source (AM 1.5).

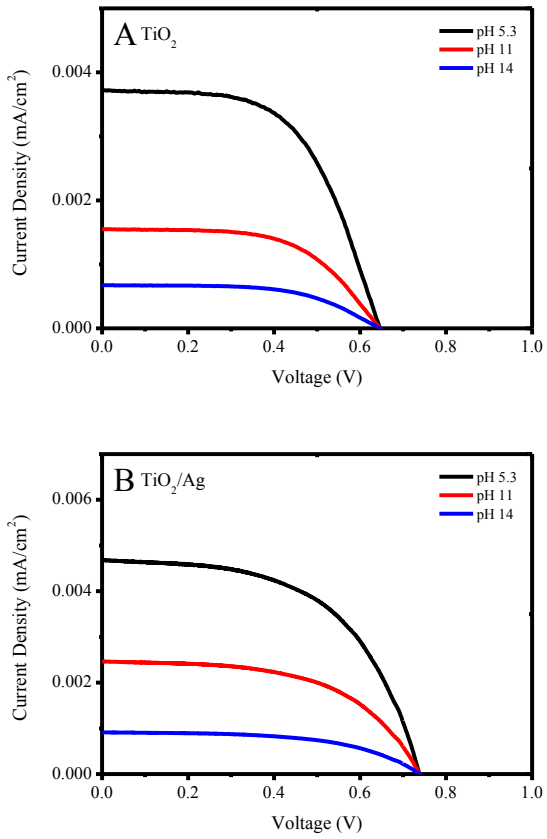

Figure 7. Current density voltage curves (J-V) of A) TiO_2 and B) TiO_2/Ag photoanodes for indigo carmine sensitizers at different pH value.

Table 3. Photovoltaic parameters of TiO_2 and TiO_2/Ag nanocomposite for indigo carmine at different pH values

	pH	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)
TiO_2	5.3	3.71	0.65	57	1.38
	11	1.54	0.65	58	0.57
	14	0.67	0.63	59	0.25
TiO_2/Ag	5.3	4.69	0.74	55	1.91
	11	2.47	0.74	54	1.01
	14	0.91	0.73	56	0.37

The current density-voltage curves (J-V) of all prepared cells are exhibited in Fig 7 and the calculated solar cell parameters of these systems are listed in Table 3. The results indicated that the Ag nanoparticles is improved the solar cell efficiency. Hence, the solar cell efficiency value of the TiO_2 and indigo carmine at pH 5.3 was found to be 1.38%, and this value is lower than TiO_2/Ag nanocomposite photoanode based cells (1.91%). Additionally, the short circuit current density (Jsc) and the open circuit voltage (Voc) values were slightly increased for TiO_2/Ag nanocomposite compared with TiO_2 photoanodes. These values are influenced by the electron mobility. Voc is also correlated with the TiO_2 conduction band and enhancement of charge recombination at the TiO_2/dye/electrolyte interface. The small doped Ag nanoparticles can be improved the electron mobility and can be improved the solar cell efficiency. When compared the solar cell efficiency values of TiO_2 and TiO_2/Ag, the Ag used in the photo anodes was increased the solar cell efficiency values by 20-45%.

4. Conclusion

The TiO_2 and TiO_2/Ag nanocomposite were prepared via microwave assisted hydrothermal methods and characterized via XRD, FE-SEM and DRS. The indigo carmine at different pH values are prepared in ultrapure water and characterized by UV-Vis and CV techniques. The TiO_2 or TiO_2/Ag photoanodes were prepared by spin coating technique. The dye sensitized solar cells were fabricated by TiO_2 or TiO_2/Ag and indigo carmine dye at different pH values. The champion solar cell efficiency was found to be a 1.91% with TiO_2/Ag photoanode and indigo carmine dye solutionat pH 5.3. The TiO_2/Ag nanocomposite photoanode based solar cells have exhibit higher conversion efficiency values than TiO_2 photoanodes. The Ag doped TiO_2 photoanodes have increased the dye sensitized solar cell efficiency values up to 20-45% for indigo carmine at different pH values.

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Author's Contributions

Soner Çakar: Drafted and wrote the manuscript, performed the experiment and result analysis.

Keziban Atacan, Nuray Güy: Assisted in analytical analysis on the structure, supervised the experiment's progress, result interpretation and helped in manuscript preparation.

Ethics

There are no ethical issues after the publication of this manuscript.

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