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Performance Evaluation of Ag Doped TiO_2 Nanoflowers in Dye-sensitized Solar Cell

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Abstract: Many attempts have been made over the last few years to create effective visible light-activated photovoltaic using Titanium dioxide as photoanode materials in Dye-sensitized solar cell (DSSC). TiO_2 possesses high photocatalytic behavior but has high charge recombination. In this study, the effect of introducing Ag dopant in TiO_2 nanoflower morphology as a blocking layer to reduce charge recombination is investigated. The fabricated Ag doped TiO_2 nanoflower was characterized using XRD, UV-Vis, IPCE, EIS analysis and Solar simulator under 1M solar illumination. Ag dopant may be considered a great approach to improving electron harvesting by suppressing electron recombination between the interface of TiO_2 and electrolyte.

Keywords: DSSC, Hydrothermal method, TiO_2 doped Ag.

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1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) are widely regarded as a viable substitute to silicon-based solar cells for photovoltaic (PV) technology in renewable energy harvesting. DSSC was first reported by Gratzel and O'Regan in 1991 recognized with low cost of fabrication, light-weight, lower handling expenses, high mechanical durability, much finer transparency, low toxicity, customizable and flexible design [1], [2]. DSSC is an environmental device as it can generate electricity from light irradiation in electrochemical cells [3]. All components in DSSC contribute significantly to the efficiency, ŋ% of the cell. DSSC comprises of two electrodes which are a working electrode consisting of a photoanode electrode (PE) and anchored dye clamped together with the counter electrode that acts as a catalyst. Redox electrolyte I^-/I_3^- is filled between them and serves as a conductor as shown in Figure 1. PE is an important layer of the DSSC because it creates a surface area for dye adsorption and electron transport. [4], [5].

Titanium dioxide (TiO_2) is the most promising PE material as its exhibits remarkable characteristics of physical and chemical properties [2]. TiO_2 able to withstand photo-corrosion and chemical corrosion and possessed high redox ability. This made TiO_2 a good prospective in a broad range of applications as well as photocatalysis [6], sensor device [7], photo-luminescence[8] and solar cell [9]. Photocatalytic activity of TiO_2 hinged on crystalline form, particle size, and particle shape. Various crystalline formations resulted in different band gaps. For instance, rutile (Eg=3.05 eV), anatase (Eg=3.23 eV), and brookite (Eg=3.26 eV) [10]. Other than that, the morphology of TiO_2 (1-Dimensional, 2-Dimensional and 3-Dimensional) is affected by the anodization state on the photon-to-current efficiency (PCE) of the electrode characteristics. Due to its high large surface area and light scattering, TiO2 with 3D nanoflower morphology can improve the PCE of DSSC. Yet, the large surface area of TiO_2 can contribute to the dark current due to the aggregation of photoelectrons with oxidized dye and electrolyte [11]. Despite this, the characteristics of TiO_2 are scarce, as spectroscopic studies indicate that approximately 90% of photogenerated electron-hole (e-/h+) pairs recombine rapidly after the excitation of photon [12]. Thus, this issue led researchers to explore material modification by introducing transition metal ion doping [8], noble metal deposition [12], surface modification [13] and modification by UV illumination to improve the efficiency of DSSC [14].

Reported studies show doping noble metal of silver (Ag) for altering the morphology of TiO_2 nanoparticle structure can reduce charge recombination and increase visible light absorption [15], [16]. In this study, TiO_2 nanoflowers (NFs) doped Ag was fabricated by facile hydrothermal process. The hydrothermal method was employed because crystallization can occur in an aqueous phase at very low temperatures and produces high-purity

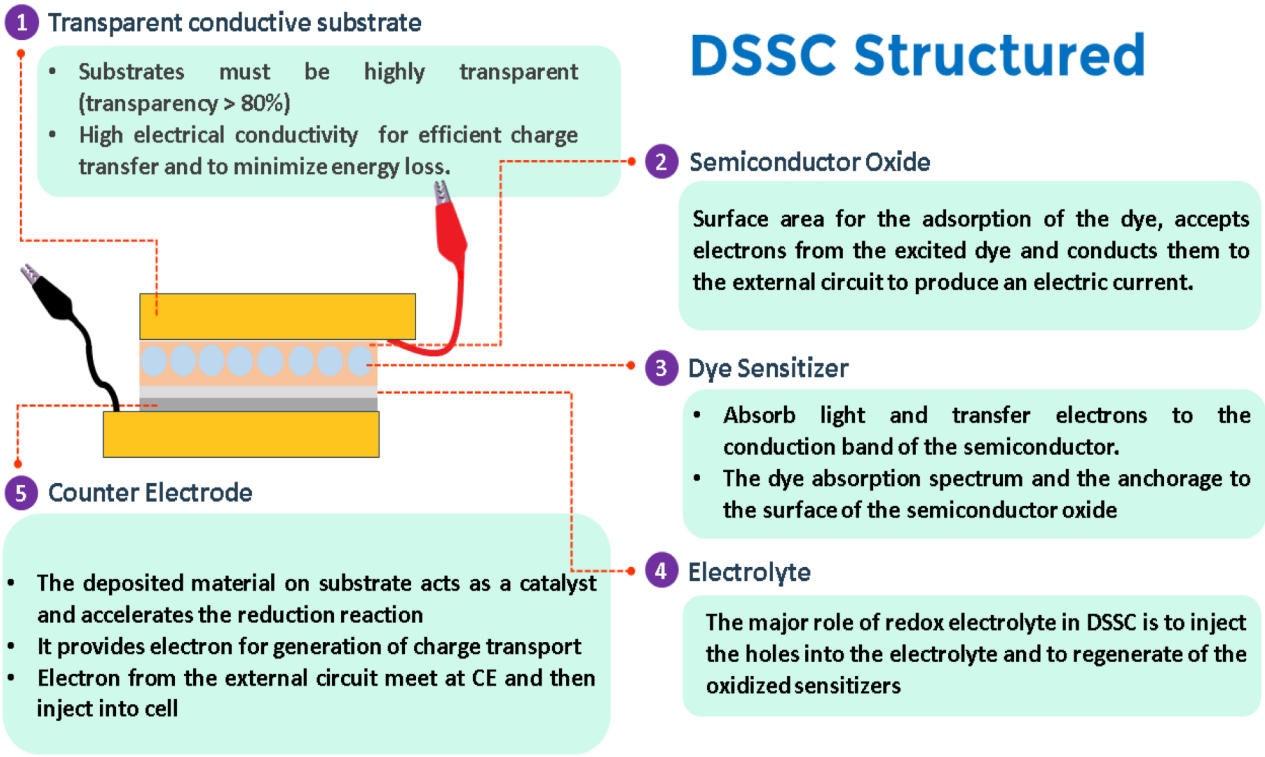

Figure 1. Mechanism of DSSC

crystals with a wide range of forms. The advantages in this work are: (1) three-dimensional TiO_2 NFs can improve the surface area for dye anchoring and light scattering on PE and (2) Ag dopant can exhibit higher visible light absorption and induces Schottky barriers at their interface resulting in lower recombination rate of photo-generated charge carriers. In this study, we investigate PCE of TiO_2 NFs by using varying concentrations of Ag dopant (0.25%, 0.5%, 1.0% and 2.0%) to improve their photovoltaic properties.

2. MATERIALS AND METHOD

TiO_2 doped Ag is synthesized by facile hydrothermal process and deposited on the flourine-doped oxide (FTO) glass with a dimension of 1.0 (L) × 0.5 (W)× 0.2 (T) cm. The solutions are mixed with 80 ml of deionized water (DI) and 80 ml of hydrochloric acid (HCl) with 36-38% purity in a beaker. Next, the mixed solution is heated at 212 °C for 20 minutes and followed by $AgNO_3$ (QRëC, USA) solution addition in different weight percentages (0.25%,0.5%, 1.0%, and 2.0%). The solutions are stirred for 30 minutes while it is heated. The solution is then cooled to room temperature before adding 0.10M $Ti(OBu)_4$ (No.5593-70-4, Sigma-Aldrich, Munich, German) dropwise. The mixed solution needs to be stirred until the solution becomes clear [17].

The prepared FTO glass is then arranged in the Teflon-lined autoclave with the sample conducting side facing up. After that, the precursor solution is placed in the autoclave, which is then placed in the oven. This hydrothermal synthesis takes 10 hours at a constant temperature of 150 ºC. Following the synthesis process, the FTO film is removed from the oven and thoroughly rinsed with DI water before being dried in the oven for 30 minutes at 100 °C. There is no post-annealing treatment.

For the preparation of electrolyte, 5 ml of veloronitrile, 10 ml of butyl pyridine (TBP), 10 ml of iodolyte AN 50, 1.597 g DMPII (1.2-dimethyl-3-propylimidazolium iodide) and 0.01g guanidine thiocyanate (GT) are mixed. After mixing the chemicals, the solution is placed in the ultrasonicator for 10 minutes to ensure thorough mixing. The dye solution is then produced using a mixture of 0.0178 g of N719, 25 ml of Acetonitrile, and 25 ml of 1-Butanol. To avoid the solution of dye evaporate, which would cause molarity changes, the solution mixture is then stored at low temperatures (refrigerator's temperature). [18]. The TiO_2 doped Ag films are submerged in the dye for 72 hours (3 days).

Each layer of DSSC is assembling and clamped as shown in Figure 1. The structural characteristics of the photoanode (PE) film at 2θ from 20° to 80° were examined using the X-ray diffraction (XRD) PANalytical X-Pert Powder and HighScore software was used to analyze the data. The optical characteristics and light absorption capabilities of the PE layer are examined using an ultraviolet-visible (UV–vis NIR) spectrophotometer (Shimadzu 3600 Plus spectrophotometer). The efficiency of DSSC is analyzed by using solar simulator (Oriel Sol 1A) with 1 M solar illumination, IPCE and EIS analysis. Table 1 is sample details in this experiment.

Table 1. Sample Details

Samples	Details
A	TiO_2 Nanoflowers with 0.25% Ag dopant
B	TiO_2 Nanoflowers with 0.5% Ag dopant
C	TiO_2 Nanoflowers with 1.0% Ag dopant
D	TiO_2 Nanoflowers with 2.0% Ag dopant

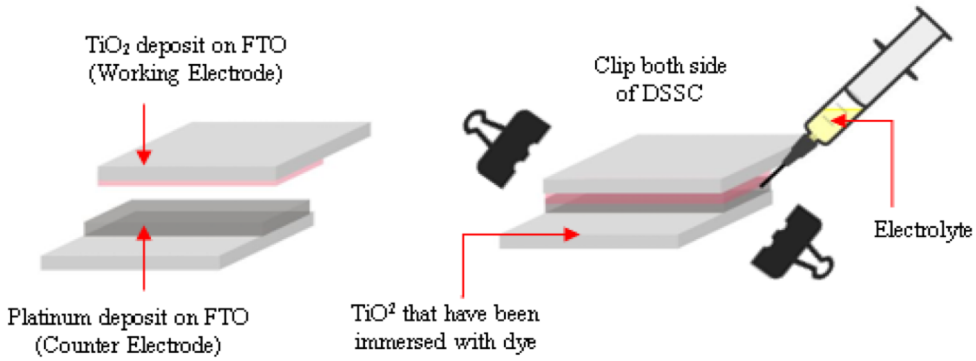

Figure 2. DSSC Assembling

3.0 RESULTS AND DISCUSSION

In this section, the characterization results of XRD, UV-Vis spectrophotometry, Solar Simulator, IPCE and EIS analysis are explained.

3.1 XRD Characterization TiO_2 doped Ag

Figure 3 depicts the crystal structure of TiO_2 doped Ag with different molarities of 0.25%, 0.5%, 1.0%, and 2.0 % estimated in the 20–80° range. There are rutile phase peaks in all of the samples, but no anatase peaks are found. The observed XRD peak corresponded to JCPDS file No. 98-016-8138. The XRD patterns revealed that the pure rutile phase was developed through a simple hydrothermal method that did not involve calcination. Peaks at 2θ of 27.42°, 36.07°, 41.22°, and 54.29° corresponded to the (110), (101), (111), and (211) planes of TiO2's rutile form, respectively. According to the studies, XRD peak unable to detect the peak of Ag doped with molarity below 4wt % because of the visibility peak of XRD [17]. Nanoflower TiO_2 in rutile form is good for light-scattering characteristics which are advantageous for DSSC application. Light scattering acts as a photon-trapping system to minimize charge recombination in the DSSC. The light-scattering gives a larger surface area for charge transport of injected electrons within the structure of PE for dye adsorption [4], [19].

3.2 UV–Vis spectral, IPCE and Solar Simulator

The capability of the DSSC to load dye has a significant effect on the incidence of photon-converted electrons (IPCE). In the adsorption of the N719 dye, visible light absorption wavelengths can be detected at 350 nm and 550 nm. Lower current density yields from less dye adsorption which can be validated by UV–Vis spectroscopy. The UV-Vis absorption, bandgap and transmittance spectra of different molarity of 0.25%,0.5%, 1.0%, and 2.0% Ag dopant of TiO_2 are shown in Figure 4, Figure 5 and Figure 6 respectively. The efficiency of DSSC is dependent on the diffusion of ejected electrons and the capability of the dye sensitizer anchored on the surface of the photoanode layer to absorb light. Thus, optical properties of substrates were observed to investigate the absorption spectra before and after immersed in the N719 dye solution. It can be observed that there is a significantly different absorption intensity between before and after immersed in dye solution in Figure 4. This is due to the degradation of dye. After immersed in the dye solution, the dye molecule is easily exposed to the surroundings and oxidized when there is no sealant attempted on it. Other than that, the light beam of UV-Vis penetrates through the photoanode layer will passing through the ultraviolet (UV) region can reduce the efficiency of dye molecules.

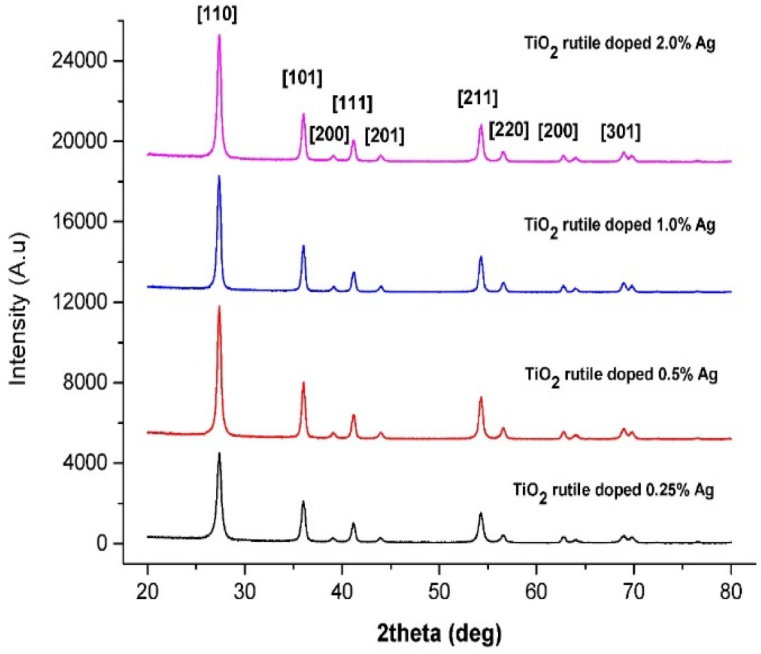

Figure 3. XRD analysis

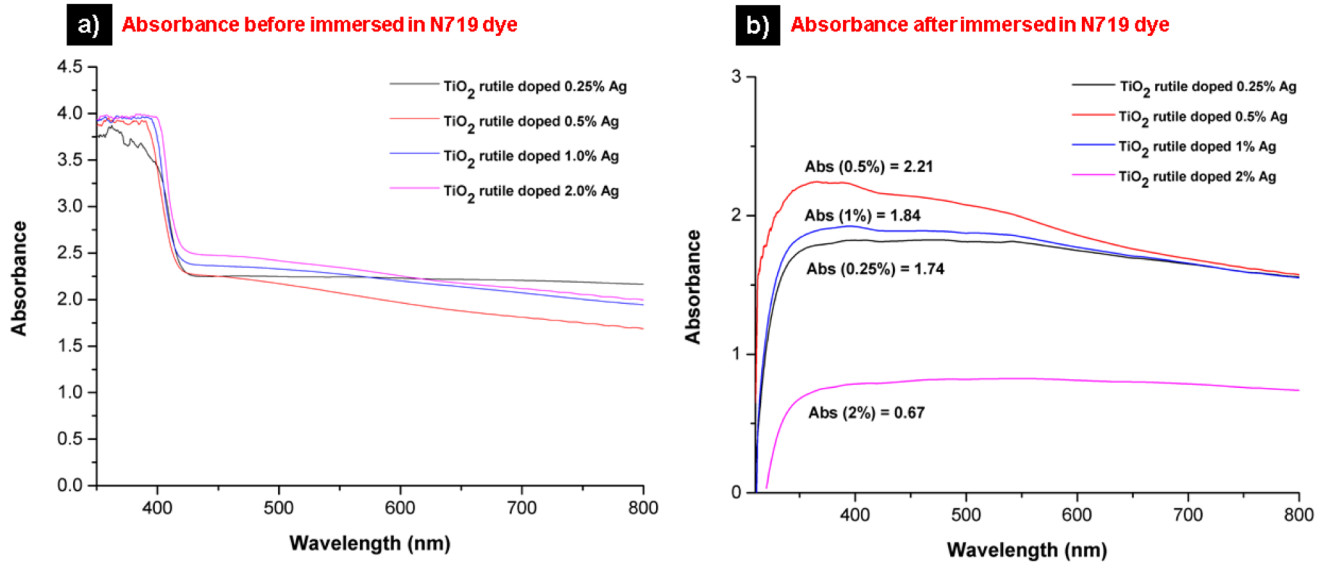

Figure 4. Absorbance before and after immersed in N719 dye

From the absorbance in Figure 4, we can find the bandgap of substrates using the Tauc Plot equation as below [20]:

$$(h\upsilon\alpha)^{\frac{1}{2}} = A(h\upsilon - Eg)$$

where hυ is the photon energy, α is the absorption coefficient, Eg is the absorption bandgap, A is constant [20].

From the Tauc plot equation above, bandgap of TiO_2 doped Ag is 2.89 eV (0.25% doped Ag and 0.5% Ag), 2.90 eV (1% doped Ag) and 2.91 eV (2% doped Ag) as Figure 6. Although TiO_2 is chemically stable in an aqueous solution, the width of the bandgap energy is the significant justification for lower conversion efficiency. Introducing noble metal not only can reduce charge recombination but bandgap energy of TiO_2 as semiconductor photoanode. These are matched with the reported studies [17], [21] that

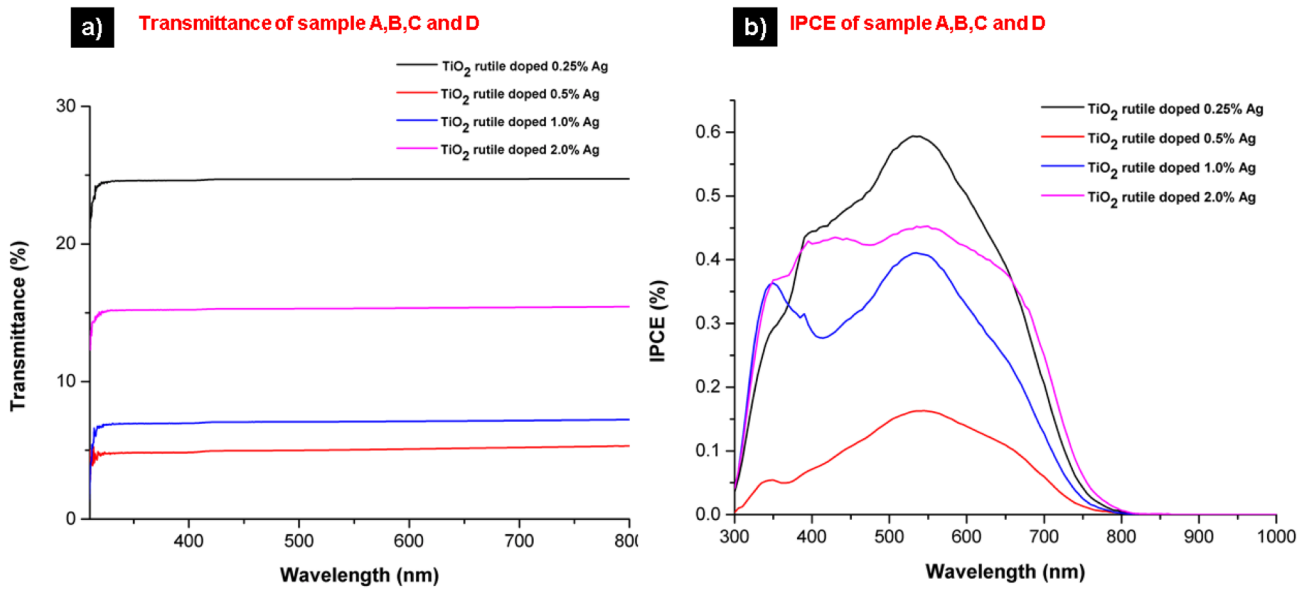

Figure 5. a) Transmittance and b) IPCE of sample A, B, C and D

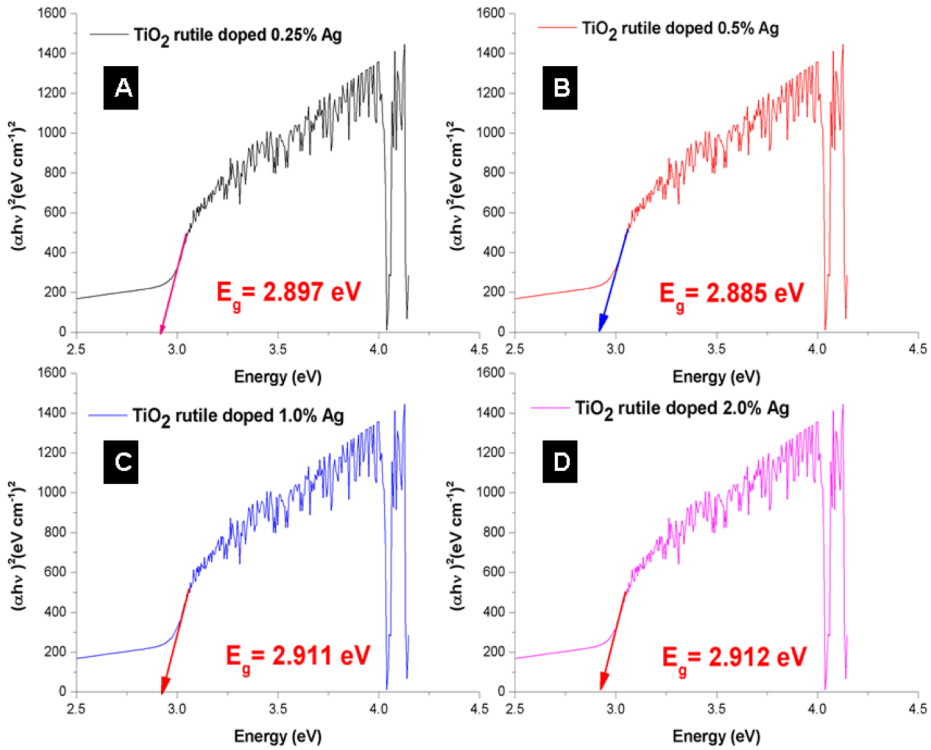

Figure 6. Bandgap sample A, B, C and D

investigate the photocatalytic properties of Ag dopant through bandgap energy.

The lowest bandgap of TiO_2 doped Ag in Figure 6, shows the highest transmittance value as shown in Figure 5 a). Transmittance quantifies the amount of light emitted by the substance and can be expressed mathematically as: [22]:

$$T\% = \frac{1}{Exp\ (\alpha t)}$$

where T, t, and denote the transmittance, thickness, and absorbance coefficients. In Figure 5a), TiO_2 doped with 0.25% Ag demonstrated the highest transmittance spectra. The value transmittance of a substance reflects on how much light irradiation passed through it.

According to Figure 5b), the smallest dopant concentration of 0.25% Ag doped has the highest IPCE, which is the ratio of the number of carriers captured by the solar cell to the number of photons with given incident energy on the solar cell. Next, Table 2 shows the photon-conversion efficiency (PCE) with the highest value using Solar Simulator. The highest 0.25% Ag doped transmittance results are matched with the result of IPCE and PCE. From the results obtained, we can analyze that the thickness of substrates in increasing dopant concentration can affect the optical transmittance, PCE and IPCE materials. Besides, the resistivity of FTO glass also contributes to low transmittance. In this experiment, the resistivity of FTO is measured to be 7 Ω/sq.

Table 2. PCE TiO_2 doped Ag

Sample	V_{oc}, (A)	I_{sc}, (A)	Jsc, (mA/cm^2)	Fill Factor	Ŋ %
A	0.669	0.0016	3.23	58.08	1.25
B	0.668	0.0013	2.70	53.36	0.96
C	0.653	0.0009	1.79	65.45	0.76
D	0.677	0.0064	2.84	32.88	0.63

3.3 EIS analysis

EIS (electrochemical impedance spectroscopy) is a reliable measure that is being used to investigate electronic and ionic mechanisms in DSSC. The resistance of the interface between electrolyte and counter electrode is represented by the first semicircle in EIS at high frequency (R_1). The resistance of the interface between the electrolyte and the TiO_2 layer is described by a second semicircle at an intermediate frequency (R_2). The third semicircle is looking into the peak frequency associated with electron transport and the back reaction of the photoanode-electrolyte interface (R_3). Table 3 represents the obtained parameters from fitting the EIS plots whereas Rct is the charge transfer resistance of the charge recombination process at the TiO_2/I_3^- in the electrolyte which is the value of the impedance in its real component; R_{Pt} is the charge transfer resistance Platinum at the counter electrode, Rd is the diffusion resistance and Rs is the resistance of solution. Figure 7 depicts the Nyquist plots from EIS analysis of various samples A, B, C, and D under light illumination.

To correlate with the highest efficiency in this experiment which is sample A (1.25%), the R_{CT} result of sample A showed the third lowest (208.5 Ω) but obtained the lowest R_d (52.55 Ω). This is a significant reason for the current density of sample A which is the highest compared to others (3.23 mA/cm^2). Compared the sample D which obtained the lowest efficiency (0.63%), the sample showed the lowest R_{CT} (89.13 Ω) but 1 magnitude higher than R_d sample A (118.4 Ω). This may due to the charge trapping effect of Ag doped and corresponded from the highest bandgap of Sample D from Tauc Plot equation.

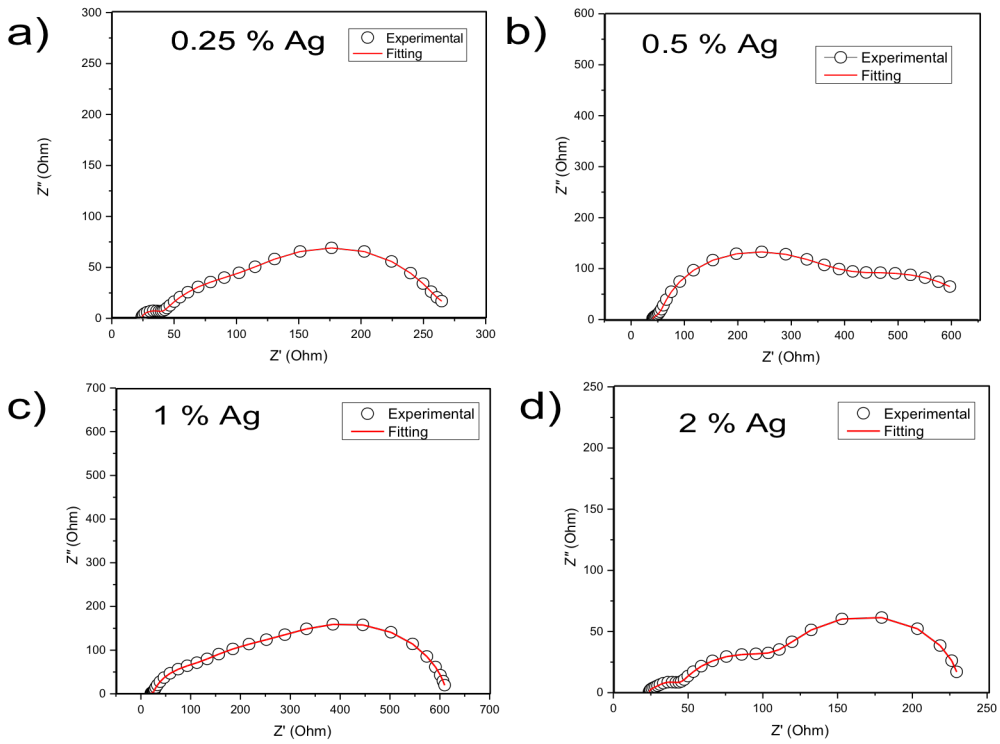

Figure 7. Nyquist plot from EIS analysis under illumination

Table 3. Parameter values of Rs, Rpt, Rct and Rd of DSSC photoanode obtained from fitting method

Sample	R_s (Ω)	R_{Pt} (Ω)	R_{ct} (Ω)	R_d (Ω)
A	23.11	16.55	208.54	52.55
B	39.8	11.88	312.83	309.1
C	19.58	5.21	251.07	339
D	23.8	4.589	89.13	114.8

4. CONCLUSION

This study shows how a hydrothermal reaction can be used to boost the morphology of TiO_2 nanoflowers doped with Ag. The addition of Ag-doping increased their surface area and visible light absorption. Among the samples, TiO_2 doped 0.25 % wt. Ag had the highest performance, ŋ% (1.25 %). Metal doping has an effect on the band structure and trap states on the surface of TiO_2. The charge injection between photoanode and dye molecule should be fast to avoid recombination. As a result, a suitable band level is needed to minimize charge recombination. For efficient electron injection, the photoanode and material band edges should match the dye's bandgap structure. To summarize, the bandgap of TiO_2 should be less than 3.0 eV to improve photocatalytic activity in DSSC applications. This is due to the lower bandgap's ability to expand TiO_2's spectral response to the visible spectrum, as the DSSC mechanism works well in the visible region but degrades in the UV region.

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