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Synthesis and characterization of Ag-doped TiO_2 nanostructure and investigation of its application as dye-sensitized solar cell

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Abstract

A new strategy for enhancing the efficiency of TiO_2 dye-sensitized solar cells (DSSCs) by doping foreign ion into TiO2 lattice via sol-gel process is reported. DSSCs are based on a semiconductor (i.e., TiO2), formed between a photo-sensitized anode and an electrolyte. In order to reach high conversion efficiency, it is important to increase the electron injection and optical absorption. One promising solution to increase the electron injection is to decrease the large band gap of TiO2 by doping a foreign ion into TiO2 lattice. In the present work, Ag- doped TiO2 nanopowders and thin films with different Ag:Ti ratios are reported. The effect of dopant WT% on photovoltaic performance of dye-sensitized solar cells were studied. The powders were synthesized via aqueous sol–gel route, followed by annealing at 500°C for 4hr. X-ray diffraction and Field emission scanning electron microscope (FE-SEM) analyses revealed that the synthesized samples had uniform grains in nanometer range. It was found that, 0.05 WT. % Ag-doped TiO2 DSSC (i.e., DSSC number 2) had the highest power conversion efficiency of 2.4%, short current density of 5.65 mA/cm2 and open circuit voltage of 761 mV. This can be related to achievement of an optimum condition balance among the electron injection, light scattering effect and dye sensitization. The applied method exhibited superior potential for synthesis of Ag-doped TiO2 nanopowders and films to utilize as DSSCs.

Keywords: Ag, Ag-doped TiO2, TiO2, Solar cell

1. Introduction

In the present age, dye-sensitized solar cells (DSSCs) have been regarded as a promising candidate for third solar cells generation owning to their ease of manufacturing, good power conversion efficiency and low cost [1]. This class of cell has reached efficiencies over 12 % recently [2]. The main stream of the research has been focusing on development of materials which would enhance the conversion efficiency, simplify the production of DSSC and assure their long-lifetime. Titanium dioxide is an n-type wide band

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gap semiconductor that absorbs in the UV region and is transparent for visible light. In a typical DSSC the dye molecules are adsorbed on the surface of the TiO_2 to assure photoelectric conversion over a broad spectral range of the solar spectrum. When sunlight radiates onto the DSSC the electrons in the dye molecules (HOMO level) absorb photons that become excited and jump to an unoccupied upper level (LUMO level). The electrons from the LUMO level are then injected into the TiO_2 semiconductor conduction band and pass through the TiO_2 layer to the transparent conductive oxide (TCO) coated glass and to a load Further, the vacant "HOMO" level is then filled with electrons supplied by the iodide (I^-) ions in the electrolyte while iodide is oxidized to tri-iodide I^{-3} [3]**.** Meanwhile the platinum counter electrode acts as a catalyst for the redox reaction of the ions in the electrolyte solution and reduces the tri-iodide back to iodide, [2] for practical application, the photocatalytic activity of TiO_2 needs further improvement [4]. An effective way to improve the TiO_2 photoactivity is to introduce foreign metal ions into TiO_2. The sol-gel process is a most attractive method to introduce foreign metal ions into TiO_2powders and films [5]. A wide range of metal ions such as iron [6], nickel [7], cupper [8], manganese [9] and cobalt [10] have been used as acceptor dopants into TiO_2 and the TiO_2 photocatalytic activity was improved to varying extents. The foreign metal ions, however, usually affect the TiO_2 phase transformation behaviour and structure while they were introduced by sol-gel method [11-13]. In this work, using the sol-gel method we prepared Ag-doped TiO_2 films and found that Ag could also effectively improve the photocatalytic activity of TiO_2 nanopowders and films in preparation of Dye-sentisized solar cells.

2. Experimental

2.1 Preparation of Ag-Doped TiO2 Sol

The desired amount of HCl, was dissolved in distilled water at 70c. Then TTIP as a titanium precursor was added to the solution under stirring for 24 hour at room temperature. For preparation of Ag-doped TiO_2 sols, $AgNO_3$ was dissolved in TiO_2 sol with various Ag atomic percentages in the range 0–3%.

2.2. Synthesis of Ag-doped TiO_2 powders

The obtained sol were then heated at 70 °C for 24 h to obtain as-synthesized Ag-doped TiO_2 powders. Subsequently, the as-synthesized powders were annealed at 500°C for 4hr under Ar atmosphere to obtained organic-free crystalline powder. The synthesized condition of TiO_2 powders in terms of mol ratio, temperature and time are shown in table 1.

2.3. Synthesise of Ag-doped TiO_2 pastes

A new formulation of TiO_2 paste was developed in our lab. Different nanostructured TiO_2 pastes with various crystal structures were prepared using the synthesized nano crystalline TiO_2 powders and dispersing agents [13].

2.4. Preparation of DSSCs

2.4.1 Preparation of photoanode electrodes

The homemade formulated Ag-doped TiO_2 pastes were coated on ITO substrate with a sheet resistance of 8 Ohm/sq by spin coating method. The films were annealed at 400°C for 2 h in Ar atmosphere.

Table 1. Characterization of the prepared TiO_2 powders

Powder	Ag at %	heat treatment	
		Temperature (°C)	Time (h)
1	0	500	4
2	0.05	500	4
3	0.3	500	4

Table 2. Characterization of the prepared TiO_2 electrodes

Electrode	Powder	Ag WT.%	$TiCl_4$ Conc. (M)	Powder Heat Treatment		Electrode Heat Treatment	
				Temperature (°C)	Time (h)	Temperature (°C)	Time (h)
1	1	0	0.004	500	4	400	2
2	2	0.05	0.004	500	4	400	2
3	3	0.3	0.004	500	4	400	2

2.4.2. $TiCl_4$ treatment

The post treated with $TiCl_4$ solution was applied to freshly annealed TiO_2 photoanode electrodes treated with $TiCl_4$ as reported in the literature [11]. TiO_2 photoanode electrodes were immersed into$TiCl_4$ solution concentration of 0.004 M and stored in an oven at 70°C for 30 min in a closed vessel. After flushing with distilled water, the photoanode electrodes were sintered again at 500°C for 30 min.

2.4.3. Preparation of sensitized electrodes

The TiO_2 electrodes were immersed into a 0.5 mM N-719 dye solution and kept at room temperature for 24 h to assure complete sensitizer uptake [13].

2.4.4 Preparation of counter electrode

The counter Pt-electrode was deposited on the FTO glass by coating with a drop of H_2PtCl_6 solution with repetition of the heat treatment at 400 °C for 15 min.

2.4.5 Preparation of the electrolyte

The electrolyte employed was a solution of 0.70 M tetra butyl ammonium iodide, 0.03 M I_2, 0.10 M lithium iodide, 0.20 M guanidinium thiocyanate and 0.50 M 4-tertbutyl- pyridine in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15).

2.4.6 DSSCs assembly

The dye-covered TiO_2 electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 60 ml thickness made of the Surlyn Meltonix 1170 (Solaronix). The size of the TiO_2 electrodes used was 0.25 cm^2. A drop of the electrolyte was put on the hole in the Surlyn frame and was introduced into the cell via vacuum backfilling. The cell was placed in a small vacum chamber to remove inside air. Exposing it again to pressure causes the electrolyte to be driven into the cell. The characteristics of the prepared TiO_2 electrodes are shown in table 2.

2.5. Characterization and measurements

The photoanode electrodes were characterized by X-ray diffraction diffractometer (XRD) using a Philips X'pert PW3020, Cu-Ka and field emission scanning electron microscope (FE-SEM) using a ZEISS 500. The density of the nanostructures was measured by a Micromeritics AccuPyc 1330 pycnometer analyzer. Photovoltaic measurements of fabricated solar cells were carried out using a solar simulator under standard test conditions (STC i.e., irradiance of 100 mW/cm2, AM 1.5 spectrum).

3. Results and Discussions

3.1. XRD analysis

The crystal structure and phase composition of the synthesized powders were studied by XRD analysis and the results were shown in figure 1. It can be observed that powders 2 and 3 had a mixture of anatase and rutile phases with dominant peaks at 2h = 25.3 (1 0 1), and 2h = 27.5 (1 1 0), respectively. The anatase to rutile phase transformation is known to be a nucleation and growth process during which rutile nuclei form within the anatase phase and grow in size. Crystallites should grow to the critical nuclei size before the transformation can proceed. Consequently, formation of rutile nuclei retards by Ag introduction since

the initial crystallites have the smaller size than the critical nuclei size. Moreover, neither silver oxide nor silver titanates were detected for Ag-doped TiO_2 powders due to low concentration of the dopant. It can be observed that the phase composition of Ag-doped TiO_2 powders depends on dopant concentration.
SEM imaging is a powerful technique for the direct elucidation of surface morphology and particle size of nanomaterials. Figure 2 and 3 shows FE-SEM images of the synthesized TiO_2 powders annealed at 500°C 4 hr. It can be observed that in all cases nanometer TiO_2 powders were obtained. The small grains represent anatase, while large grains relate to rutile phase. Figure 4 to 6 show surface morphology of deposited transparent TiO_2 electrodes. It is evident that all deposited films had uniform, homogeneous and porous structure as a result of removal of the dispersing agent and solvents. As can be observed, the porosity of doped electrodes was higher than that of undoped electrode, enhancing dye adsorption. Moreover, the porosity of doped films depended on the amount of Ag^+ concentration and decreased with increasing Ag^+ atomic percentage. Porosity is an essential parameter for a high-efficiency DSSC, because it allows adsorption of sufficiently large number of dye molecules needed for efficient light harvesting. The thickness of the film can be controlled by spin coating parameters. These parameters were tailored to obtain a total thickness of 16.1 μm.

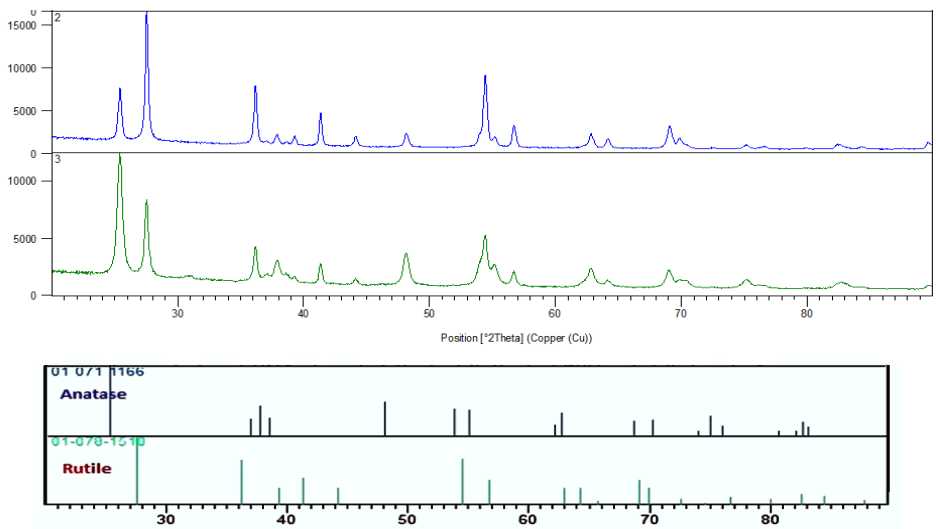

Figure 1. XRD pattern of synthesized powders: powder 2 and powder 3.

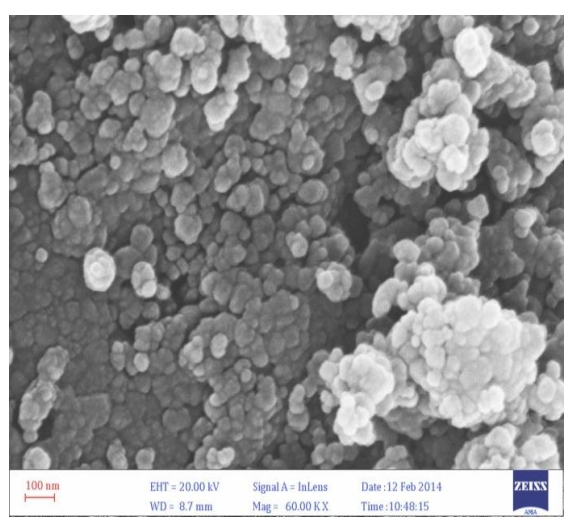

Figure 2. FE-SEM images of powder 2.

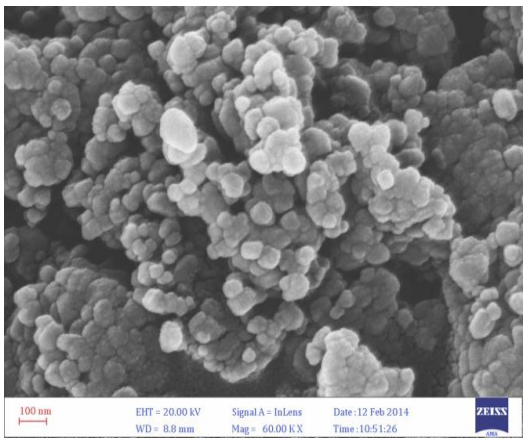

Figure 3. FE-SEM images of powder 3.

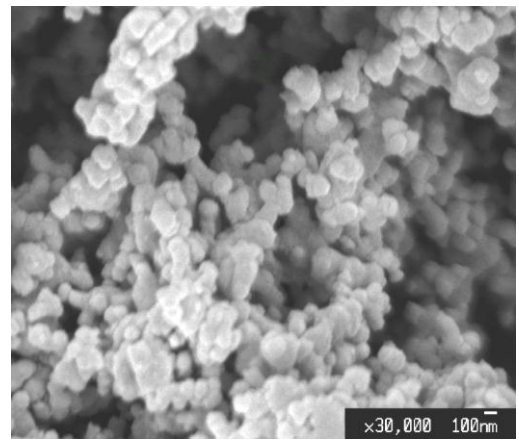

Figure 4. FE-SEM images of surface of electrode 1

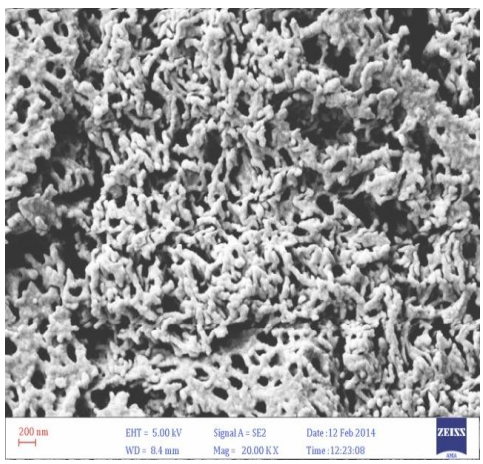

Figure 5. FE-SEM images of surface of electrode 2.

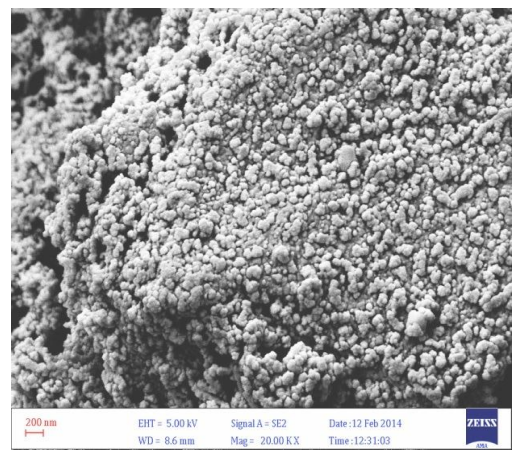

Figure 6. FE-SEM images of surface of electrode 3

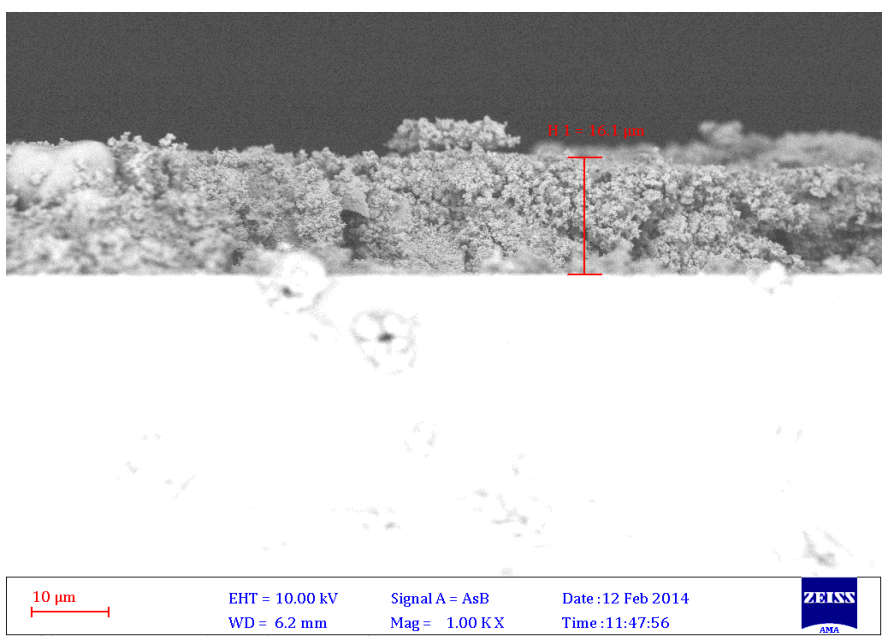

Figure 7. Cross sectional view of electrode 2.

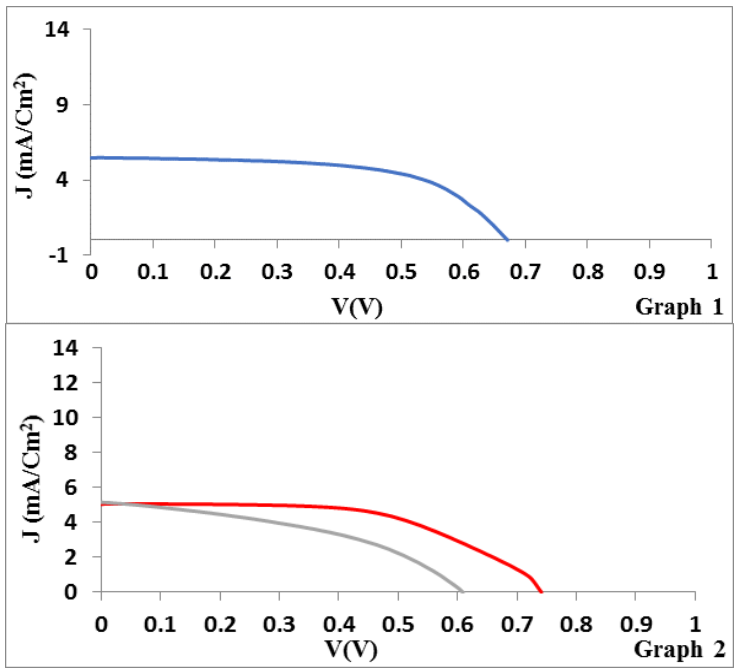

Figure 8. Graph1and 2: Photocurrent density–voltage curves of fabricated TiO_2 DSSCs doped with different Ag atomic percentages annealed at 500°C for 4 h, $TiCl_4$ 0.004 M, blue line =cell1, red line =cell2 and green line =cell3.

Table 3. Photovoltaic parameters of fabricated TiO_2 DSSCs doped with different Ag atomic percentages, annealed at 500°C for 4 h, $TiCl_4$ 0.004 M

Cell	J_{SC} (mA/cm²)	V_{OC} (mV)	FF (%)	Efficiency (%)
1	5.46	671	60.1	2.2
2	5.65	761	56.8	2.4
3	5.15	609	42.3	1.3

3.3. Photovoltaic performance of DSSCs

The photocurrent density–voltage (J-V) characteristics of fabricated monolayer TiO_2 DSSCs, with the same thickness (i.e., 16.1µm) were illustrated in figure 7. In addition, the corresponding photovoltaic parameters such as short circuit current (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), adsorbed dye and power conversion efficiency (η) were summarized in table 3. It is apparent that the short circuit current and power conversion efficiency of the solar cells changed with Ag atomic percentage, reaching a maximum at a specific value. Therefore, cell 2 showed the highest power conversion efficiency of 2.4 % amongst all fabricated solar cells. The improvement in the photovoltaic performance of cell 2 can be explained due to enhancement of J_{SC}.

4. Conclusions

The effective methods were presented in order to make a balance among electron injection, light scattering effect and dye absorption of photoanode electrode of dye-sensitized solar cells. For this purpose, a systematic study of the DSSCs by fabrication of nanostructured Ag-doped TiO_2 films with different atomic percentages (i.e., 0.5, 0.3 at.%) by sol-gel process on the photovoltaic performance of DSSCs is reported. X-ray diffraction (XRD) analysis revealed that all samples with Ag:Ti molar ratios 0.05 and 0.3 at.% showed mixtures of anatase and rutile phases. Moreover, no silver and silver oxide phases were detected after heat treatment. Field emission scanning electron microscope (FE-SEM) analyses revealed that the synthesized samples had uniform grains IN nanometer range. It was found that, 0.05 at.% Ag-doped TiO_2 DSSC had the highest power conversion efficiency of 2.4%, short current density of 5.65 mA/cm² and open circuit voltage of 761 mV.

5. References

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