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Synthesize of Carbonate Doped TiO_2 Nanomaterials to Enhance the Overall Performance of Dye Sensitized Solar Cells

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Abstract: In this study, we synthesized carbon doped TiO_2 nanoparticles as anode electrode in Dye Sensitized Solar Cells (DSSCs). TiO_2 nanopowder was doped with different amount of carbon. Carbon atoms are easily to be couples with O atoms due to the small energy barrier between them in anatase phase. Doctor blade method is used to deposit thin paste of carbon doped TiO_2 on FTO glass. Scanning electron microscope was used to study the microstructure of the samples as well as to confirm the existence of carbon. Also, x-ray diffraction used to identify the crystallite size and phases of the samples. The results showed that the 4% of carbon-doped TiO_2 was given the best performance of DSSCs as the efficiency increased as four times as the TiO_2 without doping.

Key words: C-doped TiO_2, DSSCs, synthesized carbon, nanoparticles, electrode, nanopowder

INTRODUCTION

A Dye-Sensitized Solar Cell (DSSC) was first introduced by O'Regan and Gratzel (1991). Recently, interesting in DSSCs has increased due to their simplicity in manufacturing, low cost as compared to silicon solar cells and high efficiency (Mao and Chen, 2007). DSSCs offer an effective and simply applied technology for future energy supply (Gong *et al*., 2017; Narayan, 2012). The working electrode of DSSCs is formed by depositing a TiO_2 film layer on conducting glass substrate.

Nanostructured TiO_2 has been used as a photo-anode in DSSC applications due to its conductive electronic structure (Gong *et al*., 2012; Hagfeldt *et al*., 2010). The efficiency of nano-TiO_2 is limited by its wide band gap that allows TiO_2 to absorb only UV-radiation (Khan *et al*., 2013). In order to improve its efficiency, nano-TiO_2 has been doped with metals and non-metals. The band-gap energy of TiO_2 doped with metallic and non-metallic elements is shifted into the visible region, due to induced new energy levels above the valence band (Zaleska, 2008; Roose *et al*., 2015).

Many techniques have been employed to dope TiO_2 with different elements (Patle and Chaudhari, 2016; Sakthivel *et al*., 2017; Ko *et al*., 2005). Seddigi *et al*. (2016) investigated the effect of carbonate doping in TiO_2 on performance of DSSCs. The results revealed that carbonate doping of TiO_2 mesoporous microspheres enhanced the density of light harvesting centre, photoinduced electron, light trapping, injection and electron transport without self-recombination parameters which accountable for the enhancement of solar cell efficiency. Lu *et al*. (2010) studied the performance of a DSSC in Nb-doped TiO_2 electrodes. The efficiency of a 5 mol% Nb-doped TiO_2 cell was 7.8% which was better than an un-doped cell by 18.6%. This improvement in DSSC efficiency is due to the positive shift in powder conductivity and flat-band potential which improves electrons injection and charge transfer. Yang *et al*. (2014) and his group doped TiO_2 with Co ions by a sol-hydrothermal process. Their results showed significant improvement of properties of TiO_2 at 1% Co^{+2} ion doping, due to induced abundant energy levels below the conduction band. Kang *et al*. (2010) and co-workers used a sol-gel method to prepare nitrogen-doped TiO_2 for DSSC applications. They showed improvement in DSSC efficiency up to 4.87% compared to 3.73% for un-doped TiO_2.

MATERIALS AND METHODS

Experimental work

C-doped TiO_2 preparation and characterization: C-doped TiO_2 was prepared by adding 2 grams of TiO_2 anatase

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nanoparticles (from Sigma-Aldrich) to 60 mL of deionized water. Then, specific quantity of carbon was added to suspension of TiO_2, then, the slurry stirred for 40 min. The solution was moved into a 120 mL teflon autoclave and a stainless steel lid used to seal it. Then, the mixture was aged at 160°C for of 24 h with heating and cooling rates set at 25°C/min in order to nucleate and grow the C-doped TiO_2 nano-particles. Then, the mixture solution was slowly cooled in air. The gained solid particles were centrifuged and carefully washed by distilled water and dried at 90°C in air atmosphere.

Phase identidication of carbon doped TiO_2 was carried out using X-ray diffraction (X-ray diffractometer, model PW 3040, Cu Kα). Chemical analysis and morphology of TiO_2 anatase and C-doped TiO_2 were carried out using Energy Dispersion X-ray (EDX) and Scanning Electron Microscopy (SEM) (A Zeiss-Gemini FE-SEM). A solar simulator Xeon 300 W with incident light-power intensity 100 mW/cm^2 is used to perform photovoltaic measurements.

RESULTS AND DISCUSSION

Figure 1 shows the un-doped TiO_2 nanopowder of high porosity nanoparticles. The average particles size is 20 nm. Upon adding the carbon and heat treatment, the average nanoparticle size and surface area are reduced due to the presence of carbon which restrained the growing of TiO_2 particles. Typical SEM images of 2% and 4% C-doped TiO_2 samples after heat treatment at 150° are shown in Fig. 2. Also, the particles color turn into black due to the presence of carbon. The corresponding EDS spectra confirm the presence of C and small contaminations as shown in Fig. 3.

Furthermore, the XRD patterns (Fig. 1) shows that peaks intensity of anatase decreased with increasing carbon content due the carbon atoms slow down the growth of TiO_2 crystal. Scherer's equation was used to calculate the crystallite size of anatase in the catalysts. Table 1 represents the values of TiO_2 crystalline size which reveal that the crystallite size of TiO_2 decreases with the increasing content of carbon. These results have been confirmed for similar doping and it ascribed to the restrained the growing of TiO_2 crystals because of the presence of doped material (Quinones *et al*., 2015) (Fig. 4).

Preparation and testing of a solar cell: The platinum counter electrode was prepared by depositing a 250-nm Pt film on FTO-glass substrate (fluorine-doped tin oxide, F: SnO_2) by sputtering at a rate of 34 nm/min for 6 min. The electrolyte is a solution of 0.6 m 1-butyl-3 methyleimidazolium, 0.5 m 4-tertbutyl-pyrodine, 0.03 m Iodine, 0.1 m lithium iodide, 0.1 m guanidinium-thiocyanate in a mixture of 8.5 mL acetonitrile and 1.5 mL valeronitrile.

TiO_2 paste is prepared by adding 0.43 g to 3.3 mL ethanol 0.1 mL of acetyl-acetone is added to the TiO_2 paste as a dispersing agent and to prevent its coagulation. Two drops of surfactant (Triton X-100) is added to the solution to assist spreading of the TiO_2 paste on the FTO surface and the solution is stirred

Table 1: Crystallite size of TiO_2 at different amount of carbon doping

Carbon content (%)	TiO_2 crystalline size (nm)
0	12
2	10
4	9

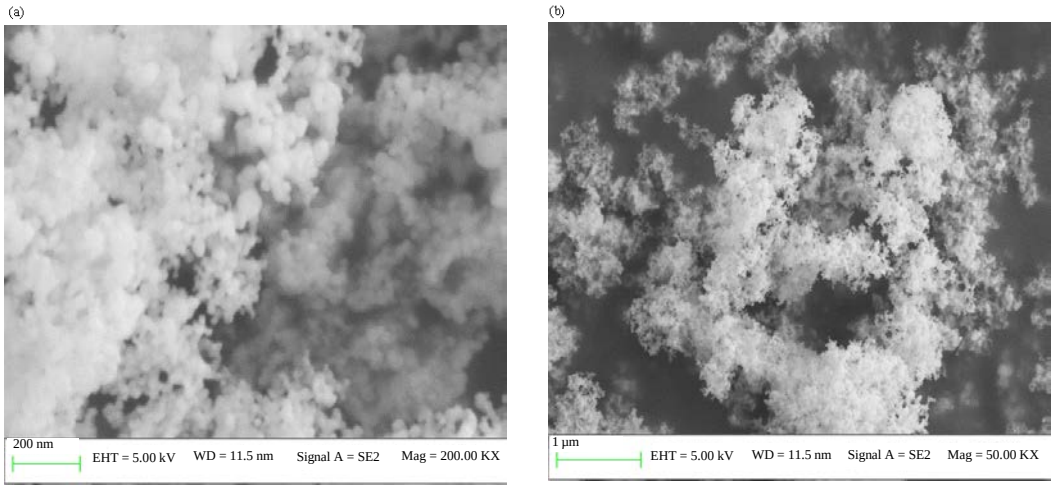

Fig. 1: SEM images of only TiO_2 nanopowder: a) High magnification and b) Low magnification

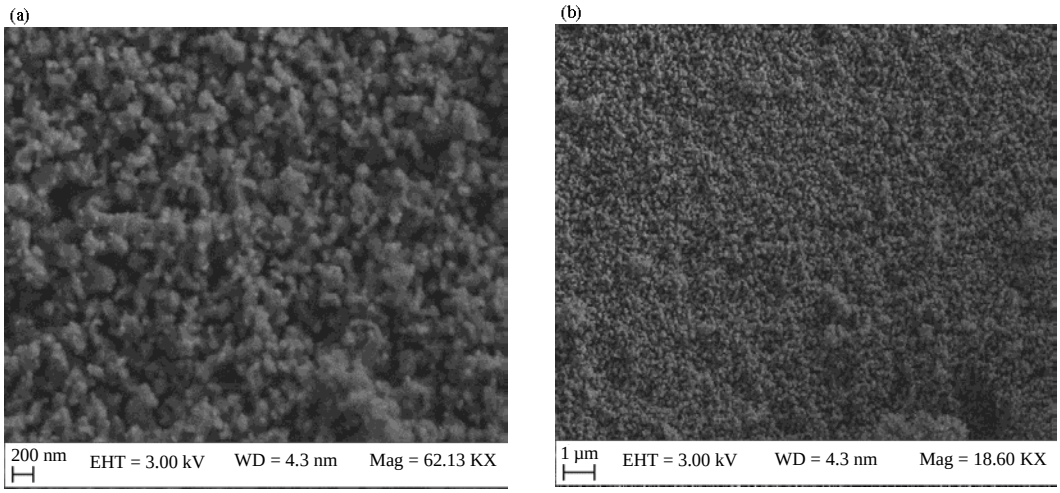

Fig. 2: SEM images C-doped TiO_2 samples after heat treatment at 150°: a) High magnification and b) Low magnification

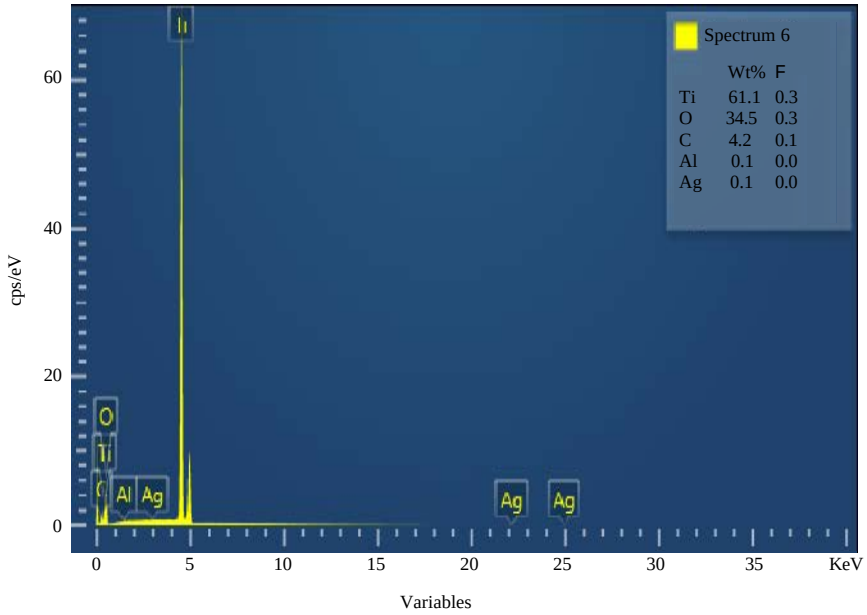

Fig. 3: EDX-SEM of C-doped TiO_2 nanopowder

for 20 min. The FTO glass is uniformly coated with a TiO_2 layer using a doctor-blade method. The coating is detached from its glass substrate using scotch tape. The coating is 2 cm^2 in area and 3-4 µm thick. After the electrode is dried in air for 30 min it is sintered at 500°C for 1 h with heating and cooling rates 5°C/min. Finally, the electrode is immersed in a solution of 0.045 g of ruthenium dye in 100 mL of ethyl alcohol for 12 h at room temperature.

The two electrodes are placed face-to-face with binder clips. To prevent a short circuit, a 40 µm teflon spacer is used to separate them. Then, electrolyte is inserted between the two electrodes by a capillary drawing action. Finally, a stainless-steel mask with a center hole 0.25 cm^2 area is placed on the TiO_2 electrode to expose a small area of film. Photovoltaic measurements are carried out by using a solar simulator (Xeon 300 W) under a light intensity 100 mW/cm^2 at room temperature. Efficiency, open voltage, short current and fill factor results for all samples tested are presented in Table 2.

As indicated, a significant increasing in the efficiency of C-doped TiO_2 samples is observed due to the doping of carbon which induced electronic states above the valence band edge. Therefore, it was considered that the

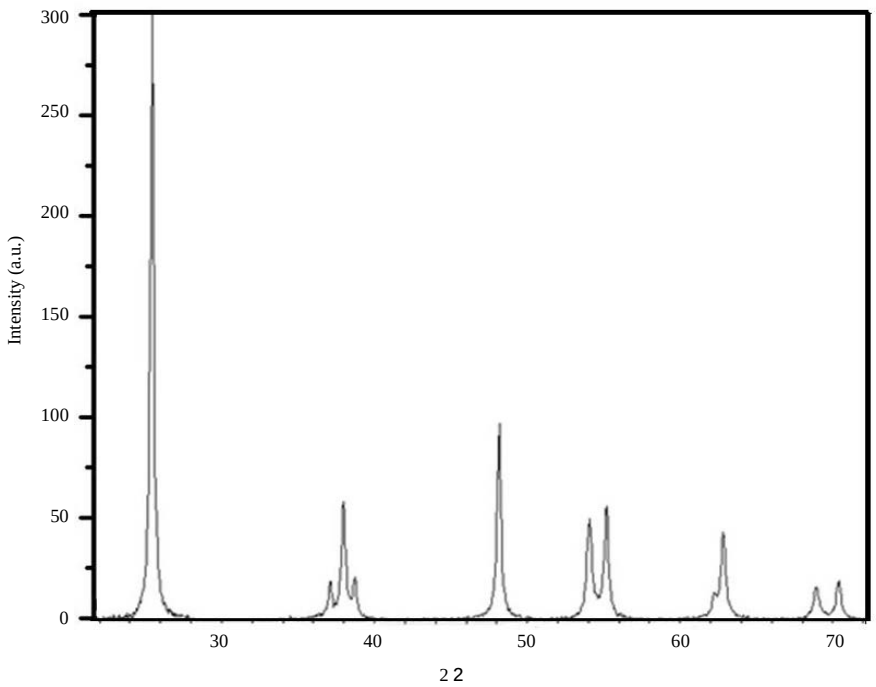

Fig. 4: XRD pattern of C-doped TiO_2

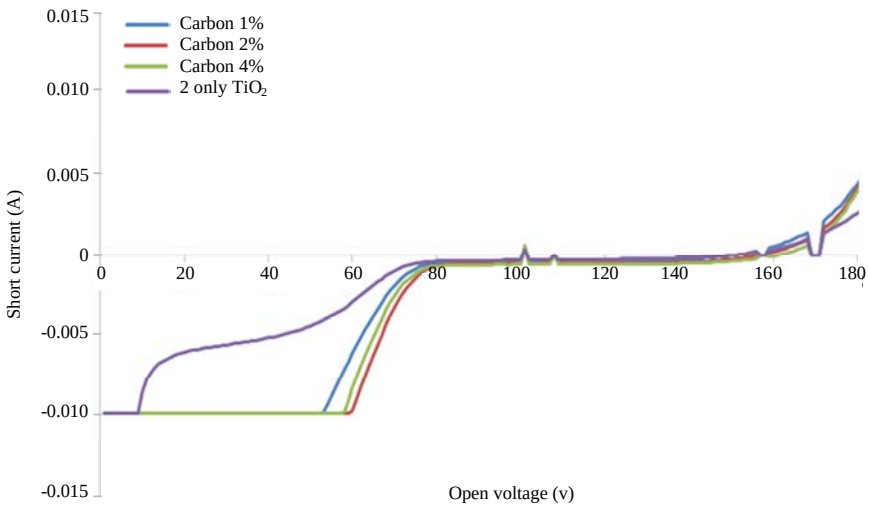

Fig. 5: Current/voltage curves for C-doped TiO_2

Table 2: DSSCs photovoltaic properties for TiO_2 and C-doped TiO_2 electrodes

Sample	Short current (A)	Open voltage (V)	Fill factor	Efficiency (%)
Only TiO_2	-0.000313	0.5	0.43015	0.26928
1% carbon-doped TiO_2	-0.000352	0.5	0.541875	0.38148
2% carbon-doped TiO_2	-0.000545	0.5600	0.57404	0.7008
4% carbon-doped TiO_2	-0.000611	0.61	0.57492	0.85712

doping leads to the visible light absorption of C-doped TiO_2. Carbon atoms are easily to be couples with O atoms due to the small energy barrier between them in anatase phase in contrast to rutile phase (Fig. 5).

CONCLUSION

Nanostructured powders C-doped TiO_2 are prepared for dye sensitized solar cells by a chemical process.

DSSCs overall efficiency is investigated which has shown similar results as approved by previous researches in the DSSCs field. As indicated, a significant increasing in the efficiency of C-doped TiO_2 samples is observed because of the doping of carbon which induced electronic levels above the valence band edge. So, the doping leads to enhance the absorption of visible light of C-doped TiO_2. Carbon atoms are easily to be couples with O atoms due to the small energy barrier between them in anatase phase in contrast to rutile phase.

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