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Photoanode Modification in DSSC Using Chromium Doped TiO$_2$ nanoparticles by sol-gel method

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ABSTRACT

TiO$_2$ nanoparaticles were prepared by acid modified sol-gel method by varying different mole % of Chromium and characterized by various advanced techniques such as powder X-ray diffraction, SEM, FESEM, UV-vis, PL and photovolatage current. Analytical results demonstrated that the pure TiO$_2$ and Cr-doped could inhibit the phase transformation, increase the surface area and decrease the crystallite size. UV-vis DRS spectrum revealed that the absorption was improved in both the ultra -violet and visible areas. Under simulated solar illumination, a short circuit current of 9.820mA and an open circuit voltage of 0.714V were attained, which were better than the absorption of N719 dyes molecules with the photoanode materials.

Keywords: Modified photoanode, N719 dye, dye-sensitized solar cells, FTO glass

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INTRODUCTION

TiO$_2$ has emerged as one of the most fascinating materials in the modern era. It has succeeded in capturing the attention of physical chemists, physicists, material scientists, and engineers in exploring unique semiconducting and catalytic properties. Inertness to chemical environment and long-term photostability have made TiO$_2$ an important component in many practical applications and in commercial products[1].DSSC usually consists of a dye-adsorbed nanocrystalline TiO$_2$ film on a fluorine-doped tin oxide (FTO) substrate, an iodide/iodine redox electrolyte and discontinuous platinum nanoparticles on a FTO substrate. In dye-sensitized solar cell, among the three important components, inorganic oxide film should be firstly considered. This is because photovoltaic performance depends significantly on kind of inorganic material, morphology of nanoparticles, band gap and inorganic oxide film porosity. Among the several candidates for photoanode materials, TiO$_2$ has been usually adapted as adequate material for DSSC since it has demonstrated best performance compared to other oxide materials [2].

However, there are limitations, such as the wide band gap and charge recombination between the TiO$_2$ electrode and the electrolyte. Doping with the proper kind of metal ion could reduce the charge recombination and narrow the band gap of TiO$_2$, thus broadening the width of absorption under sunlight. Then, the additional absorbed solar energy could increase the efficiency of the solar cells. Transition metals such as Cr, Mn, V, Fe, have been used to improve the photoresponse of TiO$_2$ [3-13]. Among these, Cr seems to be one of the most promising dopant in TiO$_2$ as it shifts the optical absorption spectrum towards the visible range and improves the photocurrent density of TiO$_2$. However, an excess of chromium leads to the recombination of charge carriers. Thanks to different colors from dye molecules and nano-sized inorganic oxide thin film, colorful and transparent appearance is possible for DSSC. Energy payback time of DSSC is analyzed to be about less than 0.8 year [14], while that of the multicrystalline

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silicon solar cell is about 3-4 years [15]. This indicates that DSSC is expected to be a promising solar cell for highly cost effective solar power system.

In the present work highly pure and stable anatase Cr- doped titanium dioxide nanopowders have been prepared by means of acid modified sol gel method. The developed synthesis technique were avoids the use of hazardous chemical compounds with large homogeneous concentration and under stoichiometry control [16-20]. The synthesized powders were structurally, morphologically and optically characterized and its photovoltaic properties were studied.

MATERIALS AND METHODS

Experimental details
Synthesis and Characterization of titanium nanoparticles
The Cr-TiO$_2$ nanopowders were prepared by means of acid modified sol-gel method. All the reagents used in the synthesis experiments were purchased from commercial sources and used without further purification. The dopant starting materials were chromium nitrate (Cr(NO$_3$)$_3$.9H$_2$O,Himedia). A titanium isopropoxide solution(C$_{12}$H$_{28}$O$_4$.Ti, Aldrich) was used as the titanium source. Chromium nitrate were dissolved in 60 mL of deionized water at room temperature, followed by adding 5 mL of glacial acetic acid to obtain solution A. 14 mL titanium isopropoxide was dissolved in 40 mL of anhydrous ethanol with constant stirring to form solution B. Then, the solution B was added drop-wise into the solution A within 60 min under vigorous stirring. Subsequently, the obtained sol was stirred continuously for 2 h and aged for 48 h at room temperature. As-prepared TiO$_2$ gels was dried for 10h at 80 ^{0}C. The obtained solids were ground and finally calcined at 450 ^{0}C for 2 h (heating rate = 3 ^{0}C/min). The undoped TiO$_2$ was prepared using the same method for comparative purposes.

Crystallographic observations of the specimens were made using an X-ray diffractometer (Model 6000-Shimadzu X-ray diffractometer) with monochromatized CuK$_\alpha$(1.5406 Å) radiation and measured under the conditions of 40 kV and 30 mA. The UV-vis spectra were recorded in the range 200-800 nm on HP338 uv-vis. The morphology and size were observed by field emission scanning electron micrographs (Model: FEI QUANTA 200F). The photovoltaic properties were measured with a computer-controlled digital source meter (Keithley, model 2400) under illumination with a Newport solar simulator (AM1.5, 100 mW/cm^2).

DSSC preparation
 The TiO$_2$ and Cr–TiO$_2$ sols were individually mixed with ethanol, acetyl acetone, Triton-X and PEG-600 giving different pastes. Each paste (pure TiO$_2$ paste and Cr–TiO$_2$ paste) was coated onto an FTO ((Flurine doped SnO$_2$, 10 Ω/sq) substrate using a doctor blade, followed by firing at 450 ºC for 30 min. In addition, the Cr–TiO$_2$ paste was also coated onto one of the sintered TiO$_2$ films and calcined again under the heating condition described above. To control film thickness, we used 3M Scotch Magic Tape in the doctor blade process, and it was found that thickness depended on how many folds of tape were used respectively. After the resultant films were cooled, they were immersed in a 0.5 mM ethanolic N719 solution for 24 h, and the dye adsorbed films (photoanodes) were rinsed with absolute ethanol. Thermally treated platinum counter electrodes were applied to the photoanodes. The redox electrolyte solution was introduced into the porous nanocrystalline TiO$_2$ film by capillary action [21].

A digital multimeter (Keithley 2000) was utilized to measure the open-circuit photovoltage and short-circuit photocurrent of the DSSC. A solar stimulator with a 500 W halogen lamp and a light intensity of 100mW/cm^2 were employed to illuminate the dye solar cells. In addition the power conversion efficiency of the solar cell was determined by

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100\%$$

$$(1)$$

In eq.(1) V_{oc}, I_{sc}, P_{in} represent the open-circuit photovoltage, the short-circuit photocurrent and the incident light power respectively. Furthermore the fill factor is given by

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}}$$

$$(2)$$

In eq. (2) V_{max} and I_{max} represents the voltage and the current at the maximum output power point respectively.

RESULTS AND DISCUSSION

XRD analysis

The XRD patterns for the pure TiO_2 and different concentration of chromium doped TiO_2 powders are shown in Fig.1. In XRD patterns of pure and Cr-doped nanoparticles the peaks at 25.32, 37.80, 48.11, 54.02, 55.18, 62.72° are assigned to the (101), (004), (200), (211) and (215) lattice planes, which are attributed to the signals of the anatase phase. There is no diffraction peaks in the XRD spectra, the doped elements diffuse in titania with a high degree form. It can be calculated that the average crystalline size of pure and Cr-doped were 8.62 nm, 8.75 nm, 8.23nm, 7.21 nm respectively by Scherrer formula. These results indicate doping Cr elements can significantly inhibit the growth and increase the specific surface area of titania grains, which is supportive for the absorption of dyes in both cases.
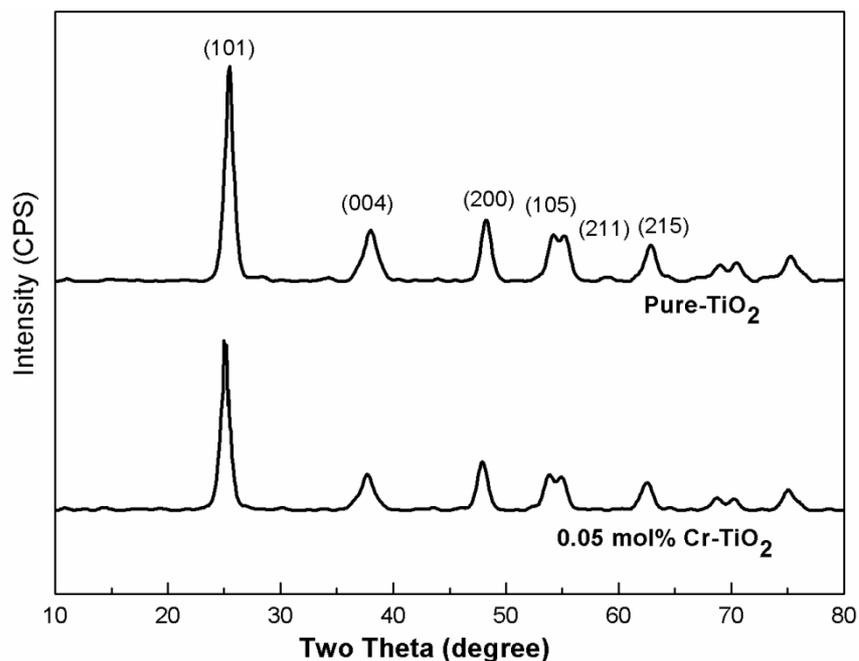

Figure 1. XRD powder diffraction patterns for (a) Pure TiO$_2$ and Cr-TiO$_2$ nanoparticles

FE-SEM analysis

Fig. 2 shows the FE-SEM images of the pure and Cr-doped TiO_2 nanoparticles. It has been observed that the samples were almost the spherical particles. For pure titania the surface with large agglorametes to be presented and for Cr doped TiO_2 nanoparticles the surface is smoother and its crystallinity is better with high porous nature.
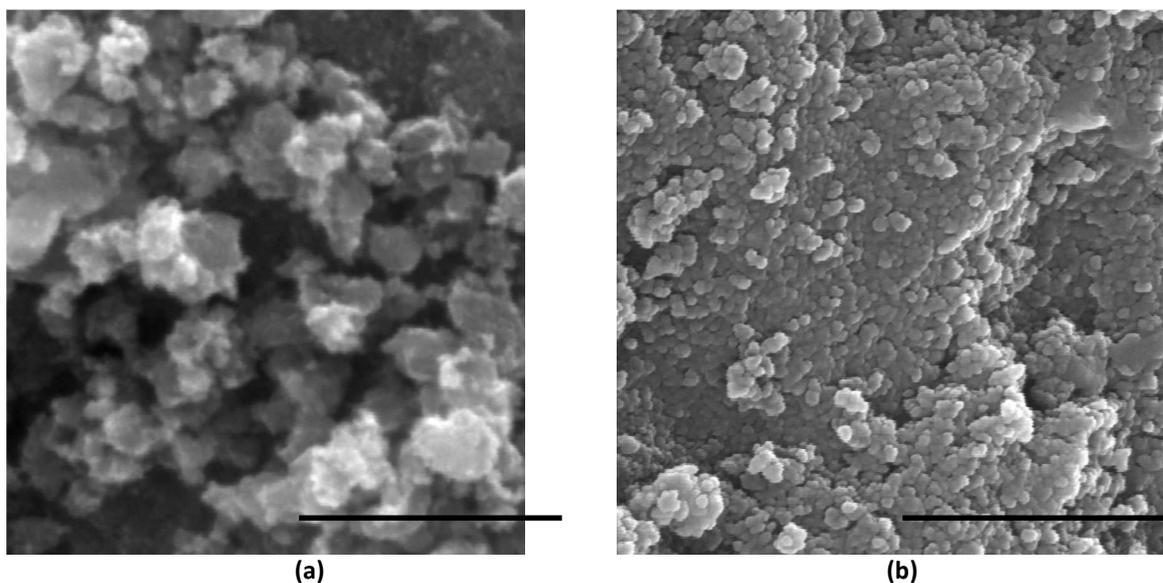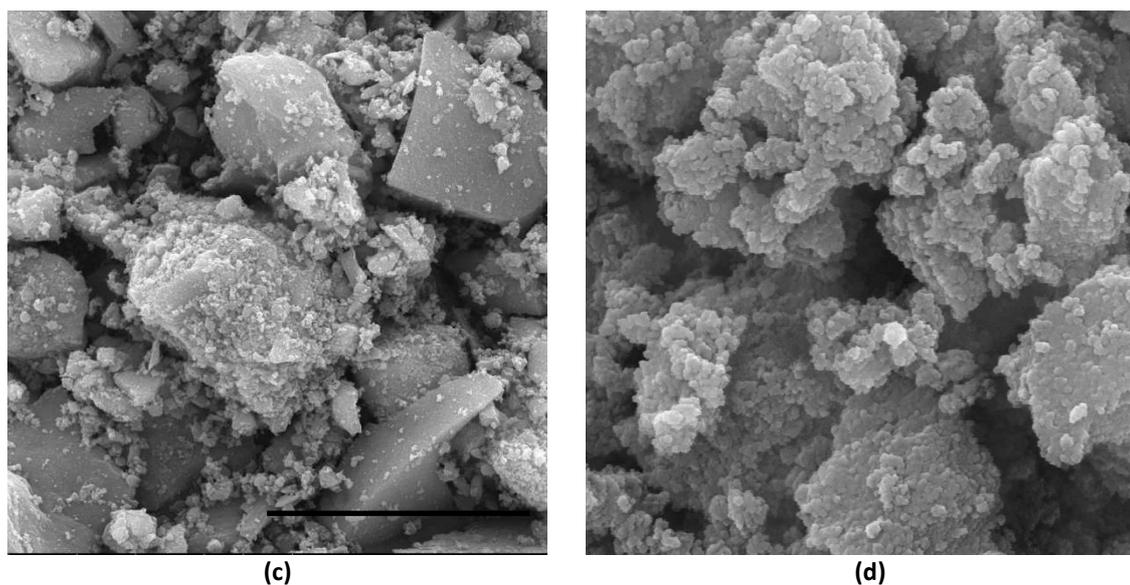

(a)   (b)

Figure 2. FE-SEM micrographs of the undoped(a) and Cr-doped TiO$_2$ ((b)0.01, (c)0.03, (d)0.05 mol%), nanoparticles(▬▬500 nm)

UV-vis absorption spectra analysis

The UV–vis spectra of Cr-doped TiO$_2$ with different concentration, together with pure TiO$_2$, are shown in Fig. 3. The photoabsorption of Cr-doped TiO$_2$ in the visible-light region was stronger than that of pure TiO$_2$. The visible-light photoabsorption of Cr-doped TiO$_2$ calcined at 450º C was the strongest. The energy gap (E$_g$) is determined by the formula [22], E$_g$ = 1239.8/ λ, where λ(nm) is the wavelength of the absorption edge in the spectrum. The energy gaps of TiO$_2$ doped with Cr-doped(0.01,0.03,0.05 mol %), shows mostly red shift and exhibits distinct synergistic effects.
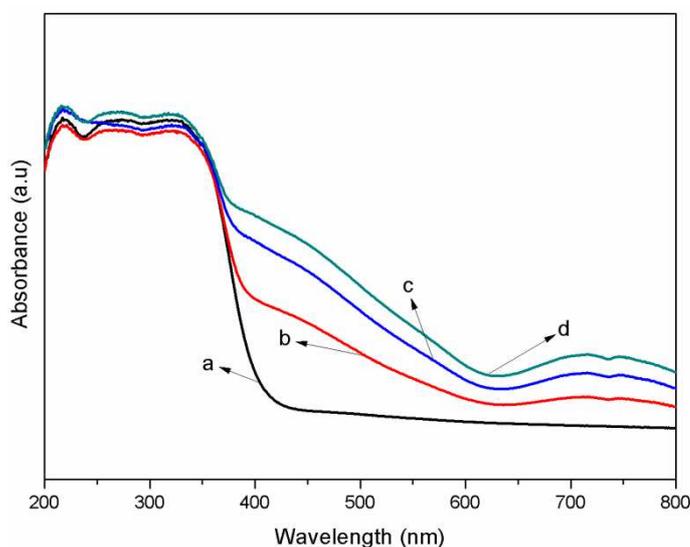

Figure 3. UV–visible spectra of pure TiO2 and Cr–TiO$_2$(0.01,0.03,0.05 mol %).

Table 1 Band gap and absorption edges of pure and modified TiO$_2$ nanopowders

Samples	First absorption edge (nm)	First band gap energy (eV)	Second absorption edge (nm)	Second band gap energy (eV)
Pure – TiO$_2$	398	3.2	-	-
0.01 mol% Cr-TiO$_2$	431	2.87	664	1.86
0.03 mol% Cr-TiO$_2$	459	2.70	711	1.74
0.05 mol% Cr-TiO$_2$	474	2.61	733	1.69

PL spectra analysis

PL emission spectra have been extensively used to observe the effectiveness of charge carrier trapping, immigration, transfer and the chance of electron-holes in semiconductor particles [23]. Fig. 4 shows the PL spectrum of pure TiO_2 and Cr doped TiO_2 and the curve pattern of $Cr-TiO_2$ was similar to that of pure anatase TiO_2 nanoparticles. However, the PL intensity decreased significantly with increasing chromium. The intensity in 0.05 mol% $Cr-TiO_2$ was the smallest, which is most likely due to Cr atoms playing the role of electrons capturers, thereby depressing the recombination process.
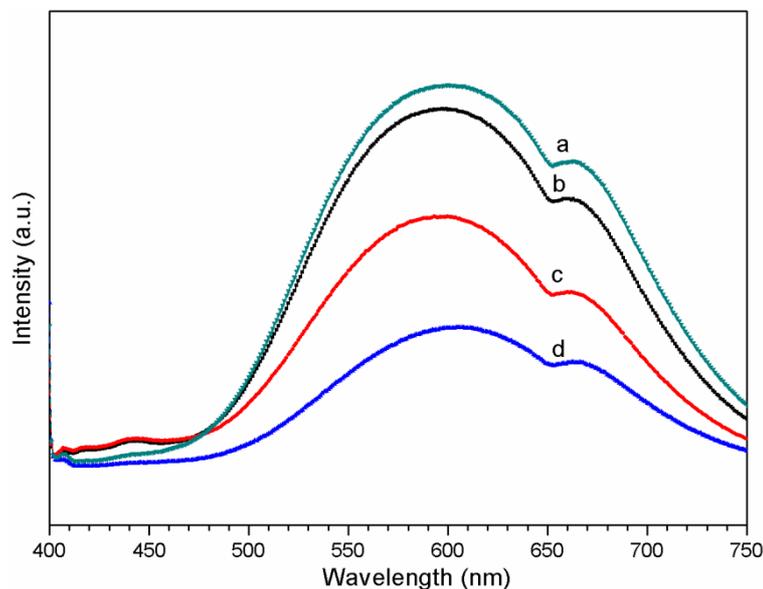

Figure 4. PL spectra of (a) pure and (b) $Cr-TiO_2$ (0.01,0.03,0.05 mol%) nanoparticles

Photovoltaic characterization of FTO based DSSCs

Fig. 4 shows the photoelectric performance of the pure TiO_2 and Cr-modified TiO_2 electrodes using N719 dye. The photocurrent is increased significantly for all the DSSCs after the addition of Chromium. For the pure TiO_2 electrode, the V_{OC} (0.681)and ff(0.601) are decreased seriously, However, for the Cr-modified TiO_2 electrodes, the conversion efficiency is improved from 2.33% to 5.02%.
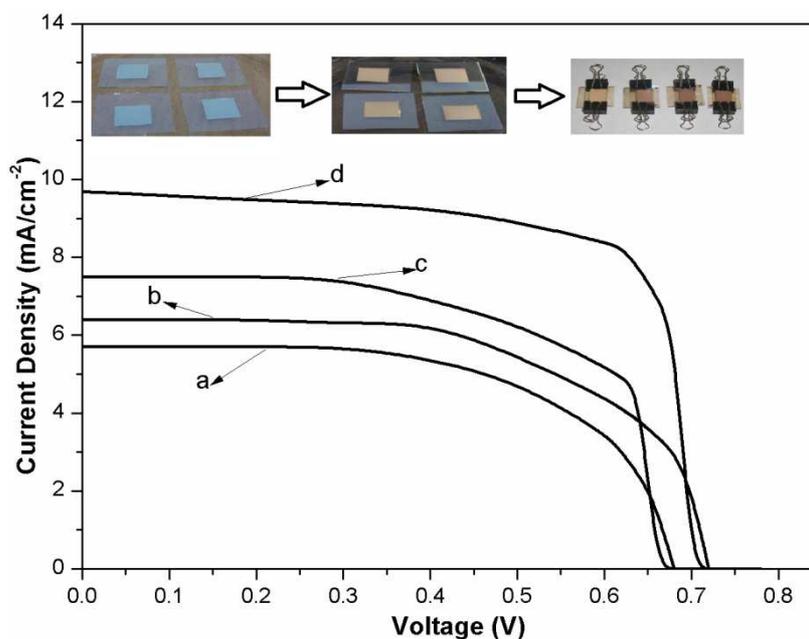

Figure 5. Solar energy conversion efficiency of the DSSC prepared by pure TiO_2 and $Cr-TiO_2$

Table 2 Photovoltaic parameters of DSSC with Chromium modified TiO$_2$nanopowders

Solar cells	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill Factor *(FF)*	Efficiency (η in %)
Pure TiO$_2$	0.681	5.710	0.601	2.33
Cr-TiO$_2$(0.01 mol%)	0.720	6.416	0.559	2.58
Cr-TiO$_2$(0.03mol%)	0.670	7.541	0.609	3.08
Cr-TiO$_2$(0.05mol%)	0.714	9.820	0.716	5.02

CONCLUSION

In summary, the present results demonstrate the improvement in the photoelectric performance of DSSC by introducing Chromium into the TiO$_2$ photoanode. With 0.05 mol% of Cr dopant in the TiO$_2$ electrode, the light-to-electric conversion efficiency of the DSSC reaches 5.02% under a simulated solar light irradiation of 100mWcm^{-2}, which is enhanced by a factor of 2.33 compared to that of the DSSC without Cr doping. XRD results suggest that the amount of impurities added has a great effect on the crystallinity and particle size of TiO$_2$.The UV-vis results shows Cr doped titanium nanoparticles extends the absorption edge to the visible light range (733 nm) and make the red shift more distinct.

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