Crystal structure, optical and electrical characteristics of rutile TiO₂ nanocrystallite-based photoanodes doped with GeO₂

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Abstract. The effect of germanium dioxide, GeO₂ doping on dye-sensitized solar cell (DSSC) TiO₂ nanocrystallite photoanodes with composition (TiO₂–(GeO₂)_x: 0 ≤ x ≤ 0.3 wt%) has been studied. The pure sample and GeO₂-doped samples have been synthesized by a conventional solid-state reaction method and analysed by means of X-ray diffraction, scanning electron microscopy, energy dispersive X-ray and ultraviolet–visible spectroscopy techniques. The photovoltaic characteristics of the prepared samples have been studied by employing *J*–*V* measurements. The pattern of XRD depicted that the dominating phase in the sample with *x* = 0 is a rutile tetragonal phase with the *P*4₂/*mmm* space group. An increase in GeO₂ concentration leads to an appearance and rise of another hexagonal phase structure of α-GeO₂ with the *P*3₂21 space group. Data obtained from the UV–visible spectroscopy measurements reflect that the optical energy gap (*E*^{optical}) increases with increasing GeO₂ content, while the optical refractive index decreases. *J*–*V* photovoltaic characteristics confirm that the DSSCs doped with low-concentration doping, *x* = 0.05 and 0.1 of GeO₂ have higher values for conversion efficiency (*η*), fill factor and short circuit current density (*J*_{sc}) compared with samples with high-concentration doping (*x* = 0.2 and 0.3) of GeO₂. The present results showed that TiO₂–(GeO₂)_x (*x* = 0.05 and 0.1 wt%) films are potential candidates for optical filter materials and optoelectrical and photo-conversion energy devices.

Keywords. TiO₂ nanocrystallites; rutile-type TiO₂; optical energy gap; refractive index; efficiency.

1. Introduction

Recently, enhancement of the efficiency of dye-sensitized solar cells (DSSCs) has been devoted by many researchers [1]. The most effectively utilized wide band gap oxide material is still titanium dioxide (TiO₂) among other wide band semiconductor oxides, such as ZnO, SnO₂, Nb₂O₅ and SrTiO₃, due to its conversion stability, immobility, non-poisonous and remarkable refractive manner [2]. The improvement of progressed photoanode materials that successfully use the visible region of solar energy is an attention challenge, especially for DSSC applications, as the light absorption and charge collection are essentially in the synthesis of the dye-sensitized mesoporous photoanodes [3,4].

One of the compelling methods to enhance the conversion efficiency of TiO₂ DSSC photoanodes is by doping TiO₂ with transition element ions or alkaline earth ions [5–10]. The transition element ions lead to expanding the absorption edge of the TiO₂ to visible-light region by embedding a sub-band into the main band gap. On the other hand, doping with alkaline earth ions leads to change in the crystal structure which modifies the physical and electronic characteristics of TiO₂.

Previously, TiO₂ films have been doped with Ag and La. These films were sensitive to the visible light and have high-photocatalytic activity [11]. Based on this knowledge, the TiO₂ nanoparticles had higher catalytic activity in the

visible-light region when it doped with silver and strontium. This is due to the intensive impact caused by a narrow band gap and an improvement in the separation of charge [12]. When TiO₂ doped with chromium and antimony, the absorption bands in the visible-light region of light had 2.4 and 2.2 eV of energy gaps for chromium and antimony, respectively [13]. The synthesized films of TiO₂ doped with Ta and Ni were found to be a sensitive for the visible-light and the charges able to transfer from the electron donor levels to the conduction bands of the host materials [14]. The effect of Mn dopant on the TiO₂-based photoanodes of DSSCs has been studied [15]. Mn dopant affected the optical properties, whereas the energy band gap of rutile TiO₂ decreases linearly with increasing dopant content. This decrease in energy gap values promises an enhancement of the transport properties of DSSCs based on TiO₂–(MnO₂)_x photoanodes.

Germanium doping on the microstructure and photoelectronchemical properties of TiO₂ films by the sol–gel method has been studied [16]. Doping of germanium reduced the grain size and the surface morphology of Ge-doped films showed higher particle density than that of pure TiO₂. TiO₂–Ge nanocomposite photoanode materials have been investigated for their performance in DSSCs [17]; it was found that there is an increase in electron transfer ability and the efficiency of solar cells changed with an increase in Ge nanoparticles.

Figure 1. XRD patterns for the $\text{TiO}_2-(\text{GeO}_2)_x$ system. The peaks of hexagonal phase $\alpha\text{-GeO}_2$ are marked with (*). The insets show peaks (110) and (101) belonging to the first rutile tetragonal phase with increasing GeO_2 .

Hence, the present work is aimed to study the impact of germanium dioxide (GeO_2) doping on the TiO_2 photoanodes by a conventional solid-state reaction method for DSSC applications to improve the properties of TiO_2 nanostructure and to enhance the photovoltaic efficiency. In addition, this study illustrates the role of GeO_2 doping concentration on the crystal structure, and optical and electrical characteristics of the rutile-type TiO_2 .

2. Experimental

TiO_2 paste was prepared by grinding nanocrystallite TiO_2 (2 g) (Aldrich 99.95%) with acetylacetone (0.25 ml) and Triton X-100 (0.25 ml) using a mortar for 1 h. Then, GeO_2 (Aldrich, 99.999%) with $0 \leq x \leq 0.3$ wt% was added and ground for 2 h to prepare $\text{TiO}_2-(\text{GeO}_2)_x$ series.

2.1 Preparation of DSSCs

To prepare a photoanode working electrode, the paste was spread over the transparent conducting glass fluorine-doped tin oxide (FTO), followed by annealing at 450°C for 30 min. Subsequently, the samples were immersed in N-719 dye solution deluted with ethanol for 1 day at room temperature and then, gently splashed with ethanol. On the other hand, to

prepare the Pt layer of the counter electrode, 20 ml of pure ethanol was added to a 0.5 ml of $\text{H}_2\text{-Hex-Pt(IV)}$. The acquired solution was spread on the FTO substrates and gradually heated to 450°C for 30 min. The DSSC samples were accumulated by placing the counter electrode (FTO substrate coated with a Pt layer) over the aperture of the working electrode. Consequently, the electrolyte KI_2 was added into the aperture by repeated additions of electrolyte drops and air suction to ensure complete filling of the hole [18].

2.2 Measurements and characterization

The study of the crystal parameters and phase identity of powder samples were conducted by analysing the powder X-ray diffraction (XRD) patterns at room temperature obtained by using a Bruker D8 Advance diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). We used the FULL-PROF program (Le Bail fit) [19] for the analysis of diffraction patterns. The optical absorption properties of the samples were investigated by UV-Vis absorption spectra recorded with a Jasco V-576 model double-beam spectrophotometer in the range of $\lambda = 190\text{--}1100 \text{ nm}$.

$J\text{--}V$ curves of DSSCs were carried out using a current amplifier (Keithley 427), multimeter (Aplab 1087) and data acquisition (DataQ: DI-158U). The DSSC devices were irradiated with a homemade solar simulator with a xenon lamp

Table 1. Lattice parameters a , b and c and crystalline size (nm) of the rutile tetragonal phase with the nominal GeO_2 content in the $\text{TiO}_2-(\text{GeO}_2)_x$ samples.

GeO_2 content (x)	a, b (Å)	c (Å)	Crystalline size (nm)
0	4.5801	2.9530	25.68
0.05	4.5815	2.9537	20.24
0.1	4.5810	2.9536	21.36
0.2	4.5799	2.9538	23.89
0.3	4.5796	2.9546	24.21

(35 W), a halogen lamp (55 W) and equipped with IR and UV filters to irradiate DSSCs with an effective area of 0.35 cm^2 . The power of the simulator was measured by using a Lutron (SPM-1116SD) solar power meter.

3. Results and discussion

3.1 XRD patterns and lattice parameters

The powder XRD patterns for $\text{TiO}_2-(\text{GeO}_2)_x$ with $0 \leq x \leq 0.3 \text{ wt\%}$ are shown in figure 1. One can notice that the dominated phase in the sample with $x = 0$ is a rutile tetragonal with the $P4_2/mnm$ space group. Doping of GeO_2 into the material leads to the appearance and rise of a hexagonal phase $\alpha\text{-GeO}_2$ with the $P3_121$ space group [20,21] (mentioned with asterisks) with lattice parameters $a = 4.872 \text{ Å}$ and $c = 5.535 \text{ Å}$. The intensity of corresponding peaks for the hexagonal phase $\alpha\text{-GeO}_2$ increases with an increase in the GeO_2 concentration. The appearance of the hexagonal phase $\alpha\text{-GeO}_2$ is due to the limit solubility of GeO_2 in TiO_2 . As seen from the insertions on the figure, there are no shifts of both peaks (101) and (110) corresponding to the rutile tetragonal one with increasing GeO_2 . Table 1 shows the dependence of rutile TiO_2 crystal lattice parameters of the $\text{TiO}_2-(\text{GeO}_2)_x$ system on the GeO_2 concentration, indicating that there is no effect caused by increasing GeO_2 concentration. The stability in the lattice parameters a and c of the rutile TiO_2 phase with an increase in x could be attributed to the convergence in ionic radii values of Ti (0.42 Å) and Ge (0.40 Å) [22].

The Rietveld refinement of diffraction patterns is shown in figure 2 for the system under study with $0 \leq x \leq 0.30$. As seen from figure 2, the sample with $x = 0$ contains only the peaks of the main rutile tetragonal phase (space group $P4_2/mnm$). In addition, with increasing GeO_2 content ($x = 0.05, 0.1, 0.2$ and 0.3), the samples are mixed with two phases: the main rutile tetragonal phase and another hexagonal phase $\alpha\text{-GeO}_2$ [20,21].

The particle size (L) for all sample powders was calculated by using the Scherrer equation:

$$L = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where K is a dimensionless shape factor (0.9) for nanoparticles. λ the X-ray wavelength, β the full-width at half the maximum intensity in radians and θ the Bragg angle, whereas this equation is limited to nanoscale particles.

The calculated values of the crystallite size are collected in table 1 which reflects that nanocrystallites of doped samples have been decreased as compared with that of pure TiO_2 . It could be attributed to crystallite growth suppression due to the presence of Ge^{4+} at the grain boundary [23]. Thus, the surface area of TiO_2 will be expected to increase and consequently, increases dye loading and photogenerated electrons [24].

3.2 SEM and EDX results

Scanning electron microscopy (SEM) images in figure 3 show the surface morphology of the pure and GeO_2 -doped TiO_2 samples with $x = 0, 0.1$ and 0.3 . It has been observed in figure 3a that the top-view of the SEM image for $x = 0$ was characterized by high porosity which decreased with increasing GeO_2 content (figure 3b and c). The decrease in porosity with increasing GeO_2 content could be attributed to a decrease in the particle size of GeO_2 (table 1).

Table 2 shows the doping ratio analysis results of $\text{TiO}_2-(\text{GeO}_2)_x$ photoanodes with mass fraction $x = 0, 0.05, 0.1, 0.2$ and 0.3 measured using energy dispersive X-ray spectroscopy (EDX). The pure sample, $x = 0$, displayed the absence of Ge element or any other impurity elements and the Ge ratio increases by increasing Ge content. The EDX results show that GeO_2 does not affect the crystal structure of rutile TiO_2 as confirmed by XRD charts in figures 1 and 2. As a result, the Ge doping element would have an effect only on the DSSC photovoltaic characteristics.

3.3 Optical measurements

Figure 4 shows the spectral distributions of absorbance for the studied film system. UV-Vis spectra depict that the basic absorption of the Ti-O bond in the UV light range around 400 nm , which is consistent with a band gap of rutile TiO_2 (3 eV) [25], while the absorption spectra of $\text{TiO}_2-(\text{GeO}_2)_x$ films are successfully extended to the visible wavelength range at around 650 nm .

In the fact that near the fundamental edge of the absorption coefficient spectrum is very useful to investigate the type of the optical transition [26]. Therefore, the optical band gap can be deduced from the dependence of the absorption coefficient on the photon energy ($h\nu$) which reflects the importance to study the band-to-band transition theory. It can be used to analyse the absorption coefficient at the fundamental edge for such materials [26,27].

According to Tauc's equation which is modified by Mott and Davis, the absorption data follow a power-law behaviour

Figure 2. Observed (symbols) and calculated (line) XRD patterns for $\text{TiO}_2-(\text{GeO}_2)_x$ samples. The positions of Bragg reflections for both tetragonal and hexagonal phases are indicated in the first and second rows, respectively.

Figure 3. SEM micrographs of $\text{TiO}_2-(\text{GeO}_2)_x$ photoanodes with $x =$ (a) 0, (b) 0.1 and (c) 0.3.

as in the following equation [28,29]:

$$\alpha h\nu = G(h\nu - E^{\text{optical}})^m. \quad (2)$$

In equation (2), using Beer–Lambert’s law, the absorption coefficient (α) can be calculated. G is a constant, $h\nu$ represents the energy of the incident photons, E^{optical} is

the optical band gap energy and power (m) characterizes electronic transition, where $m = 2$ and $1/2$ for indirect and direct allowed transitions, respectively [26]. In the present work, the optical energy band gap for the studied films has been calculated using the absorption spectrum fitting method. In this method, the optical absorption coefficient (α) expressed as a function of the wavelength (λ) of the incident

Table 2. EDX analysis of $\text{TiO}_2-(\text{GeO}_2)_x$ ($x = 0.0, 0.05, 0.1, 0.2$ and 0.3 wt%) photoanodes.

Sample	Element	wt%	Real Ge content
$x = 0$	Ti	28.75	0.0
	O	71.25	
$x = 0.05$	Ti	67.64	0.048
	O	29.13	
	Ge	3.23	
$x = 0.1$	Ti	62.88	0.11
	O	30.08	
	Ge	7.04	
$x = 0.2$	Ti	57.78	0.21
	O	30.08	
	Ge	12.14	
$x = 0.3$	Ti	53.53	0.31
	O	29.42	
	Ge	17.05

Figure 4. UV absorption spectra of $\text{TiO}_2-(\text{GeO}_2)_x$ ($x = 0.0, 0.05, 0.1, 0.2$ and 0.3 wt%) film samples.

photon and equation (2) can be rewritten as [30,31]:

$$\alpha(\lambda) = G(hc)^{m-1} \lambda \left(\frac{1}{\lambda} - \frac{1}{\lambda_{\text{cut}}} \right)^m, \quad (3)$$

where λ_{cut} is the cut-off wavelength corresponding to the optical band gap, c the light velocity and h the Planck's constant. Equation (3) can be simplified and rewritten as:

$$A(\lambda) = D\lambda \left(\frac{1}{\lambda} - \frac{1}{\lambda_{\text{cut}}} \right)^m, \quad (4)$$

$D = [C(hc)^{m-1}d/2.303]$. Equation (4) helps to calculate the optical band gap only by using the absorbance data avoiding the thin film thickness. Thus, the energy band gap

can be calculated directly from λ_{cut} using the following equation:

$$E_{\text{ASF}}^{\text{optical}} = \frac{hc}{\lambda_{\text{cut}}} = \frac{1239.83}{\lambda_{\text{cut}}}. \quad (5)$$

The value of λ_{cut} can be deduced from extrapolating the linear region of $(A/\lambda)^{1/m}$ against (λ^{-1}) curve at $(A/\lambda)^{1/m} = 0$. The variation of $(A/\lambda)^{1/2}$ with $(1/\lambda)$ for indirect allowed transition is shown in figure 5. The values of E^{optical} for the studied $\text{TiO}_2-(\text{GeO}_2)_x$ films are listed in table 3. Energy gap values depend on the concentration of GeO_2 in the formed film and it varies from 2.80 to 3.34 eV.

The refractive index of $\text{TiO}_2-(\text{GeO}_2)_x$ films was calculated by the following equation [32]:

$$\left(\frac{n^2 - 1}{n^2 + 2} \right) = 1 - \sqrt{\frac{E^{\text{optical}}}{20}}. \quad (6)$$

The values of the calculated refractive index, n are tabulated in table 3. The values reveal that the refractive index of all studied films is considerably high. Figure 7 shows the variation in the energy band gap and refractive index with GeO_2 content in the studied films. As seen from figure 6, the energy band gap increased with increasing GeO_2 . An increase in the optical band gap of the prepared samples $\text{TiO}_2-(\text{GeO}_2)_x$ can be related to the size effect that appears in nanocrystalline structures [33]. The optical properties of the $\text{TiO}_2-(\text{GeO}_2)_x$ thin films indicate that they are suitable for use in fabricating DSSCs.

3.4 Electrical measurements

The photocurrent density–voltage curves of DSSCs with different concentrations of GeO_2 in the TiO_2 photoanode under a simulated solar irradiation of 55 W cm^{-2} are shown in figure 7. The conversion efficiency (η) of the DSSCs was determined by short-circuit current density (J_{sc}), open circuit potential (V_{oc}) and the intensity of the incident light per unit area (P_{in}). The overall conversion efficiency was calculated according to the equation below:

$$\eta = \frac{J_{\text{sc}} \cdot V_{\text{oc}} \cdot \text{FF}}{P_{\text{in}}} \times 100\%. \quad (7)$$

The fill factor (FF) can be calculated according to the following equation:

$$\text{FF} = \frac{J_{\text{max}} \cdot V_{\text{max}}}{P_{\text{in}}}, \quad (8)$$

where J_{max} and V_{max} are the current density and potential at the point of the maximum power, respectively. The photovoltaic parameters were calculated and indicated in table 4.

We noted that the doping with GeO_2 , the short-circuit photocurrent density (J_{sc}) was increased in comparison with the

Figure 5. Relation between $(A/\lambda)^{1/2}$ and (λ^{-1}) for $\text{TiO}_2-(\text{GeO}_2)_x$ ($x = 0.0, 0.05, 0.1, 0.2$ and 0.3 mol%, respectively) film samples.

Table 3. Energy band gap (E^{optical}) and refractive index (n) for $\text{TiO}_2-(\text{GeO}_2)_x$ ($x = 0.0, 0.05, 0.1, 0.2$ and 0.3 wt%) films.

GeO ₂ content (x)	Energy band gap (E^{optical})	Refractive index, n
0	3.13	2.36
0.05	3.16	2.35
0.1	3.22	2.34
0.2	3.24	2.33
0.3	3.26	2.32

undoped sample ($x = 0$) as shown in figure 8, this can be attributed to the decrease in the energy gap of the samples. On the other hand, at low concentration of doping with GeO₂

doping at $x = 0.05$ and 0.1 , open-circuit voltage (V_{oc}) was increased in comparison with the undoped sample as shown in figure 7 and at high concentration of doping at $x = 0.2$ and 0.3 , open-circuit voltage (V_{oc}) was decreased. As a result, the efficiency (η) of doped-DSSC devices at low concentrations is higher than that of the undoped cells.

Because of the decrease in the crystal size for doped films, their surface area will be increased, leading to expansion in the number of absorbed dyes which increase the number of injected electrons in photoanodes, and therefore, increase in J_{sc} [34,35]. As GeO₂ content is <0.1 wt, it could assist as a crystal growth inhibitor that can cause a higher surface area. This is expected to increase the surface area of TiO₂

Table 4. Photovoltaic characteristics of DSSCs for $\text{TiO}_2-(\text{GeO}_2)_x$ ($x = 0.0, 0.05, 0.1, 0.2$ and 0.3 wt%) films.

GeO ₂ content (x)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	Power	Efficiency (%)
0	7.6094	0.3698	0.4475	1.25938	3.73982
0.05	9.1313	0.3882	0.4574	1.58661	4.71155
0.1	8.6752	0.4067	0.4574	1.57906	4.68913
0.2	8.5236	0.3328	0.4474	1.2693	3.76927
0.3	8.3703	0.2588	0.44749	0.9696	2.87929

Figure 6. Relation between the energy band gap (E^{optical}) and refractive index, n for $\text{TiO}_2\text{-(GeO}_2)_x$ ($x = 0.0, 0.05, 0.1, 0.2$ and 0.3 mol%) film samples.

Figure 7. Photocurrent density–voltage curves (J – V) of DSSCs with different GeO_2 -doping concentrations of TiO_2 photoanodes.

and consequently, increases dye loading and photogenerated electrons [24]. In contrast, if the amount of added GeO_2 is >0.1 wt%, a distinctive decrease in η of the binary oxide

Figure 8. Dependence of DSSC characteristics on GeO_2 content: (a) short-circuit photocurrent density of photoanode (J_{sc}), (b) open-circuit voltage (V_{oc}) and (c) conversion efficiency (η).

electrodes was observed. This corresponds to the property of the pure GeO_2 electrode [36].

4. Conclusion

In this study, the effect of $(\text{GeO}_2)_x$ co-doped on DSSC TiO_2 nanocrystallite photoanodes at low concentrations ($x = 0, 0.05, 0.1, 0.2$ and 0.3 wt%) has been studied. XRD, SEM, EDX and UV–visible data analysis were used to examine the synthesized samples. The photovoltaic characteristics of the prepared cells have been studied by employing J – V

measurements. The obtained results have been revealed that:

1. The XRD pattern showed that the dominated phase in the undoped sample is a rutile tetragonal type with the $P4_2/mnm$ space group, while in doped samples, the increase in the GeO_2 ratio leads to the appearance and rise of another hexagonal phase $\alpha\text{-GeO}_2$ with the $P3_221$ space group.
2. The optical energy gap (E^{optical}) for the studied films increases with increasing GeO_2 content and takes values in the range from 2.80 to 3.34 eV, while the optical refractive index decreases.
3. The crystal size of doped films has been decreased as compared with that of pure TiO_2 . This will increase the surface area of TiO_2 and consequently, increases dye loading and photogenerated electrons.
4. J - V photovoltaic characteristics confirm that the DSSCs co-doped with low-concentration doping $x = 0.05$ and 0.1 of GeO_2 have higher power conversion efficiency (η), FF and short circuit current density (J_{sc}) in comparison with high-concentration doping samples $x = 0.2$ and 0.3 of GeO_2 .

Thus, it is reasonable to infer that $\text{TiO}_2\text{-(GeO}_2)_x$ ($x = 0.05$ and 0.1 wt%) films are potential candidates for optoelectrical devices and DSSCs.

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