Characteristic Properties of Dy-Eu-Ag co-Doped TiO₂ Nanoparticles Prepared by Electrospinning Processes

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TiO₂ with high photoactive wide band gap energy semiconductor has been studied intensively for its attractive applications as photo catalyst and solar cell. TiO₂ has three kinds of different crystal structures; anatase, brookite and rutile. TiO₂-nanoparticles could become valuable light emitting materials when they are doped with highly luminescent rare earth ions. In this study, Dy-Eu-Ag co-doped TiO₂ nano particles were prepared by electrospinning method. The crystal structures of nanofibers were determined X-Ray Diffraction device (XRD), morphology of the samples were analyzed by scanning electron microscope (SEM), and the optical properties of the samples were determined by ultraviolet/visible spectrometer (UV/VIS) measurements. Electrical and electronic properties of the sampled were determined using the data obtained from four point prob technique (FPPT).

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1. Introduction

Recently, many types of nanofibers and nanowires have attracted a great attention due to their potential applications in many fields, such photovoltaic devices, integrated electronic circuits, solar cells, lithography, and health [1–6]. Researchers have used different methods for the fabrication of the nanofibers and nanowires, such molecular beam epitaxy (MBE) [7], vapor-liquid-solid mechanism (VLS) [8], solution-phase, shadow sputtering, and sol-gel methods [9].

In this work, we, firstly, developed Dy-Eu-Ag co-doped TiO₂ nano particles and nanofibers on aluminium foil substrates using electrospinning method. Crystal structure, surface morphology, composition, and optical properties of Dy-Eu-Ag co-doped TiO₂ nanoparticles and nanofibers were characterized by means of XRD, SEM, and UV/VIS spectrometer, respectively.

2. Experimental

Preparation of Dy-Eu-Ag co-doped TiO₂ nano particles and nanofibers has been achieved as following: Dy(NO₃)₃ · xH₂O (Aldrich, 99.9%, Mw = 348.51 (anhydrous basis) g/mol), Eu(NO₃)₃ · 55H₂O (Aldrich 99.9% Mw = 428.06 g/mol), AgNO₃ (Sigma-Aldrich ≥99.0% , Mw = 169.87 g/mol), Ti[OCH(CH₃)₂]₄ (Aldrich, 99.999%, Mw = 284.22 g/mol) and CH₃CH₂OH (Sigma-Aldrich absolute ≥ 99.8% Mw = 46.07 g/mol) were used as precursors. In the preparation of each sample solution, the ratio of each doped material in solution is 1%.

Each of them was dissolved in absolute ethanol vigorously stirring for 15 min at room temperature. Completing the dissolution of all the compounds, these precursor solutions were mixed in a container. Afterwards, another solution was prepared dissolving 1 g polyvinylpyrrolidone (Aldrich, (C₆H₉NO)_x, PVP, Mw = 1,300,000) in 12.5 mL absolute ethanol. The obtained solution was added into the first solution and stirred for 2 h at room temperature. Hence, we obtained an homogeneous polymer solution and loaded it into a plastic syringe of the pump (Fig. 1). All samples have been developed constant voltage (25 kV), at a height (8 cm), and with constant flow rate (1 mL/hr).

Fig. 1. Electrospinning experimental set-up [1].

3. Results and discussions

XRD patterns of the Dy-Eu-Ag doped and undoped TiO₂ powders are seen in Fig. 2a,b, respectively. As seen from the XRD pattern of the undoped TiO₂ powder (Fig. 2b), it include both anatase and rutile phases. But, as seen from XRD pattern of the Dy-Eu-Ag doped TiO₂

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powder (Fig. 2a), anatase phase increases while rutile phase decreases. This result is in a good agreement with the results obtained from similar studies in literature [10–13].

Fig. 2. XRD patterns of powders of (a) Dy-Eu-Ag doped and (b) Undoped TiO_2 .

SEM images of the undoped and Dy-Eu-Ag doped TiO_2 powders are given in Fig. 3a,b, respectively. As seen from Fig. 3b, the distribution of the added dopants is very homogeneous and the sizes of powders of the added materials are less than micrometer. These SEM results are in a good agreement with the results obtained from similar studies in literature [14, 15]

Fig. 3. SEM images of powders of (a) undoped and (b) Dy-Eu-Ag doped TiO_2 .

SEM images of electrospun nanofibers of undoped, Ag doped, Ag-Eu doped, Ag-Dy doped, and Ag-Dy-Eu doped TiO_2 are given in Fig. 4a–e, respectively. As seen from Fig. 4, all electrospun nanofiber samples are in the form of uniform fibers, but their diameters differ. The measured minimum and maximum diameter values of the nanofibers of each sample are given in Table I.

We found the optical band gap energies of the nanofiber samples using the data obtained from UV/VIS

Fig. 4. SEM images of electrospun nanofibers of (a) undoped, (b) Ag doped, (c) Ag-Eu doped, (d) Ag-Dy doped, and (e) Ag-Dy-Eu doped TiO_2 .

TABLE I

The measured values of minimum and maximum diameter of the nanofibers of undoped, Ag, AgDy, AgEuDy, and AgEu doped TiO_2 samples.

nanofiber sample	minimal	maximal
	diameter [nm]	
undoped TiO_2	93	517
Ag doped TiO_2	103	506
Ag-Eu doped TiO_2	120	515
Ag-Dy doped TiO_2	125	386
Ag-Eu-Dy doped TiO_2	117	647

measurements. The optical band gap energy values of the samples were determined by extrapolating the linear portions of respective curves corresponding samples (Fig. 5). As seen from Fig. 5, the band gap energy of the undoped nanofiber sample is the largest one (≈ 3 eV) and the Ag sample doped has the smallest value (≈ 1.4 eV). This is the expected result [16–18]. The band gap energy values of the other samples lie between ≈ 1.0 and 3.2 eV.

The activation energy of the samples were calculated using $\ln \sigma$ curve versus $1000/T$ plotted using the data from FPPT measurements performed in the temperature

Fig. 5. $\alpha(h\nu)^2 - h\nu$ graphics of nanofibers Undoped TiO₂, Ag doped TiO₂, Ag-Eu doped TiO₂, Ag-Dy doped TiO₂, Ag-Dy-Eu doped TiO₂ in visible region of UV/VIS.

range 300–900 °C (Fig. 6). As seen from Fig. 6, conductivity of all the samples remain without not much changing until around 500 °C. But after 500 °C, it is seen that their conductivities increases abruptly. This is the expected result since the samples behave as the semiconducting materials.

Fig. 6. The temperature dependence of electrical conductivity for the Ag, AgDy, AgEuDy, and AgEu doped TiO₂ nanofiber samples.

We can prove this result according to their activation energies. Using the Arrhenius curves (Fig. 6), we calculated the activation energy of the samples. The calculated numerical values of the activation energies of the samples are given in Table II. As seen from Table II,

AgEu doped TiO₂ sample has the highest conductivity ($1.06 \times 10^{-2} \text{ Scm}^{-1}$) and activation energy (2.80 eV).

TABLE II

Conductivities of Ag, AgDy, AgEuDy, and AgEu doped TiO₂ corresponding to T_1 and T_2 and their activation energies belonging to the temperature region between T_1 and T_2 .

Samples	T_1 [°C]	T_2 [°C]	σ_1 [Scm ⁻¹]	σ_2 [Scm ⁻¹]	$T_{\max}$ [°C]	$\sigma_{\max}$ [Scm ⁻¹]	E_a [eV]
Ag	630	653	2.82×10^{-5}	4.12×10^{-5}	653	4.12×10^{-5}	1.18
AgDy	690	740	5.51×10^{-3}	2.37×10^{-3}	740	2.37×10^{-3}	2.69
AgEuDy	778	812	3.27×10^{-4}	1.17×10^{-3}	812	1.17×10^{-3}	3.68
AgEu	606	741	7.72×10^{-5}	1.06×10^{-2}	741	1.06×10^{-2}	2.80

4. Conclusion

In this study, we developed undoped TiO₂ and doped (Ag, AgEu, AgDy, AgEuDy) TiO₂ nanofiber samples and investigated their structural, morphological, electrical and electronic, and optical properties. Obtained results are as following;

1. Band gap energy values of all the samples are as expected and they are in a good agreement with literature.
2. Band gap energy of Ag doped TiO₂ nanofiber is suitable for these samples to be used as an antibacterial material according to the literature.
3. Band gap energy of Eu and Dy doped TiO₂ nanofibers decrease compared undoped TiO₂ nanofiber [19–20].
4. Activation energy of the samples have been calculated from the Arrhenius conductivity curves of the samples.

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