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Synthesis and characterisation of titanium dioxide nanoparticles sensitised with natural chlorophyll dye extracted from *Mentha* leaves

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For this study a facile ultrasounds assisted method was used for synthesis of chlorophyll-sensitised titanium dioxide nanoparticles. The chlorophyll was extracted from *Mintha* leaves by a solvent extraction method and based on ultraviolet-visible spectroscopy it was showed that was extracted chlorophyll (*a*+*b*) mixture with concentration of 87 mg/L. Based on X-ray diffraction patterns analysis was demonstrated that chlorophyll does not change the structural matrix of titanium dioxide. Field emission – scanning electron microscopy images revealed the formation of nanoparticles with dimensions between 3 nm and 36 nm. Ultraviolet-visible and photoluminescence spectra confirmed that all chlorophyll-sensitised titanium dioxide nanoparticles absorb the radiation from the visible range. Also, we have proposed a sensitisation mechanism of titanium dioxide particles with natural chlorophyll dye.

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1. Introduction

Titanium dioxide (TiO_2) has attracted much attention due to its various possible applications in: water splitting [1,2] heterogeneous photocatalysis processes used for degradation of organic pollutants [3-5] and solar cell devices [6,7]. However, TiO_2 present limitations mostly by the fact that it can absorb light only in the ultraviolet region, neglecting the visible and infrared regions, thus, neglecting near 95% from the available solar energy. In order to utilise more effective the sunlight as a renewable energy, natural dye sensitisation is a promising technique for extension of the excitation energy of TiO_2 into visible region [8-11]. Sensitisation with organic dyes of the semiconductors process implies three steps: (1) adsorption of the sensitizer dye at the semiconductor surface; (2) absorption of the radiation from the visible range by dye molecules and electrons generation; (3) the electrons generated by the dye molecules are injected into the conduction band of the semiconducting material [8,9]. In 1991, O'Regan and Gratzel [8] has sensitised titanium dioxide film with ruthenium complex dye in order to obtain photovoltaic cell with high efficiency in conversion of solar energy into electrical current (nearly 11%), known today as "Gratzel solar cell". Since then, a series of researchers reports the sensitisation of semiconductor with natural dyes like: antocyanine [9,12], carmine and morin [13] or curcumin [14], sensitised-systems utilised in fabrication of solar cell devices or used as photocatalyst in environment remediation. Beside these dyes, chlorophyll can be an excellent sensitiser for semiconductors due to the non-toxic nature, can be extracted from renewable bio-resources (mostly from all the green leaves), having a minimum impact on environment. Moreover, chlorophyll presents two strong absorption peaks in the visible range located at 430 and 660 nm wavelengths, which make it to be a suitable sensitiser of semiconductors with photoactive properties in the visible range [15-17]. Al-Alwani et al. [15] extracted different natural dyes, namely chlorophyll and betanin dyes, from *Cordyline fruticosa*, *Pandannus amaryllifolius* leaves and *Hylocereus polyrhizus* fruits. With these dyes authors sensitised TiO_2 commercial powder and confirmed the absorption of the natural dyes at titanium dioxide powder surface by optical and infrared spectroscopy analysis. Kathiravan et al. [16] sensitised colloidal titanium dioxide with chlorophyll extracted from green algae and described the interaction between chlorophyll and colloidal TiO_2 nanoparticle surface by absorption and fluorescent analysis which confirmed the electron transfer from excited state of chlorophyll to the conduction band of TiO_2. Benjamin et al. [17] enhance the photocatalytic activity of zinc oxide by coating of semiconductor surface with chlorophyll and anthocyanin dyes. It was observed the shifting of the optical response from ultraviolet to the visible range, a decrease of the energy band gap and a increase of the rate of photocatalytic degradation of rose bengal (used as pollutant model) of the dye coated semiconductor.

In this paper we described a facile method for sensitisation of titanium dioxide nanoparticles with chlorophyll extract, using an ultrasound-assisted method. The structural, morphological, optical and fluorescent properties of the chlorophyll-sensitised TiO_2 nanoparticles have been evaluated.

2. Materials and method

2.1. Synthesis of chlorophyll-sensitised titanium dioxide nanoparticles

In the first stage of the studies, the chlorophyll dye was extracted from *Mentha* leaves, using solvent extraction method. Thus, 3 g of leaves were washed, steamed in order to enhance the extraction process and added 50 ml ethanol heated at 60 ^{0}C, for 7 minutes. The extract was kept in a 50 ml volumetric flask.

Titanium dioxide nanoparticles were synthesised by a hydrolysis method, using as precursor titanium III-chloride, followed by heating at different temperatures i.e. 200 ^{0}C, 400 ^{0}C, 600 ^{0}C and 800^{0}C, respectively. The synthesis process and characterisation of TiO_2 un-sensitised nanoparticles, annealed at different temperatures, are presented, in details, in our previous published article [18]. Sensitisation with chlorophyll extract of TiO_2 nanoparticles annealed at different temperatures was made by an ultrasound-assisted method. Thus, a volume of 5 ml chlorophyll extract was mixed with 0.5 g TiO_2 nanoparticles. The mixtures were subjected to ultrasounds for 30 min, followed by a slow drying at 40 ^{0}C, for 24 h in order to remove the solvent. The obtained samples were aged for 48 h, at 40 ^{0}C, in order to stabilise the natural dye at TiO_2 nanoparticles surfaces.

2.2. Characterization of chlorophyll-sensitised titanium dioxide nanoparticles

The chlorophyll extract was analysed using UV-Vis spectroscopy in order to determine the chlorophyll types and the concentration of the extract [19].

For the determination of the structural properties of chlorophyll-sensitised TiO_2 nanoparticles a Bruker D8 Advance X-ray diffractometer working with CuKα radiation was used. The patterns were evaluated using a standard X-ray powder diffraction data file, JCPDS 12-1272 (space group I_41/amd, a_0=3.78(5) [Å], c_0=9.51(3) [Å]) for anatase crystalline phase and JCPDS 21-1276 (space group P_42/mnm), a_0=4.59(3) [Å], c_0=2.95(9) [Å]) for rutile crystalline phase. Using the Powder Cell software, the structural parameters were calculated using the Pseudo-Voigt refinement and the average of crystallite size and strain was calculated by the Williamson-Hall method [20].

Morphological properties of chlorophyll-sensitised TiO_2 nanoparticles were emphasised using Scanning electron microscopy. The samples were examined using a field emission scanning electron microscope (FE-SEM) – Raith e_Line with in-lens electron detection capabilities.

UV-Vis spectroscopy studies were carried out in order to determine the optical properties of the chlorophyll-sensitised TiO_2 nanoparticles. The total transmittance of the materials was recorded using a Lambda 35 Perkin-Elmer spectrometer equipped with an integrated sphere, using a spectralon as a reference. Based on the spectra, the energy band gap of the materials was determined using the Tauc's relation [21]:

$$\alpha h\nu = A\left(h\nu - E_g\right)^m \tag{1}$$

where: α is absorption coefficient, hν is photon energy, E_g is the energy band gap, A is an energy dependent constant and m is an integer depending on the nature of electronic transitions. For the direct allowed transitions, m has a value of 1/2 while for indirect allowed transitions, n=2.

Also, the Urbach energy was determined based on the absorption tail, which can be correlated with the structural disorder and strain caused by the synthesis method of the chlorophyll-sensitised TiO_2 nanoparticles [22]:

$$\ln \alpha = \alpha_0 \exp\left(\frac{h\nu}{E_U}\right) \tag{2}$$

where: α_0 is a constant and the E_u is the Urbach energy. E_u was determined from the slope of lnα versus (hν).

Photoluminescence measurements were carried out using an Able & Jasco FP 6500 spectrofluorometer with a xenon lamp of 150 W as the excitation source and a photomultiplier tube (PMT) as detector. For comparison, all emission spectra were measured at room temperature with the same instrumental parameters using an excitation at 285 nm for chlorophyll and 405 nm for chlorophyll-sensitised TiO_2 nanoparticles, emission originated from the luminescent centres. All spectra were registered exactly in the same conditions: excitation/reflection into 5 mg of powder samples with identical incidence intensity, the excitation slit (5 mm) and emission slit (5 mm).

3. Results and discussion

The UV-Vis absorption spectrum of the chlorophyll extract from *Mentha* leaves is presented in Figure 1. Based on the spectrum it was observed that chlorophyll *a* and *b* types, with chlorophyll *a*:*b* ratio 3:1 were extracted from the leaves, having the total concentration of chlorophyll (*a*+*b*) of 87 mg/L.

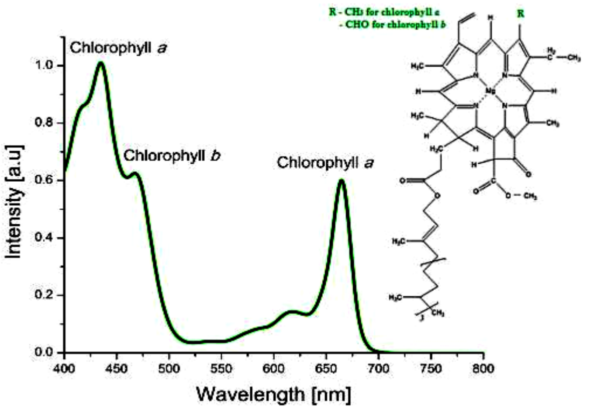

Fig. 1. UV-Vis absorption spectra of chlorophyll extract

X-ray patterns of chlorophyll-sensitised TiO_2 nanoparticles are presented in Fig. 2 and in Table 1 are summarised the results following the calculations of the average crystallite size, strain and cell parameters. It has been remarked the amorphous state of the sample treated at 200 ^{0}C and the formation of the anatase crystalline phase with increasing of the temperature to 600 ^{0}C. At 800 ^{0}C a large part of anatase it's transformed into rutile. This behaviour is also observed for the un-sensitised TiO_2 nanoparticles [18]. However, a small decrease of strain can be observed compared with the un-sensitised materials. It was not detected any diffraction peaks characteristic for chlorophyll.

Based on the obtained data, we can affirm that the sensitisation assisted by ultrasounds process, does not change the structural phases of chlorophyll-sensitised TiO_2 materials (Table 1) compared with un-sensitised materials [18], so the chlorophyll do not interacted with titanium dioxide structural matrix. Shang et al. [23] obtained Benzimidazolone Yellow-sensitised TiO_2 photocatalyst thought solvothermal method and observed that the sensitizer do not changed the crystalline structure of original TiO_2.

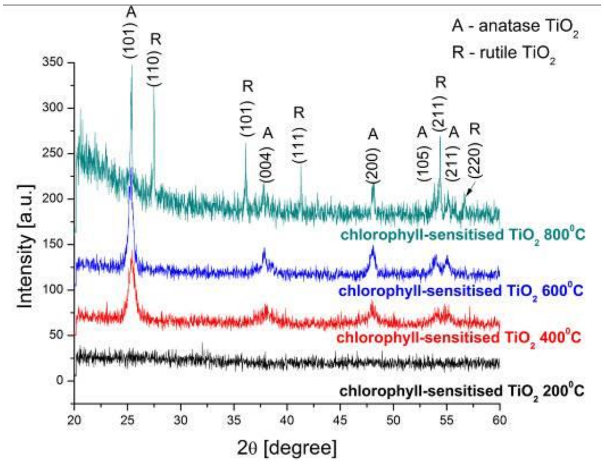

Fig. 2. XRD patterns of chlorophyll-sensitised TiO_2 particles

Table 1. Structural parameters of chlorophyll-sensitised TiO_2 nanoparticles

Sample name	Crystalline phase	Phases ratio [%]	Average crystallite size [nm]	Strain [%]	Structural parameters		Cell volume [Å^3]
					a [Å]	**c [Å]**	
Chlorophyll-sensitised TiO_2 200 ^{0}C	Amorphous	100	-	-	-	-	-
Chlorophyll-sensitised TiO_2 400 ^{0}C	Anatase	100	15	0.5	3.78(5)	9.51(3)	135.88
Chlorophyll-sensitised TiO_2 600 ^{0}C	Anatase	100	19	0.1	3.78(7)	9.50(3)	135.73
Chlorophyll-sensitised TiO_2 800 ^{0}C	Anatase Rutile	46 54	70 21	0.3 0.2	3.78(9) 4.61(7)	9.52(1) 2.97(7)	136.02 63.11
TiO_2 anatase JCPDS 12-1272	Anatase	-	-		3.78(5)	9.51(3)	135.88
TiO_2 rutile JCPDS 21-1276	Rutile	-	-		4.59(3)	2.95(9)	62.15

Fig. 3 shows the FE-SEM images of chlorophyll-sensitized TiO_2 nanoparticles. It can be observed that at low calcinations temperature (i.e. 200 ^{0}C) the particles are spherical and uniform in size, while at 800 ^{0}C particles appear irregular. The change in morphology can be attributed to the crystals grow during the calcinations and to the transformation of the crystalline phases from amorphous to anatase to rutile with the increase of the temperature. For the chlorophyll-sensitised TiO_2 200 ^{0}C sample particles dimensions were near 3 nm and increased to 36 nm for the chlorophyll-sensitised TiO_2 800 ^{0}C sample.

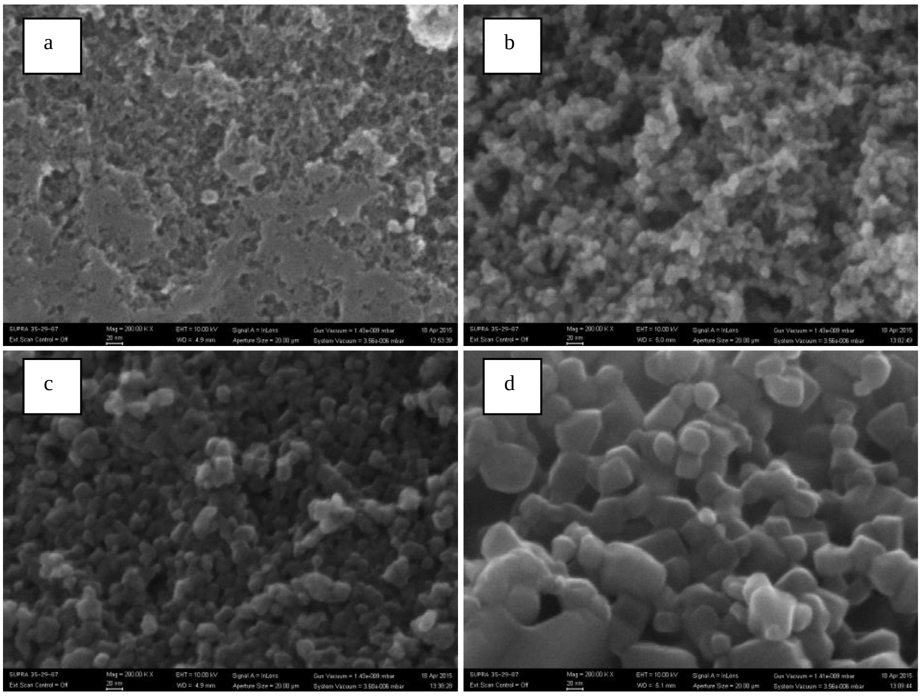

Fig. 3. SEM images of: (a) chlorophyll-sensitised TiO_2 200^0C; (b) chlorophyll-sensitised TiO_2 400^0C; (c) chlorophyll-sensitised TiO_2 600^0C and (d) chlorophyll-sensitised TiO_2 800^0C

UV-Vis absorption spectra of chlorophyll-sensitised TiO_2 materials are presented in Fig. 4. It is well known that pure TiO_2 exhibits an absorption maximum in the UV region (near 360 nm) [18] and from Fig. 4 is obvious that all the chlorophyll-sensitised TiO_2 materials shows absorption bands in the visible region, between 400 and 800 nm, besides the characteristic UV absorption of TiO_2, indicating the extension of the absorption spectra of TiO_2 into visible region by sensitisation with chlorophyll. Also, visually, it was seen that all the samples, after sensitisation with chlorophyll, change their colours from white to green. Similarly, in the literature, a series of studies highlighted the fact that the dye-sensitised or metal doped materials presents absorption bands in the visible spectrum, attributed to the dyes, which indicates that the sensitised-material can absorb the radiation from the visible range [13,24,25].

The energy band gaps of the chlorophyll-sensitised TiO_2 materials are between 3.04 eV for the sample treated at 200 ^{0}C and decrease to 2.71 eV for the sample treated at 800 ^{0}C (Fig. 5(a)). Comparing the obtained values of the energy band gap with the one for un-sensitised materials [18] (with energy band gap between 3.47 eV and 2.87 eV), it was observed that the chlorophyll-sensitised material presents smaller values (Table 2). Ananth et al. [26] sensitised titanium dioxide powders with *Henna* dye and observed that in the UV-Vis absorption spectra appear an absorption broad band between 350 and 570 nm, and the energy gap decrease from 3.48 eV for pure TiO_2 to 3.01 eV for the sensitised sample.

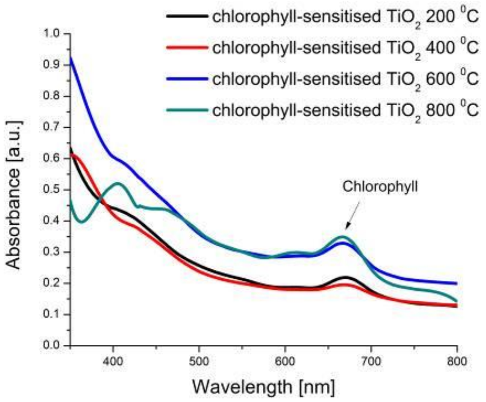

Fig. 4. UV-Vis absorption spectra of chlorophyll-sensitised TiO_2 particles

Urbach energy results showed that (Figure 5(b) and Table 2) all the chlorophyll-sensitised TiO_2 nanoparticles exhibits lower values (near 1 eV) than the un-sensitised TiO_2 materials (between 1 and 2.6 eV) [18]. In this case, we suppose that by sensitisation process, i.e. treatment with ultrasounds, a relaxation of crystalline matrix of TiO_2 acquired, which implies a decrease of the strain.

Chlorophyll fluorescence analysis allows non-invasive, near instantaneous measurement of key aspects of photosynthetic light capture and electron transport. In the case of chlorophyll (*a*+*b*) characterised by UV-Vis absorption spectroscopy it's still not known if the various forms are identical in peak position and remained obscure because is difficult separating of the chlorophyll types without destruction [27,28]. The noticeable degradation [29] of the intensity with time can be observed under excitation of the chlorophyll photoluminescence in plants. As a result, this phenomenon can affect the data obtained during the measurements and the researchers are faced with a problem of reliability [30].

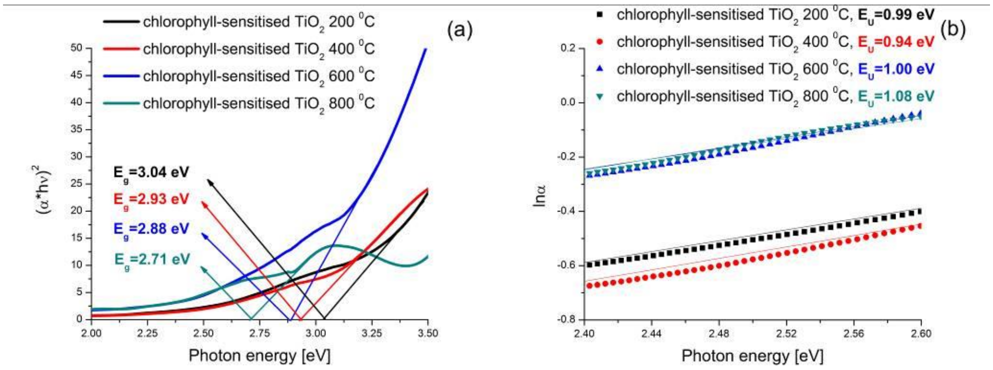

Fig. 5 (a) Determination of energy band gap; (b) Determination of Urbach energy

Table 2 . Energy band gap and Urbach energy values of chlorophyll-sensitised TiO_2 nanoparticles

Sample name	E_g [eV]	E_U [eV]
Chlorophyll-sensitised TiO_2 200 ^{0}C	3.04	0.99
Chlorophyll-sensitised TiO_2 400 ^{0}C	2.93	0.94
Chlorophyll-sensitised TiO_2 600 ^{0}C	2.88	1.00
Chlorophyll-sensitised TiO_2 800 ^{0}C	2.71	1.08

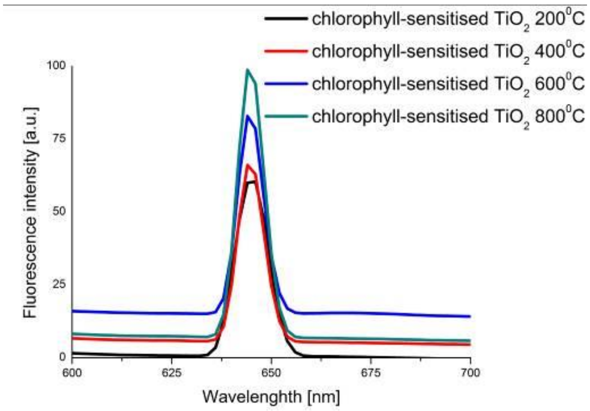

Fig. 6. PL spectra of chlorophyll

One band with peak position at 643 nm is observed at room temperature in the PL spectra which is characteristic to chlorophyll stabilised at TiO_2 nanoparticles surface (Fig. 6). Fluorescence emission of chlorophyll presents one dominant peak at 684 nm, which is attributed, principally, to the fluorescence emission by the PSII-core complex and, further, a shoulder between 710-740 nm corresponding to several fluorescence emission sources – particularly PSI-LHCI (Light harvesting complex II) and several minor PSII bands (PSII - Photosystem II) [30] and chlorophyll *a* absorbs at 430 nm and 662, whereas chlorophyll *b* absorbs at 453 nm and 642 nm [31], fact confirmed by our UV-Vis absorption spectra of chlorophyll-sensitised TiO_2 nanoparticles (Fig. 1). The fluorescence emission of different types of chlorophyll complements leading to a high photon absorbance in the visible range.

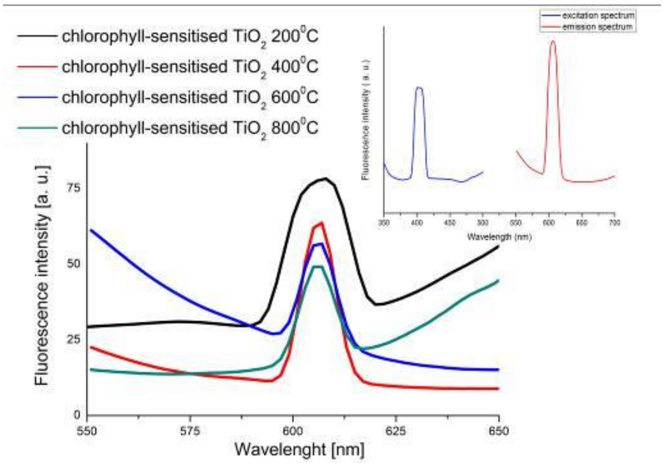

Fig. 7. PL spectra of chlorophyll-sensitised TiO_2 particles. Insert: Excitation and emission spectra of chlorophyll-sensitised TiO_2 particles

Fig. 7 shows the PL spectra recorded at room temperature of chlorophyll-sensitised TiO_2 nanoparticles, excited at 404 nm, emission originated from the luminescent centres (insert). Temperature was found to reduce the fluorescence intensity and shift emission band to a smaller wavelength compared with the chlorophyll photoluminescence spectra.

4. Conclusion

The chlorophyll-sensitised titanium dioxide nanoparticles were successfully synthesised by a facile ultrasounds assisted method. XRD analysis showed that chlorophyll do not change the structural matrix of TiO_2, although, a small decrease of strain has been observed comparing with un-sensitized materials. In this case we suppose that the treatment with ultrasounds can reduce the strain by relaxation of the matrix. FE-SEM images reveal the formation of nanoparticles with dimensions between 3 nm and 36 nm. UV-Vis and photoluminescence spectra confirmed that all chlorophyll-sensitised titanium dioxide nanoparticles absorb the radiation from the visible range, so these materials can be used in various applications such as optoelectronics devices or visible light-catalysts.

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