Synthesis of TiO$_2$-based photoelectrode and natural dye for dye sensitized solar cell (DSSC)

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Abstract. Synthesis and characterization of Mg and La doped TiO$_2$ photoelectrodes and natural dye have been studied. This study aimed to analyze the effect of Mg and La concentration on the characteristics of Mg and La doped TiO$_2$ and to investigate the characteristic of natural dye extracted from green spinach, red spinach, and mangosteen rind. Mg and La doped TiO$_2$ were synthesize by sol-gel method using titanium (IV) isopropoxide, magnesium acetate and lanthanum (III) acetate as precursors. The concentration of Mg and La were varied from 0 – 4% mol. Mg and La doped TiO$_2$ films were deposited on glass substrate by using doctor blade technique and annealed at 500°C for 1 h. The films were then characterized using X-Ray Diffractometer and UV-Vis spectrometer measurement to investigate its characteristics. The results showed that dopant concentration strongly affected the structural and optical properties of Mg and La doped TiO$_2$. The UV-Vis measurement of the natural dye extracted from green spinach, red spinach, and mangosteen rind showed a different absorption spectrum. However, FTIR measurement of these dyes showed relatively the similar spectrum. This shows that each dye has different optical properties, even though it has relatively the same functional group.

1. Introduction

The need for energy (electricity) continues to increase from year to year in line with the increasing population and technological developments. On the other hand, the use of conventional energy sources (fossil energy: petroleum, coal) which cannot be renewed continuously has caused the supply of these conventional energy sources to decrease. Therefore, it takes efforts to find and utilize alternative energy sources as a substitute for conventional energy sources. One of the most promising renewable energy sources is solar energy. This is because the supply is unlimited, environmentally friendly, cheap, and safe. To convert solar energy into electrical energy, solar cells are needed. However, the high cost of production and the low efficiency of solar cells are still issuing that need to be resolved. Therefore, researchers are still making various efforts to overcome these problems. One type of solar cell that is currently being studied intensively is dye-sensitized solar cell (DSSC). Since its introduction by O'Reagan and Gratzel in 1991 [1], DSSC has attracted the attention of researchers. This is because DSSC has several advantages, including low production costs, simple fabrication processes, environmentally friendly, and promising efficiency [2-5]. The DSSC solar cell consists of four components, namely a transparent conductive electrode and a counter conductive electrode, a semiconductor layer of nanoparticles (usually titanium dioxide), dye, and electrolyte solutions [6]. The performance of the DSSC is strongly influenced by the characteristics of the dye and the photoelectrode layer [7]. TiO$_2$ is a
semiconductor material that is applied as a photoelectrode layer on the DSSC because of its several properties, including having a fairly wide bandgap (3.2 - 3.8 eV) [3].

The application of TiO$_2$ in DSSC still has problems, namely the inability to transfer electrons due to premature recombination (return of electrons from the conduction band to the valence band) in cells, so that the resulting DSSC efficiency is low [8]. Another obstacle is the low efficiency of photon absorption by TiO$_2$-based photoelectrodes caused by the very wide energy gap of TiO$_2$, which is 3.2 -3.8 eV. One of the efforts to overcome these obstacles is by adding the element magnesium (Mg) and lanthanum (La) to TiO$_2$. Mg is an alkaline metal which can increase the light absorption activity in the material and reduce the occurrence of premature recombination in the material. Mg is also the best material that can replace Ti in large quantities and is able to increase the injection and transport of electrons in the material [9]. The use of natural dyes has attracted the attention of researchers, because the DSSC is designed based on the principles of photosynthesis [10]. To obtain high DSSC efficiency, photo sensitizers in the form of natural dyes must have the ability to absorb high photons, be environmentally friendly and inexpensive. The ability of natural dyes to absorb light is influenced by the anthocyanin properties contained in dyes [11, 12]. Anthocyanins are natural dyes that are responsible for the coloring of several fruits and plant leaves [13]. In the anthocyanin molecule, there are carbonyls and hydroxyl which can easily bind to the surface of TiO$_2$ nanoparticles [11]. Among the types of natural dyes that have been used are Oryza sativa glutinosa extract [14], lemon and morula leaves [15].

To overcome the problems described above, in this paper we report our study about developed natural dyes from plant and fruit extracts (green spinach, red spinach, mangosteen rind) as an active element of DSSC. In addition, the TiO$_2$-based photoelectrode layer will be synthesized and added with magnesium (Mg), and lanthanum (La). Thus, it is expected to increase light absorption activity by photoelectrodes and reduce the occurrence of premature recombination in DSSC.

2. Materials and method

2.1. Substrate preparation
The substrate used to deposit TiO$_2$-based photo electrodes was corning glass 7059 coated with transparent conducting oxide (TCO). The substrate is cut and washed using methanol and distilled water.

2.2. Synthesis of Mg and La doped TiO$_2$
Titanium (IV) Isopropoxide and Magnesium acetate were used as precursors to obtain Mg doped TiO$_2$. Titanium (IV) Isopropoxide dissolved in a mixture of aquades and isopropanol, then added Magnesium acetate tetrahydrate powder and HCl and stirred for 2 h. The resulting solution was precipitated to become a gel. Then, the gel was dried at 60°C until it becomes powder. This powder was then washed twice with ethanol and dried again at 60°C for 12 h. After the drying process the powder is sintered at a temperature of 500°C for 1 h. Mg doping concentrations varied from 0 - 4 mol%. The same process has been done to obtain La doped TiO$_2$. Titanium (IV) Isopropoxide and Lanthanum (III) Acetate hydrate (sigma aldric 98%) were used as precursors.

2.3. Preparation of Mg and La doped TiO$_2$ films
The Mg and La doped TiO$_2$ films were deposited on glass substrate. Before the deposition process, substrate was cleaned using methanol and aquades alternately, and dried. TiO$_2$ and Mg, La doped TiO$_2$ powder was dissolved with ethanol, acetic acid, and triton X-100 and stirred until it becomes a paste. The paste was then deposited on a glass substrate by doctor blade technique. Subsequently the Mg and La doped TiO$_2$ film was dried and annealed at 500°C for 1 hour.
2.4. Synthesis of natural dye
The dye solution was obtained from extracts of green spinach, red spinach and mangosteen rind. All the dye agents in this study were obtained from traditional markets in Banda Aceh. Green spinach, red spinach and mangosteen rind was dried and crushed with a mortar, then soaked with a solution of methanol, acetic acid, and water for 24 h. During soaking, the extract solution was stored in a dark place and stirred using a magnetic stirrer. The solution was then filtered using Whatman filter paper.

2.5. Characterization and measurement
The structural and crystallinity of Mg and La doped TiO\textsubscript{2} films were characterized by X-ray diffractometer (Shimadzu XRD-7000) using CuK\textalpha\ λ = 1.54060 Å. The given voltage was 40 kV, the current was 30 mA, and the detected angle (2θ) was set from 10 to 80°. The optical properties of Mg and La doped TiO\textsubscript{2} were analyzed from the ultraviolet-visible (UV-Vis) spectrometer measurement. From UV-Vis measurement obtained the wavelength (λ) and the λ\textsubscript{cutoff} value so that the energy gap can be determined using the equation $E = \frac{hc}{\lambda}$, where $E$ is the photon energy (eV), $h$ is the Planck constant (6.626 x 10\textsuperscript{-34} J.s), $c$ is the speed of light (3 x 10\textsuperscript{8} m/s), and $\lambda$ is the wavelength of the incident light (m). The optical properties of the dye solution were also analyzed based on the UV-Vis spectrum. Furthermore, the Fourier Transform Infrared (FTIR) test was carried out to find the functional groups of the natural dye solution.

![X-ray diffraction pattern of samples](image)

**Figure 1.** X-ray diffraction pattern of samples (a) pure TiO\textsubscript{2}, (b) 1% mol Mg doped TiO\textsubscript{2}, (c) 1% mol La doped TiO\textsubscript{2}.

3. Results and Discussion
Figure 1 (a) showed that the dominant phase that appears in pure TiO\textsubscript{2} samples is TiO\textsubscript{2}. In the Mg doped TiO\textsubscript{2} sample (Figure 1 (b)), there are three phases of the compound was found, namely TiO\textsubscript{2}, MgO, and MgTiO\textsubscript{3}. Meanwhile, the La doped TiO\textsubscript{2} sample (Figure 1 (c)) showed that there are two main phases, namely TiO\textsubscript{2} and La\textsubscript{2}O\textsubscript{3}. The most visible diffraction peaks are TiO\textsubscript{2}, this is influenced by the large concentration of TiO\textsubscript{2} in the sample. The highest TiO\textsubscript{2} peak is observed at an angle of 25.2580° both in pure TiO\textsubscript{2} samples, as well as in Mg doped TiO\textsubscript{2} and La doped TiO\textsubscript{2} samples. However, it can be seen that the peak intensity of TiO\textsubscript{2} at 25.3380° is different for each sample. A significant difference is seen in the La doped TiO\textsubscript{2} sample, where the main intensity of the TiO\textsubscript{2} peak is relatively low. This indicates
a change in the crystal structure or the degree of crystallization of these samples. The presence of the La atom has caused disturbances in the TiO₂ crystal structure.

**Table 1.** The energy gap of pure TiO₂ and Mg doped TiO₂

| Samples                  | λ_{cutoff} (x10⁻⁹ m) | Energy gap (eV) |
|--------------------------|-----------------------|-----------------|
| Pure TiO₂                | 352.0                 | 3.52            |
| 0.5% Mg doped TiO₂       | 365.0                 | 3.40            |
| 1% Mg doped TiO₂         | 370.5                 | 3.34            |
| 2% Mg doped TiO₂         | 366.5                 | 3.38            |
| 3% Mg doped TiO₂         | 359.0                 | 3.45            |
| 4% Mg doped TiO₂         | 349.5                 | 3.55            |

**Table 2.** The energy gap of pure TiO₂ and La doped TiO₂

| Samples                  | λ_{cutoff} (x10⁻⁹ m) | Energy gap (eV) |
|--------------------------|-----------------------|-----------------|
| Pure TiO₂                | 352.0                 | 3.52            |
| 0.5% La doped TiO₂       | 369.0                 | 3.36            |
| 1% La doped TiO₂         | 374.0                 | 3.31            |
| 2% La doped TiO₂         | 360.5                 | 3.44            |
| 3% La doped TiO₂         | 347.0                 | 3.57            |
| 4% La doped TiO₂         | 349.5                 | 3.55            |

![Figure 2. The effect of La concentration on the optical properties of La doped TiO₂.](image)
The energy gap value of Mg doped TiO\textsubscript{2} is shown in Table 1. In the table, it can be seen that the greater the Mg doping concentration, the smaller the energy gap value. However, this change in value is not linear. At 2 - 4\% Mg doping concentrations, the energy gap widened again. The same trend also happened to the La doped TiO\textsubscript{2} sample as shown in Table 2. The difference was seen in the La doped TiO\textsubscript{2} sample with a concentration of 4\%, where the energy gap value drops again. The energy gap value of a material is influenced by several factors, including crystal structure, atomic concentration of the constituents of the material, and the surface of the material. In the above case, the change in the energy gap value is caused by differences in atomic concentrations due to differences in doping concentrations and changes in the crystal structure as seen in the XRD pattern in Figure 1.

The Uv-Vis spectrum of La doped TiO\textsubscript{2} is presented in Figure 2. The picture showed a very significant change in the transmittance value due to the difference in the concentration of La doping. The highest transmittance value was obtained in samples with a doping concentration of 0.5\% La, while the lowest transmittance value was obtained in samples with a doping concentration of 3\% La. It is clear that the doping concentration greatly affects the optical transmittance value of the La doped TiO\textsubscript{2} films, but the transmission value does not have a linear relationship with the doping concentration. The variation in La doping concentration also causes changes in the optical response of La doped TiO\textsubscript{2} samples. Samples with a La doping concentration of 0.5\% showed an optical response in the wavelength range 320 - 375 nm. While samples with a La doping concentration of 3\% showed an optical response in the wavelength range of 300 - 350 nm.

![Figure 3. UV-Vis spectrum of natural dye.](image)

Figure 3 showed the absorption spectrum of Uv-Vis from several sensitzers derived from the extract of natural dyes used in this study. From Figure 3 it can be observed that the maximum Uv-Vis absorption peak of green spinach, red spinach, red spinach + mangosteen rind, and mangosteen rind occurs at wavelengths of 655.5 nm, 663.5, 667, and 668.5 nm, respectively.
Figure 4. FTIR spectrum of (a) green spinach (b) red spinach, (c) mangosteen rind, and (d) red spinach+mangosteen rind.

FTIR measurement showed that there are several absorption peaks in the spectrum range of wave numbers from 4000 to 400 cm\(^{-1}\) as shown in Figure 4. The absorption peak between 3500 - 3300 cm\(^{-1}\) indicates an intermolecular H bond. The absorption peak between 1600 - 1700 cm\(^{-1}\) indicates a stretching of C=O vibrations. The absorption peak between 1000-1060 cm\(^{-1}\) is the C–O–C vibrational stretching.

Based on the results of FTIR measurement, it is proven that the natural dye extract contains anthocyanins which are the main compositions of leaf and fruit extracts. The carbonyl and hydroxyl gums contained in the dye extract can bind to the TiO\(_2\) based photoelectrode.

4. Conclusions
In this research, we have been successfully synthesized pure TiO\(_2\), Mg and La doped TiO\(_2\) photoelectrode. We found that doping concentration strongly effected the characteristic both of Mg doped TiO\(_2\) and La doped TiO\(_2\) photoelectrodes. The diffraction peak intensity of La doped TiO\(_2\) is relatively lower than that of pure and Mg doped TiO\(_2\) diffraction peaks. This showed that La doping has a very significant effect on changes in the crystal structure of La doped TiO\(_2\). The doping concentration also greatly affects the optical properties of Mg and La doped TiO\(_2\) films. This research has also successfully synthesized and analyzed natural dyes derived from leaf and fruit peels extracts. There is a very significant difference in the UV-Vis spectrum of each of these dyes. Green spinach extract dye showed the highest absorption peak compared to other dyes. FTIR measurement of those natural dye showed the spectra with a relatively the same pattern. This shows that the dye has relatively the same content (functional group).

5. References
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