Effect of hexamethylenetetramine surfactant in morphology and optical properties of TiO$_2$ nanoparticle for dye-sensitized solar cells

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Abstract. The past few decades Dye-Sensitized Solar Cells (DSSC) based on TiO$_2$ nanoparticle have attracted much attention from researchers because of their promising physico-chemical properties and high photoconversion efficiency. In this research, TiO$_2$ nanoparticles mediated with hexamethylenetetramine surfactant were successfully synthesized by the hydrolysis method. The influence of hexamethylenetetramine surfactant precursor concentration on DSSC photovoltaic performance was investigated. The prepared samples are characterized by field emission scanning electron microscopy, X-ray diffraction, and UV–vis absorption spectroscopy. SEM analysis results show that the HMT surfactant has a big influence on the morphology, particle size, and crystal phase of TiO$_2$ particles. The surface morphology exhibited the nanorice grain particles in all samples. By spectrophotometry, it was shown that the films had a bandgap of about 2.9 eV. The film promoted by HMT 0.3 M from DSSC showed a power conversion efficiency of 1.7%.

1. Introduction

The demand for world energy needs is predicted to continue to increase by 70% between 2000-2030 along with technological advances and human populations. The availability of energy in the world today is one of the biggest challenges for meeting future energy needs. The energy problem will be the main challenge in the next 50 years [1,2]. The most widely used energy source so far is fossil energy that non-renewable. The International Energy Agency (IEA) states that energy demand is projected to increase by 55% until 2030[3]. Fossil fuels accounted for the largest energy consumption by 80% of total world energy consumption. It is estimated that fossil fuel reserves throughout the world can only last 40 years for oil, 60 years for natural gas, and 200 years for coal[4,5]. With the state of the depletion of fossil energy sources, in today’s world has occurred is a shift from the use of non-renewable energy sources to renewable energy sources[6].

In recent years the development of renewable energy sources is needed because of the reduced availability of fossil fuels globally. From several alternative energy sources, solar energy becomes one of the very potential and promising energy sources to be developed[7]. If solar energy is converted into electrical energy, then that energy can function as alternative energy that can replace fossil fuels. Current solar cell technology has experienced very significant development, marked by the emergence of a new generation of solar cells ranging from conventional silicon-based solar cells, then thin-film...
solar cells to Dye-Sensitized Solar Cell (DSSC) cells [8–11]. Unlike the previous generation of solar cells, in DSSC solar energy is converted into electrical energy through photoelectrochemical cells.

DSSC development is currently more focused on photoanode semiconductors which have relatively wide bandgap energy such as TiO$_2$[12–15]. TiO$_2$ nanoparticle is more suitable for the dye-sensitized solar cells (DSSCs) due to their good chemical stabilities, good optical properties, inert, non-toxic, and better dye adsorption abilities[16–20]. Xu et al. [21] reported that the existence of TiO$_2$ nanosheets in the hierarchical submicroflowers from anatase TiO$_2$, which enhanced the electron transport process in DSSC. So et al. [22] reported that TiO$_2$ nanotubes inducing nanotwinned grain structures can increase electron transport and DSSC efficiency. Recently, Lepket et al. [23] have developed different shapes of nanostructured TiO$_2$ such as a star, flower, rod, and scree-shaped TiO$_2$ particles utilizing the four types of surfactants liketetramethylelammonium hydroxide (TMAH), tetraethylammonium hydroxide (TEAH), tetrpropylammomium hydroxide (TPAH), and tetrabutylammonium hydroxide (TBAH). A similar study has been conducted by Shah et al. [24] using surfactant ammonium hexafluorotitanate and hexamethylenetetramine. It was found that surfactants with different alkyl chain lengths had a large influence on the morphology, particle size, and crystalline phase of TiO$_2$ particles.

In this work, we have successfully synthesized TiO$_2$ powders with various morphologies using the hydrolysis process by the addition of hexamethylenetetramine (HMT) as surfactants. The use of these HMT surfactants purposes to reduce crystal size. The objective of this work is to investigate the effect of hexamethylenetetramine content on the properties, morphology and performance parameters of the DSSC. The new idea in this work is the utilization of TiO$_2$-coated HMT films prepared via doctor blade deposition assisted with immersion techniques as a photoanode for DSSC.

2. Experimental Methods

2.1. Preparation of FTO substrate

Substrate preparation begins by cutting the substrate with a size of 1×2.5 cm, then rinsed with distilled water, each substrate is arranged complete with clean glass bottles and immersed in sequential water, acetone (CH$_3$)$_2$CO70%, ethanol (C$_2$H$_5$OH)70%, and lastly in the Deionized water using sonication process for 15 minutes. After that, it is transferred in a petri dish and dried with a hairdryer.

2.2. Synthesis of TiO$_2$ paste with the addition of hexamethylenetetramine (HMT) surfactant

The synthesis of TiO$_2$-HMT paste was carried out by a simple hydrolysis method. Where the TiO$_2$ Degussa P25 powder was weighed as much as 0.5 gram and dissolved with 5 mL ammonium fluoride solution in a glass bottle. HMT solution is made with a concentration variation of 1 M; 2 M; 3 M are then added to the glass bottle as much as 1 mL. The mixture is then stirred for 20 hours at a speed of 1000 rpm and a temperature of 80°C.

2.3. Fabrication of dye-sensitized solar cell

Dye-Sensitized Solar Cell assembly is done with a working electrode (FTO glass that has been coated with TiO$_2$-HMT paste soaked in dye N719 for 15 hours). Then it is stacked with a comparison electrode (FTO glass that has been coated with platinum) and is clamped on both sides using paper clips to join the two electrodes. The final stage dropped 2-3 drops of triiodide electrolyte solution from both ends of the offset prototype Dye-Sensitized Solar Cell.

3. Results and Discussion

3.1. Characterization using x-ray diffraction (XRD)

Characterization of X-Ray Diffraction (XRD) was carried out to determine the crystal structure of TiO$_2$ and TiO$_2$-HMT composite.
Figure 1. XRD spectra of TiO$_2$ nanoparticle prepared using HMT surfactant

Figure 1 shows that the TiO$_2$-HMT composite has a high degree of crystallinity. TiO$_2$ diffractogram shows the success of anatase TiO$_2$ synthesis by a simple hydrolysis method. By comparing with the JCPDS data, the TiO$_2$ nanoparticle XRD spectrum peaks can be labeled as (101), (004), (200), (105) and (211) for peaks at 2$\theta$ of 25.7, 38.4, 48.1, 54.3 and 55.3, respectively[24,25]. Electron diffraction patterns indicated that the anatase TiO$_2$ nanoparticle is characterized by a dominant (101) lattice plane, in the surface energy.

TiO$_2$ anatase has an indirect bandgap type. The indirect bandgap in anatase makes the lifetime of the charge carrier ($e/h^+$) longer[26,27]. In addition, anatase has the smallest effective mass ($e/h^+$) compared to rutile and brookite. Although anatase TiO$_2$ has slightly greater bandgap energy than rutile, anatase has a larger surface area than rutile[28]. This makes the anatase TiO$_2$ adsorption capacity of the dye molecules larger so that it can increase DSSC performance more optimally[29–31]. Thus, we expect that enhanced performance in applications, such as solar cell can be obtained from this TiO$_2$ anatase.

3.2. Characterization using field emission scanning electron microscope (FESEM)

TiO$_2$ thin layer was made from TiO$_2$ P25 Degussa which has undergone several treatments, including the addition of hexamethylenetetraminesurfactants and the heating process on the hot plate. The existence of the heating process aims to increase the adhesion of thin layers on FTO glass substrates. Results of TiO$_2$-HMT thin layer FESEM at a calcination temperature of 400°C are shown in Figure 2.
Figure 2. FE-SEM of TiO$_2$ nanoparticle treated with various concentrations HMT (A) 1M; (B) 2M; (C) 3M)

Figure 2 (A-C) showed that the FE-SEM images of TiO$_2$ treated at various concentrations HMT (1M, 2M, and 3M) and reveals to different morphological characteristics. In the HMT 2M and HMT 3M samples, the nanorice particles were aggregated and clumped together. These results are consistent with what was done by Shah et al. [24] that the addition of HMT surfactants can form nanorice particles. With further increase concentration of hexamethylenetetramine (HMT) surfactant, the rice-shaped TiO$_2$ particles stacked together and lead to the formation of TiO$_2$ microstructures (Figure. 2C). The presence of a surfactant may assist to stack a large number of particles to form bulk microstructured morphologies[32]. The surfactant plays an important role in controlling the growth of the TiO$_2$ crystals with a specific morphology [33].

3.3. Ultra Violet-Visible Diffuse Reflectance Spectrophotometry (UV-Vis DRS)
Figure 2 illustrates the diffused reflection spectra (DRS) for all samples. Figure 3 shows the diffuse reflectance spectra of pure TiO$_2$ and TiO$_2$ treated at various concentrations of HMT (1M, 2M, and 3M) photoanodes. Through the% R-value, it can be seen that the concentration of HMT used affects the thickness of the TiO$_2$-HMT film. The thicker the TiO$_2$-HMT layer produced, the smaller the reflection value, meaning that more photons are absorbed and less is reflected.
Figure 3. UV-Vis diffuse reflectance spectra of different TiO$_2$ morphological photoanodes.

Figure 4. The relationship between ($a$hv) and energy for TiO$_2$-HMT composite film and TiO$_2$ film.

Figure 4 shows that pure TiO$_2$ prepared by simple hydrolysis method has a bandgap energy of 3.2 eV. These results are consistent with research conducted by Nurdin and Maulidiyah [34]. The addition of HMT surfactant has also been shown to significantly reduce the TiO$_2$ band gap energy from 3.2 eV to 2.9 eV. This reduction will reduce the energy needed to activate the TiO$_2$ photocatalyst so that electrons will be more easily excited from the valence band to the conduction band. The more electrons in the conduction band, the greater the chance of charge carriers (e$^-$ and h$^+$) to reach the photocatalyst surface. This will improve TiO$_2$ performance which is potential for solar cell application.
3.4. DSSC Performance

Figure 5 shows a typical J-V curve for the DSSC device that was fabricated using different concentrations of HMT such as 1M, 2M, 3M and then pure TiO$_2$ of which their images are shown in Figure 5. With some testing parameters as follows; short circuit current $I_{sc}$ (short circuit), open-circuit voltage $V_{oc}$ (open circuit voltage), $V_{max}$, and $I_{max}$[35,36].

![Figure 5](image_url)

**Figure 5.** J–V curves of the devices utilizing TiO$_2$-HMT composite coated N719 dye with various HMT concentrations

Figure 5 shows the analysis of J-V testing on DSSC solar cells using pure TiO$_2$ and TiO$_2$ with different HMT addition treatments, showing that the addition of HMT surfactants can increase the efficiency of solar cells. The highest efficiency solar cell is the TiO$_2$-HMT 3M solar cell of 1.7%. So the efficiency value of the TiO$_2$-HMT photoanode is still better than pure TiO$_2$, it is shown in table 1.

| Photoanode        | $V_{oc}$ (Volt) | $I_{sc}$ (Am$^2$) | $V_{max}$ | $I_{max}$ | FF | (%) |
|-------------------|----------------|-------------------|-----------|-----------|----|-----|
| Pure TiO$_2$      | 0.48           | 2.5               | 0.12      | 2.2       | 0.22 | 0.26 |
| TiO$_2$-HMT (1 M) | 0.53           | 3.4               | 0.29      | 3.2       | 0.5  | 0.9  |
| TiO$_2$-HMT (2 M) | 0.57           | 4.0               | 0.37      | 3.7       | 0.6  | 1.3  |
| TiO$_2$-HMT (3 M) | 0.61           | 4.5               | 0.40      | 4.3       | 0.62 | 1.7  |

Based on Table 1 it can be seen that DSSC with HMT concentration of 0.3 M is the cell with the highest efficiency, which is equal to 1.7%. It can be seen in table 1 that the value of short circuit current ($I_{sc}$) and open-circuit voltage ($V_{oc}$) of DSSC solar cells has increased with increasing HMT surfactant concentration. The increase in current and voltage is due to the smaller crystal size with an increasing percentage of HMT on TiO$_2$[37,38]. The smaller the crystal size, the larger the surface area of particles per volume[39,40]. Thus, the pores between particles will be more and more and more dye N719 molecules can be absorbed. This causes the value of the resulting efficiency can increase.

4. Conclusion

In this research, TiO$_2$ nanoparticles mediated with hexamethylenetetramine surfactants were successfully synthesized by the hydrolysis method. The addition of HMT surfactant on TiO$_2$ was able
to reduce the gap energy and crystal size of TiO$_2$, the smallest was obtained in the addition of 3M HMT which was 2.9 eV. The surface morphology exhibited the nanorice grain particles in all samples. From the efficiency calculation formula, the highest efficiency value is obtained from TiO$_2$-HMT 3M solar cells at 1.7%.

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