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Synthesis and Bioactivity of TiO$_2$/PPy Micelle with *Pachyrhizus erosus* Extract as UV Absorbent Material

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**Abstract.** Indonesia is a tropical country with high intensity and duration of sunlight throughout the year. The condition causes the average UV index in Indonesia is at the level of $9$ up to $11^+$ so that the power of the sun is extreme invade the human body. This condition makes Indonesia one of the countries with the highest UV index in the world. UV rays exposure can be harmful to humans and become one of the most significant factors causing the existing of skin cancer. Researchers have studied many efforts. Unfortunately, the use of oxidic nanoparticles combined with natural products is not yet explored comprehensively. TiO$_2$ nanoparticles are materials that have excellent absorbability of UV light. In this study the TiO$_2$ nanoparticles as core and combined with Polypyrrole polymer as shell form a micelle structure. The modification of TiO$_2$ nanoparticles with Polypyrrole aims to enhance its UV protection, biocompatibility, and nontoxicity on the body. The addition of *Pachyrhizus erosus* extract as an enhancer of UV absorbent agent because it has the phenolic to skin softening properties. The synthesis of micelle TiO$_2$/PPy was performed using in situ method, followed by stirring and sonication process to mix the *Pachyrhizus erosus* extract with micelle. The XRD analysis of Micelle synthesis shows that the addition of polypyrrole polymer does not affect the crystallinity of TiO$_2$ nanoparticles. The results of testing the antibacterial properties of sunblock samples showed a clear zone with glycerine solvent.

**Keyword:** Micelle TiO$_2$/PPy, *Pachyrhizus erosus* extract, UV light, sunblock

1. **Introduction**

Cancer is one type of disease which arises from the abnormal growth of body tissue cells. Cancer has become the number one deadliest disease in the world to date. Skin cancer is one of a kind of cancer, the type of skin cancer itself also several of which one of the most deadly is the kind of melanoma. This type of melanoma skin cancer is the most dangerous, which accounts for about 75 percent of all skin cancer-related deaths. Melanoma cancer influenced by multiple genetic and epigenetic factors, one of the most significant factors causing the growth of skin cancer is UV exposure [1]. Indonesia is a tropical country with sunlight throughout the year. This condition causes the average UV index in Indonesia to
be at the level of 9 to 11+, or the power of the sun is extreme. Therefore, it makes Indonesia one of the highest UV indexes in the world. To overcome the obstacle, people use natural products as a protective ingredient as well as to beautify the skin. Unfortunately, the natural products may degrade under Sun irradiation.

TiO$_2$ has been widely developed in both industry and medicine. The TiO$_2$ nanoparticles have shown an excellent performance in solar cells [2] and cancer therapy [3]. TiO$_2$ also has a sensitivity to UV light, as evidenced by the study that TiO$_2$ thin films indicate a sharp transmittance change in the wavelength range of 300 to 400 nm which is the area of ultraviolet wavelength. The change in the value of this transmittance indicates a considerable absorption at that wavelength.

The encapsulating of nano TiO$_2$ with biocompatible polymer PPy aims to obtain the right choice of sunblock ingredients with an excellent safety for the body. The reason for using PPy is that the PPy polymer itself has proven effective as a safe drug carrier when applied in the human body. So when used for sunblock is not going to irritate, even if absorbed into the body will not be harmful to the body. With the addition of *Pachyrhizus erosus* extract may expect to increase the efficacy of sunblock to maintain the beauty of the skin. TiO$_2$ nanoparticles wrapped in a PPy polymer with the final step method is by blending *Pachyrhizus erosus* extract on micelle. The resulting sample is a gel that can be identified by the UV absorption, antibacterial, and biocompatibility before applied directly to the body.

2. Materials and Methods

2.1. Synthesis of the TiO$_2$/PPy micelle

The fabrication of micelle TiO$_2$/PPy was performed by using in situ method as previously reported [4,5]. A 1 gram of TiO$_2$ nanoparticles was suspended in HCl (1.5 M, 50 mL) and followed by ultrasonic radiation for 30 min. The subsequent step was the injection of polypyrrole polymer (PPy) with the ratio of TiO$_2$:PPy is 100:1 under constant stirring. We also prepared a solution of FeCl$_3$ (0.1 gram) in HCl (1.5 M, one mL) which was then gently dropped into the previous suspension. The mixed solution was then stirred for 4 hours at 0 °C and followed by centrifugation. The obtained sediment was washed using 1.5 M HCl and DI water until it reached a neutral pH. The washed precipitated materials were then dried at 100 °C to remove the residual solvent.

2.2. Preparation of *Pachyrhizus erosus* Extract

Preparation of *Pachyrhizus erosus* extract began with the heating of *Pachyrhizus erosus* fruit from 1 kg to reach a dry weight of 1.5 ounces. The dry *Pachyrhizus erosus* was subsequently blended and transformed into flour. A total of 400 grams of *Pachyrhizus erosus* flour was macerated using 800 mL of 96% ethanol. The maceration process took for 1-2 days with interfered by shaking every 6 hours. The macerated materials were then put in a rotary evaporator to separate the extract using the ethanol solvent. The evaporator extract was placed in an open container to remove the remaining solvent.

2.3. Processing of TiO$_2$/PPy with extract *Pachyrhizus erosus* sunblock

The micelle TiO$_2$/PPy powder was dissolved using *Pachyrhizus erosus* extract with a different solvent, PEG-6000, and glycerin. The final product was distilled for 30 min at 50 °C followed by sonication for 30 min.

2.4. Characterization

The samples were then characterized to determine the structure and biophysical properties of the material. The samples’ information associated with crystal phase, morphology and grain size were characterized by XRD, FTIR, and SEM. The sample bioactivity included the test of irritation was measured using the mice as the animal test. The anti-bacterial properties tested using the diffusion method on *E.coli*. We also measure the sample absorption using UV-Vis.
3. Results and Discussion

3.1. FTIR Spectra of the TiO$_2$/Ppy micelle

The results of the characterization of the IR spectra of the micelle TiO$_2$/Ppy are shown in Figure 1. It is obtained that the FTIR peak of TiO$_2$ nanoparticles exists in the range of 450 to 600 cm$^{-1}$ which indicate the presence of a Ti-O bond vibration in the TiO$_2$ lattice [6–8]. The peaks between 3100 to 3600 cm$^{-1}$ show vibrations of the hydroxyl (O-H) group [6,7,9] of the remaining solvent water during the synthesis.

![Figure 1. IR spectra of the TiO$_2$/Ppy micelle](image1)

![Figure 2. Phase analyses using HighScorePlus of TiO$_2$ nanoparticles utilizing the model of 01-078-2486](image2)
3.2. Structure of TiO$_2$/Ppy micelle

The analysis of TiO$_2$ XRD patterns was performed using Rietica and high score plus analysis (HSP). Figure 2 shows the results of HSP analysis with 100% purity of nanoparticles TiO$_2$. The matching results of the COD model number 2310710 of the TiO$_2$ nanoparticles with Rietica software show a matched peak. The good of fitness fitting value ($\chi^2$) reached 1.175 which was obtained from Rietica analysis (Figure 3).

![Figure 3. Crystal structure analysis of TiO$_2$ Nanoparticles.](image)

The X-ray diffraction pattern of the TiO$_2$/PPy micelle nanoparticles compared to the TiO$_2$ nanoparticles are shown in Figure 4. From the fitting, we obtain the FWHM values, which were then used to calculate the grain size with the use of the Scherrer equation (Equation 1) [10].

$$D = \frac{k \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $k = \text{Scherrer constant}$, $\lambda$ = wavelength radiation Cu- Ka (1.5406 Å), $\beta$ = FWHM (radians), and $\theta$ = Bragg’s position (radian).

![Figure 4. Histogram of TiO$_2$ and micelle TiO$_2$/PPy](image)

Figure 4 shows the X-ray diffraction patterns of TiO$_2$ nanoparticles with TiO$_2$/PPy micelle. The diffraction peaks have corresponded to the model of the crystal peak of nanoparticles of TiO$_2$ anatase. The PPy-wrapped nanoparticles exhibit a diffraction pattern similar to those of TiO$_2$ nanoparticles, indicating that the addition of the PPy polymer as a wrap does not decrease the crystallinity of the TiO$_2$ nanoparticles. Analysis of the main peak of X-ray diffraction of nanoparticles TiO$_2$ using Equation 1 yields a grain size of 15.78 nm. This value is associated with the FWHM of 0.57608 under Lorentzian fittings. Using the same way, we obtain that the micelle TiO$_2$/PPy shows a grain size of 17.38 nm. The
micelle TiO$_2$/PPy grain size shows a greater value than the grain size of TiO$_2$ nanoparticles. This is because of the effect of coating the particles with polymer PPy.

3.3. Morphology Analysis of micelle TiO$_2$/PPy using Scanning Electron Microscope (SEM)

The nanomorphology of TiO$_2$ which was obtained from the SEM analysis is shown in Figure 5. From the morphological results of the SEM of the TiO$_2$ and TiO$_2$/PPy nanoparticles, it is seen that after the particles enclosed by the polymer PPy still have a shape like nanoparticles TiO$_2$. These results support the results of XRD analysis showing that the addition of PPy does not alter crystallinity, which is seen from nearly the same morphology. The elemental composition of the TiO$_2$ nanoparticles was performed using EDAX is shown in Figure 6.

![Figure 5. SEM Morphology a) TiO$_2$ nanoparticles and b) TiO$_2$/PPy micelle (100.000 x).](image)

![Figure 6. SEM-EDAX result of TiO$_2$ nanoparticles.](image)

We observed that comparing the ratio of atomic percentage content of oxygen in K-band and titanium in K-band falls as 64.32 to 35.68. This ratio is close to 1 to 2 for respectively for Ti to O. We could conclude that the obtained synthesized material is TiO$_2$ nanoparticles. The size of nanoparticles has been confirmed from X-RD pattern analysis. Figure 5, as well as Figure 6, show that the TiO$_2$ shows agglomeration which is also reported for several oxidic nanoparticles [11,12].

3.4. Absorbance performance

The UV-Vis spectra of *Pachyrhizus erosus* extract and various TiO$_2$ of micelle TiO$_2$/ Ppy is shown in Figure 6. We found that *Pachyrhizus erosus* extract has a good uptake in the starting range of UV rays of 350-400 nm and have a high absorbance on 400-900 nm. The highest absorbance shows by the lower transmittance [11]. UV-Vis showed the same results from micelle TiO$_2$/ PPy and sunblock for the sample with 0.05-gram TiO$_2$/PPy content. Further analysis related to the variation of mass of TiO$_2$/PPy micelle of 0.05, 0.1, 0.15, 0.20, and 0.25 grams it was revealed that the most appropriate sunblock composition (which has a good uptake) shows by the sample with 0.05 grams micelle.
3.5. *Anti-Bacterial Activity of TiO$_2$/PPy micelle with Pachyrhizus erosus Extract*

The result of the antibacterial activity of TiO$_2$/PPy micelle with *Pachyrhizus erosus* extract is shown in Table 1.

![UV-Vis spectra of TiO$_2$/PPy micelle with Pachyrhizus erosus extract.](image)

**Figure 7.** UV-Vis spectra of TiO$_2$/PPy micelle with *Pachyrhizus erosus* extract.

| No   | Sample                        | Active Zone Diameter (cm) |
|------|-------------------------------|---------------------------|
| 1.   | TiO$_2$-PEG                   | -                         |
| 2.   | TiO$_2$-Glycerin              | 0.9                       |
| 3.   | TiO$_2$/Ppy-PEG               | -                         |
| 4.   | TiO$_2$/Ppy-Glycerin          | 2.10                      |
| 5.   | Pachyrhizus extract           | -                         |
| 6.   | TiO$_2$/Ppy-PEG-P.extract     | 0.225                     |
| 7.   | TiO$_2$/Ppy- P.extract -Glycerin | 0.295                 |
| 8.   | TiO$_2$/Ppy- P.extract-PEG-Glycerin | -                 |

The observation of *E. Coli* bacterial inhibition zone was performed on the different sample. The width of the inhibitory region indicates the antibacterial power of the material. The wider area exhibits, the more significant of the antibacterial strength. Antibacterial of various samples showed that the inhibitory zone diameter of the TiO$_2$/Ppy-Glycerin sample shows the highest drag zone. The hygroscopic property of glycerin may provide better absorption of water molecules allow a more effective interaction of the sample. The hygroscopic nature of glycerin causes the sample to diffuse easily into the medium part of Nutrient Agar. The micelle TiO$_2$/PEG particle diffuses to the maximum in the medium to have more significant contact with the bacterial wall. Glycerin has been widely used in the industry of producing soap, detergent, and cosmetics as a suitable and safe solvent.

3.6. *Irritation test of TiO$_2$/PPy micelle with Pachyrhizus erosus extract*

We performed a skin irritation test on mice. We used six young mice which one of them as a control. We found that the skin of mice which were treated of all samples indicate no difference in skin color with the control sample. These results suggest that the sample is not irritating to the skin of test animals. A good performance as antibacterial as well as the nonirritating materials gives the TiO$_2$/Ppy micelle a great potential to develop and further investigation.
4. Conclusion
We conclude that the TiO$_2$/PPy micelle samples with *Pachyrhizus erosus* extract have been successfully synthesized. The samples show excellent potential for sunblock prevention of skin cancer that works by optimizing UV light absorption. It is shown that TiO$_2$/PPy micelle samples with *Pachyrhizus erosus* extract exhibit anti-bacterial properties and nonirritating.

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