Surface Compositional, Structural and Optical Properties of Nanohybrid TiO$_2$/ZnO Coated Silicone Surface

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Abstract. This paper reports on preparation and characterizations of nanohybrid TiO$_2$/ZnO using sol-gel spin-coating techniques. The study involved of modification band-gap energy of Titanium dioxide (TiO$_2$) at different precursor molecular concentration of Zinc oxide (ZnO). The Field Emission Scanning Electron Microscope (FESEM) for morphological characterization showed the existence of TiO$_2$ and ZnO particles at 20 nm scale of magnification. The compositional of both particles were then confirmed using Energy Disperse Analyzer X-Ray (EDAX) analysis which indicates the elements of Ti, O and Zn exhibited EDAX spectras at about 0.5 and 1.0 keV while silicone (Si) at 1.75 keV. The X-Ray diffraction (XRD) characterized the structural properties of anatase and rutile for TiO$_2$, and zincite for ZnO, then crystallite size for both elements. At optimum molar concentration ratio of nanohybrid TiO$_2$/ZnO is 1:4 (0.20M), the crystallite size, $d$, is 23.71 nm with peak of anatase found at diffraction angle of 48.05$^\circ$ and 62.50$^\circ$ while at 33.25$^\circ$ and 55.06$^\circ$ is rutile phase, respectively. We have found the distribution of nanohybrid TiO$_2$/ZnO particles dispersed homogeneously since the particles were not bonded together with increasing ZnO molar concentration. From Ultra-Violet/Visible-near-infrared spectroscopy (UV-Vis-NiR), we have found the optical band-gap energy of nanohybrid TiO$_2$/ZnO was increased at 3.38 eV, while the transmittance percentage is 88.67%. This studied was successfully improved the optical band-gap energy of TiO$_2$ and the results suggests for improvement of optical band-gap energy TiO$_2$.

1. Introduction.

TiO$_2$ has shown good optical properties with optical band-gap energy of anatase about 3.1 eV until 3.2 eV while ZnO has optical band-gap energy about 3.37 eV [1, 2]. These two material are suitable to hybrid together not only due to their similar band-gap energy, but they also has a similarities in their properties such as high chemical and thermal stability, high refractive indices and share a high transmittance in the visible region although they transmittance relatively different in UV region [3]. Moreover, both materials have good photocatalytic efficiency. TiO$_2$ has mostly been used for photocatalyst, photoelectrodes, gas sensors and electrochromic display devices [4] while the attractive application of ZnO used for forming various forms of nanostructures, such as nanorods, nanowires, and nanobelts.

The hybrid of TiO$_2$/ZnO has been done via many methods such as hydrothermal method [5], magnetron sputtering method [6], and in-situ mixing [7]. In this study, sol-gel spin coating method has been used because this method allow a higher surface activity, low-temperature synthesis and easily control reaction condition besides of safe and low cost method [8]. The purpose in this study was to
improve the optical band-gap and structural quality of TiO$_2$ with ZnO material grown on Si substrate and further increase the application of this nanohybrid material.

2. Methodology.

![Figure 1. Flow chart process diagram of methodology.](image)

2.1. Material.
The following chemicals were obtained from commercial sources and used as received: Titanium Tetra Isobutoxide (TTIB; grade 99.99%, metal basis from Aldrich), Ethanol (EtOH; 99.99% purity, R&M Chemicals), Glacial Acetic Acid (CH$_3$COOH; J.T. Baker Analyzed; grade 48%), Triton-X 100 (R&M; C$_{34}$H$_{62}$O$_{11}$), Zinc Acetate Dihydrate (Zn(CH$_3$COO)$_2$.2H$_2$O; 99.5% purity; Merck), Isopropanol (CH$_3$CHOHCH$_3$; 99.99% purity, Merck), Diatehanolamine (NH(CH$_2$CH$_2$OH)$_2$; 99.5% purity; Merck), Distilled Water (DI; H$_2$O), Acetone (C$_3$H$_6$O; ChemAR), Methanol (CH$_3$OH; 98.99% purity, Merck), Hydrofluoric Acid (48% purity; Merck), Silicon wafer (p-type, thickness 25 µm) and Glass Substrate (Microscope slide borosilicate glass; Sail brand).

2.2. Preparation of the nanohybrid samples.
The Si substrate was cleaned using acetone, methanol and hydrofluoric acid respectively in ultrasonic bath. The glass substrate for deposited TiO$_2$/ZnO nanohybrid was also used to determine optical band-gap, the cleaning process was involved acetone and methanol solution respectively, and was then cleaned by using distilled water. Lastly, the substrate was dried using nitrogen gas.

The TiO$_2$ solution was prepared via sol-gel process where TTIB (titanium tetra isobutoxide) was used as precursor while ethanol as the solvent. Firstly, TTIB was dissolved in ethanol. Next, glacial acetic acid (GAA), Triton-X 100 and distilled water was dropped in the precursor solution. After that, the solution were stirred for 1 hour with applied heating and was then continue stirred without heating with ageing time of 24 hours. The similar method was used to prepare ZnO solution where zinc acetate dehydrate as a precursor was dissolved in isopropanol solution. Next, diatehanolamine (DEA) and distilled water was dropped in the precursor solution. Then, the solution was also stirred for 1 hour with applied heating and was then continues stirred without heating, and leaved 24 hours. After that, the two solutions were directly mixed gradually until finish and was again the solution stirred for 1 hour with heating and were then continue stirred without heat for 24 hours. For spin coating technique, speed of 5000 rpm for 30 second was used to deposit nanohybrid TiO$_2$/ZnO on Si surface. Next, the sample was dried using microwave oven for 10 minutes at 150°C and was then annealed at 450°C for 90 minutes using furnace.
2.3. Characterization of samples.
After completing the process of producing nanohybrid sample, the characterization techniques were used Field Emission Scanning Electron Microscope (FESEM; Zeiss Supra 40VP) and Energy Disperse Analyzer X-ray (EDAX; 200.0 kV) mapping analysis, applied on the nanohybrid sample. This characterization was done to observe the surface morphology and confirmed the existence element of nanohybrid sample. Then, X-Ray Diffraction (XRD; Siemens D5000) characterization was done to characterize the compositional of crystal structures, peaks and then, determines the crystallite size. The Ultraviolet-Visible Near-infrared spectroscop (UV-Vis-NiR; Varian Cary 5000) characterization was done to determine the changes on optical band-gap energy ($E_g$) and observe the percentage optical transmittance of nanohybrid.

3. Result and Discussion.
3.1. Structural Properties.
The surface morphology of each sample was characterized using FESEM with an accelerated voltage of 5 kV. Figure 2 shows the FESEM morphologies of pure TiO$_2$ and pure ZnO, respectively. Figure 2 (a) shows seem smooth surface while Figure 2 (b) shows existence of ZnO particles at 20 nm scale of magnification. Both Figures have small of particle size.

![Figure 2. FESEM morphologies of the (a) pure TiO$_2$ and (b) pure ZnO. Scale bars are 20 nm.](image)

Figure 3 shows the FESEM morphologies of the nanoparticles of TiO$_2$/ZnO can be seen appeared in each sample. Figure 3 (a) shows low concentration of Zn, the particles formed a small agglomerates and the size of these agglomerated particles increased with an increasing in ZnO sol concentration. As can be observe in Figure 3 (d), the agglomeration of particles was clearly observed. This is due to the particles dispersed homogeneously and exhibited near and close each other of particle size distribution [9]. Since the formation agglomerated particles is due to the electrostatic interaction between the solute particles, hence the increase in ZnO sol concentration, will also increase the amount of solute. While, Figure 3 (e) indicates at higher concentration of sol ZnO, the particles are less likely to form agglomeration, and these particles are rather form only particles or small agglomeration [9].
Figure 3. The FESEM morphologies of the nanohybrid TiO$_2$/ZnO with different precursor molar concentration (a) 1:1 (0.05M); (b) 1:2 (0.10M); (c) 1:3 (0.15M); (d) 1:4 (0.20M) and (e) 1:5 (0.25M). Scale bars are 20 nm.

The EDAX analysis shows the atomic percentage of each element detected. Observe Table 1, the element of Si has highest peak and the energy dispersive of Si element was found in between of 1.6 and 2.0 keV indicates the substrate of Si. It was used because of higher conductivity, it was thus reduced the probability of sample charging. Furthermore, Ti and O elements were found bonded together. Since the energy dispersive between the two elements is relatively close. This result proved the existence both of TiO$_2$ and ZnO particles that distributed on the Si surface in Figure 3.

Table 1. The analysis data of atomic percentage for each element composition taken from EDAX.

| No. | Elements | Atomic percentage for each element composition (%) |
|-----|----------|---------------------------------------------------|
|     |          | (a) Pure TiO$_2$ | (b) Pure ZnO | (c) Ratio of 1:1 (0.05M) | (d) Ratio of 1:2 (0.10M) | (e) Ratio of 1:3 (0.15M) | (f) Ratio of 1:4 (0.20M) | (g) Ratio of 1:5 (0.25M) |
| 1.  | Ti       | 12.11   | none    | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2.  | Zn       | none    | 2.37    | 0.61 | 2.38 | 2.39 | 9.71 | 9.71 |
| 3.  | O        | 7.36    | 7.11    | 6.18 | 8.90 | 7.71 | 19.14 | 19.14 |
| 4.  | Si       | 80.54   | 90.53   | 93.21 | 88.71 | 89.89 | 71.15 | 71.15 |

Figure 4 indicate the XRD peak of Si at diffraction angle of 62.5°. Observed optimum sample in Figure 4 (d), with ratio of nanohybrid TiO$_2$/ZnO 1:4 (0.20M), the XRD measurement has detected 4 obvious peaks contains of zincite (002), anatase (200), rutile (211) and silicon (100) at diffraction angle of 33.35°, 48.05°, 55.06° and 62.50°, respectively. These result expressed the particle formation was not bonded together and had less effect to the crystallization of the particles. A narrow peak for anatase and rutile phase was found indicates a smaller crystallite while the broaden peak represent the zincite particle distribution. This statement consistent with the result of surface morphology where ZnO particles found disposed throughout TiO$_2$ particles. This result in agreement with Tian et. al. [7].
Figure 4. XRD pattern of nanohybrid TiO$_2$/ZnO with different precursor molar concentration: (a) 1:1 (0.05M); (b) 1:2 (0.10M); (c) 1:3 (0.15M); (d) 1:4 (0.20M) and (e) 1:5 (0.25M).

Figure 5 indicates the effect of increasing ZnO sol concentration on the crystallite size. When the concentration of ZnO increased from 0.05 to 0.20 M, the crystallite size was decreased. The smallest crystallite size was observed for nanohybrid TiO$_2$/ZnO 1:4 (0.20M) with an average crystallite size is 23.71 nm and was smaller. It was proved the sample was prepared below 100 nm ranged which indicates a better crystallinity of the surface sample as reported by M Dutta et. al., (2008) [10]. Observed optimum sample of ratio 1:4 (0.20M) was calculated by using the Scherer’s formula:

$$d = \frac{0.94 \lambda}{\beta \cos \theta}$$  

where $d$: crystallite size, $\lambda$: x-ray wavelength, $\beta$: full-width at the half-maximum (FWHM) of the peak, and $\theta$: peak of diffraction angle.

Figure 5. Effect of variation ZnO sol concentration of the nanohybrid TiO$_2$/ZnO with average crystallite size, $d$. 

23.71 nm
3.2. Optical Properties.

Figure 6 shows the transmittance of pure TiO₂ and ZnO and 5 ratios of varied nanohybrid TiO₂/ZnO. The data roughly emphasize that almost no transmission were detected on the wavelength from range 200 nm to 300 nm. Conversely, in this region, the absorption of UV wavelength occurs with high band-gap energy (E_g). However, obvious increases in transmittance for each nanohybrid ratio as can be seen in the range of ultraviolet (UV) region causes absorbed UV light contain of electron. Then, the maximum and more consistent transmittance were detected in the visible (Vis) region. Figure 6, shows the sample ratio of nanohybrid TiO₂/ZnO 1:4 (0.20M) roughly shows a better transmittance in both regions compares to the other samples. It was proved this sample was mixed well an obviously better than the pure samples.

![Figure 6](image)

**Figure 6.** The graph of transmittance (%) versus wavelength (nm) of (a) pure TiO₂; (b) pure ZnO and nanohybrid TiO₂/ZnO with different precursor molar concentration (c) 1:1 (0.05M); (d) 1:2 (0.10M); (e) 1:3 (0.15M); (f) 1:4 (0.20M) and (g) 1:5 (0.25M) in Uv-Vis-NiR region.

Figure 7 shows the transmittance of optimum nanohybrid TiO₂/ZnO (1:4) (0.20M)). Since the optimum result works well in both regions, this sample has remarkably shown the dual abilities and even better in transmittance region compared to pure TiO₂ and ZnO in UV region and visible region, respectively. The shift in UV region of pure TiO₂ and ZnO indicates the differences in the surface sample due to the lower energy needed to be excited that lead to an improvement in irradiation energy efficiency. The optical band-gap determined on Figure 8 by plotting graph of absorption coefficient from transmission data against optical band-gap energy. From this graph, the optical band-gap energy for sample nanohybrid TiO₂/ZnO 1:4 (0.20M) was 3.38 eV which is higher compared with the theoretical band-gap of anatase. This indicates the sample has successfully improved its optical band-gap energy that suitable for coated glass application, where the percentage of transmittance in UV region and visible region increased and subsequently increases the efficiency of photocatalytic activity. The details about the experimental value of optical band-gap for each samples is tabulated in Table 2.
Figure 7. The graph comparison of transmittance (%) against wavelength (nm) compares to pure for optimum sample, ratio of nanohybrid TiO$_2$/ZnO 1:4 (0.20M).

Figure 8. The optical band-gap ratio of nanohybrid TiO$_2$/ZnO 1:4 (0.20M).

Table 2. Optical band-gap of the nanohybrid TiO$_2$/ZnO calculated from T$(\alpha,\nu')$ noting and using (2).

| Name of samples TiO$_2$/ZnO | Ratio (TiO$_2$/ZnO) | Optical Band-gap, $E_g$ (e.V.) |
|-----------------------------|---------------------|---------------------------------|
| (a)                         | Pure TiO$_2$        | 3.09                            |
| (b)                         | Pure ZnO            | 3.43                            |
| (c)                         | 1 : 1 (0.05M)       | 3.11                            |
| (d)                         | 1 : 2 (0.10M)       | 3.22                            |
| (e)                         | 1 : 3 (0.15M)       | 3.33                            |
| (f)                         | 1 : 4 (0.20M)       | 3.38                            |
| (g)                         | 1 : 5 (0.25M)       | 3.40                            |
The value of an optical band gap can be obtained by using the formula:

\[ E = \frac{hc}{\lambda} \]  

Where \( h v \) is \((\alpha \times hv)^2\), \( r \) is considered indirect band gap energy which equal to 2, \( h \) is Planck’s constant, \( c \) is speed of light and \( \lambda \) represent wavelength.

4. Conclusion.
Nanohybrid TiO\(_2\)/ZnO has been successfully prepared on top of silicon and glass substrate via hybridization process and spin-coating. For this study, we have been varied the concentration of ZnO and identified the optimum sample was the hybrid ratio of TiO\(_2\)/ZnO 1:4 (0.20M). The morphological characterization has confirmed the ZnO particle dispose throughout TiO\(_2\) particle at scale of magnification 20 nm while the EDAX analysis confirmed the atomic percentage of element composition for this sample. From the XRD characterization, we found the peaks of anatase and rutile from TiO\(_2\), zincite from ZnO and Si from Si substrate. This sample also shown a better crystallization and a smaller crystallite size that is much improved compares to TiO\(_2\) itself with value of 23.71 nm. Lastly, the Uv-Vis-NiR characterization has detected this sample has a better transmittance in both region of Uv and Vis region compared pure TiO\(_2\) and ZnO. The optical band-gap energy for this sample was 3.38 eV also increased compared pure TiO\(_2\) that noted the modification of optical band-gap energy has successfully affect the transmittance and efficiency of its photocatalytic activity in Uv and Vis region. Hence, this result suggest for improvement of TiO\(_2\) optical band-gap energy.

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