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Preliminary Study on Different Calcination Temperature of TiO_2/Eggshell Composite Using Sol-Gel Method

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ABSTRACT

The study investigated the impact of varying calcination temperatures on the band gap of a TiO_2/eggshell (TE) composite. The composites were synthesized via the sol-gel method and subjected to different calcination temperatures (400°C, 450°C, and 500°C). Characterization techniques, including Thermogravimetric Analysis (TGA), UV-visible spectroscopy (UV-Vis), and X-ray diffraction (XRD), were employed. Among the different calcination temperatures, the TE 450°C composite exhibited optimal absorbance, indicating a potential enhancement in photocatalytic performance. This suggests that the calcination at 450°C provided favourable conditions for the composite properties. Furthermore, the band gap measurements of the composites ranged from 3.25 eV to 3.48 eV. This range indicates the ability to maintain the inherent stability of TiO_2 while ensuring sufficient light absorption, which is crucial for effective photocatalysis. Overall, the study highlights the significance of calcination temperature in tailoring the properties of TiO_2-Eggshell composites, with the calcination temperature at 450°C composite demonstrating promising characteristics for photovoltaic applications and requiring more exploration.

Keywords: TiO_2/eggshell; Calcination Temperature; Composite; Band Gap

1. Introduction

The large band gap, suitable band edge levels for charge injection and extraction, the long lifetime of excited electrons, exceptional resistance to photo corrosion, non-toxicity, and low cost have made TiO_2 a popular material for solar energy applications. TiO_2 occurs naturally in three crystalline forms: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). TiO_2 has a variety of properties, including chemical stability, a high refraction index of visible light, semi-conductivity, and photosensitivity, making it an excellent material for photocatalytic applications and as the anode of photovoltaic cells in energy generation systems [1]. Adding composite into TiO_2 with certain elements can modify its electronic properties, including the band gap. By narrowing the band gap, more photons from the solar spectrum can be absorbed, leading to increased efficiency in converting light energy into electrical energy. Pure TiO_2 exhibits strong photocatalytic activity, which can cause unwanted side reactions in DSSCs, leading to decreased stability

and efficiency over time. Therefore, adding other elements to TiO_2 can reduce its photocatalytic activity, making the semiconductor more stable and less prone to degradation under prolonged exposure to light and other environmental factors. Modification of TiO_2 can also mitigate the recombination of photo-generated electron-hole pairs, which is a major loss mechanism in DSSCs [2]. Recombination occurs when electrons and holes recombine before reaching the external circuit, thus reducing the overall photocurrent and efficiency of the solar cell. Modification of TiO_2 can alter the electronic structure of TiO_2, creating energy states that trap charge carriers and reduce their mobility, thereby suppressing recombination and improving charge collection efficiency.

Another modification of the photoanode is a higher surface area. Increasing the surface area of a photoanode can indeed have significant effects on its performance in dye-sensitized solar cells (DSSCs) or other similar devices by modifying the photoanode to have a higher surface area and more active sites for the dye molecules to adsorb onto. This, in turn, increases the total number of photogenerated carriers, which can enhance the efficiency of the solar cell. One common method to increase surface area is by reducing the size of the photoanode particles to the nanoscale [3]. Nanomaterials typically have high surface area-to-volume ratios due to their small size and large number of exposed surface atoms. This increased surface area provides more sites for dye molecules to attach, leading to a higher dye loading and, therefore, more efficient light absorption and charge generation.

Therefore, in this research, chicken eggshells were used as composite materials because eggshells contain calcium carbonate ($CaCO_3$) and hydroxyapatite (HA) [4]. Eggshell waste has been offered as a source of the substance for photocatalytic applications that accelerate the pace of photoreaction. Photocatalysis has been utilized to eliminate organic pollutants from the water in advanced methods of oxidation [5]. The use of eggshell, a natural protein-membrane composed of protein with highly crosslinked fibres, could potentially be an excellent support to photocatalyst due to its porous structure and large surface area from the fibrous network [6]. Further investigation of the TiO_2/eggshell (TE) composite was prepared using the sol-gel method, and the properties of the TiO_2/eggshell composite were investigated.

2. Materials and Methods

The synthesis of the TE composite was done via the sol-gel method with the ratio 6:4. First, the 4g eggshell powder was mixed together with 6g TiO_2 powder and put in the 100 mL beaker. Then, 100 mL ethanol was added and stirred until the mixture of TE powder dissolved. A few drops of nitric acid (HNO_3) were added into the solution of TiO_2 incorporated with Eggshell (CaO). 50 mL distilled water was added into the beaker and stirred for 3 hours to ensure the proper mixing and interaction between the eggshell and TiO_2 particles.

The samples were dried in an oven at 60 °C for about 2 hours in order to evaporate the solvent and remove the organic residuals. The mixture of TE was ground using mortar and pestle before being calcined for 4 hours at different calcination temperatures, which were 400, 450, and 500 °C, respectively. All the samples were characterized using XRD and UV-Vis.

3. Results and Discussion

3.1 XRD Analysis

Fig. 1 shows XRD patterns of patterns of pure TiO_2, Eggshell, TE 400 °C, TE 450 °C, and TE 500 °C. The prominent TiO_2 peak observed at $2\theta = 25.4°$ indicates of anatase structure. The constituent of eggshell is mainly $Ca(OH)_2$, where the highest diffraction peaks exist at $2\theta=34.10°$. The XRD peaks of the $Ca(OH)_2$ appear at 2θ equal to 18.066°,28.675°, 34.101°, 47.145°, 50.798°, 56.201°, 64.223°, 64.298°,71.811°, and 84.916° which could delegated to the diffraction of (0 0 1), (1 0 0), (1 0 1), (1 0 2), (1 1 0), (0 0 3), (1 1 2), (1 0 3), (2 0 2), and (1 0 4) planes respectively. This demonstrated that $Ca(OH)_2$ with portlandite structure (hexagonal) with unit cell parameters (a=3.592 Å, c=4.906 Å). The diffraction patterns corresponding to the (0 0 1), (1 0 0), (1 0 1), and (1 0 2) planes are evident through peaks observed at 2θ angles of 18.066°, 28.675°, 34.101°, and 47.145°, respectively.

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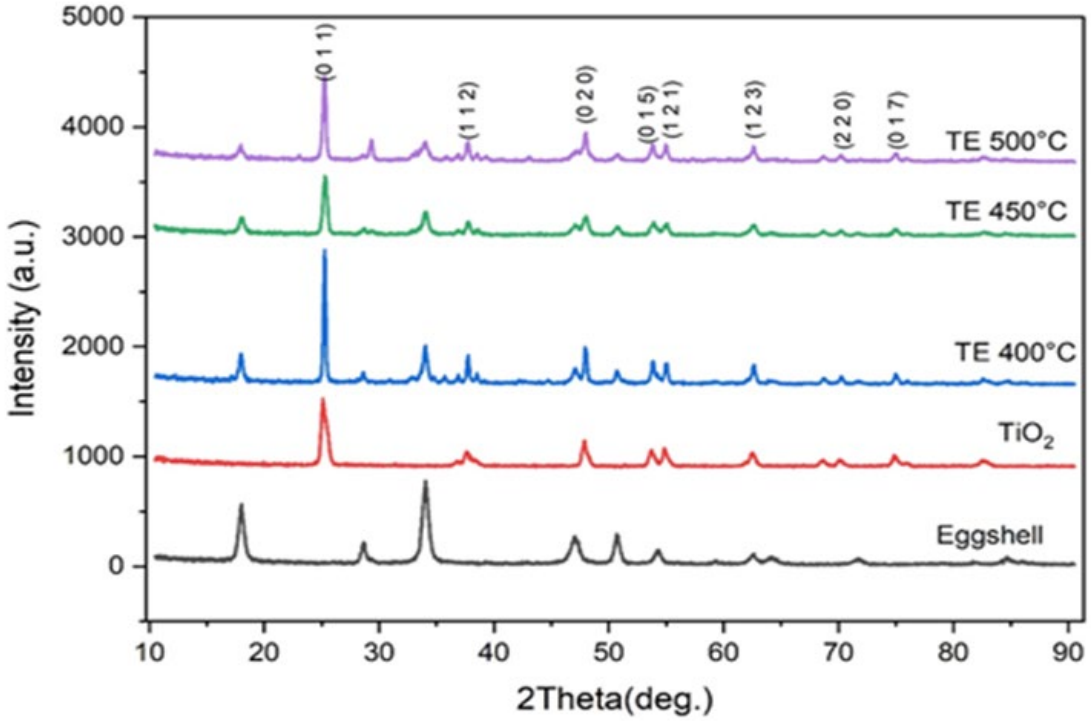

Fig. 1: XRD patterns of pure TiO_2, Eggshell, TE 400 °C, TE 450 °C, and TE 500 °C

The lattice constants (a and c) and cell volume were measured using the basic formula of the tetragonal crystal lattice, while the crystallite size was measured using Scherer's equation. Based on **Table 1**, the change in lattice constant can occur due to the incorporation of Ca atoms into the TiO_2 lattice structure. Since Ca atoms may have a different atomic radius compared to titanium atoms, their presence can lead to a distortion in the lattice, causing an increase in the lattice constant. The introduction of Ca into a material can alter the lattice structure due to its different atomic size and properties compared to the host material. This alteration can lead to changes in the crystal structure and lattice parameters, ultimately affecting the size of the crystallites. As the temperature increases, it can cause lattice expansion, which in turn affects the arrangement of atoms within the crystal lattice. This alteration may result in larger crystallites because the lattice becomes less constrained or more favourable for larger grain growth. Increased temperature also has the potential to enhance the crystallite size. Due to an increase in thermal energy, lattices gain more atomic mobility, allowing atoms to rearrange themselves into more stable configurations. In the context of crystalline materials, higher temperatures can facilitate the movement of atoms within the crystal lattice, leading to the growth of crystallites [7].

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Table 1: Lattice Parameter, the average crystallite size of TE with different calcination temperatures (400, 450, and 500 °C)

Samples	Average crystallite size, D (nm)	Cell Volume ($Å^3$)	a(Å)	c(Å)
Eggshell	16.86	54.82	3.59	4.91
TiO_2	18.29	136.27	3.76	9.51
TE400	27.80	136.31	3.76	9.51
TE450	27.10	136.37	3.76	9.51
TE500	27.06	136.34	3.76	9.51

3.2 Optical Properties Analysis

Studying the optical properties of TE is crucial for understanding its behaviour as a photoanode material, as shown in Fig. 2. Based on Fig. 2, the increased calcination temperature expands the absorption spectrum window with strong absorption indicated at between 400 nm and 500 nm. By comparing, TE 450 °C produced the highest and widest absorption compared to others. A wider absorption spectrum means that the material can absorb a broader range of light wavelengths. In the context of photovoltaics, this is advantageous because it allows the material to capture more sunlight, increasing the overall efficiency of the solar cell. Meanwhile, higher peaks indicate stronger absorption at specific wavelengths. Again, in the context of photovoltaics, this is beneficial because it means the material can efficiently convert light energy into electrical energy at specific wavelengths. Therefore, TE 450 °C gave an advantage in the performance of solar cell applications [8].

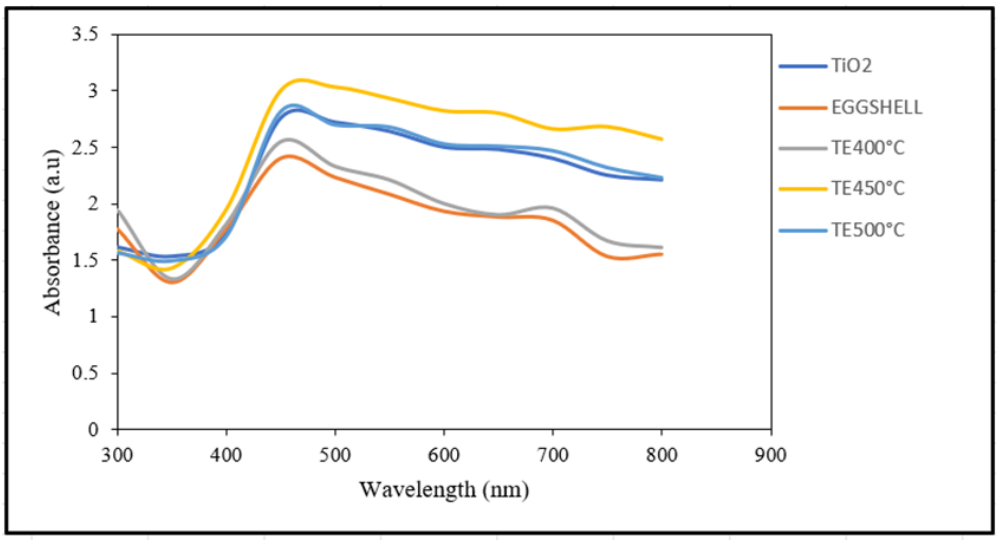

Fig. 2: UV–vis absorbance spectra of TE at different calcination temperatures

The results of the optical band gap (Eg) illustrated in **Table 2** were calculated using the UV–vis spectra, as shown in Equation (1).

$$\alpha hv = A(hv - E_g)^n \quad (1)$$

Where α is the optical absorption coefficient, hv is the photon energy, Eg is the absorption band gap, A and n are constants. For the indirect semiconductor of anatase TiO_2, n is equal to 2 [9].

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Table 2: Band gap with different calcination temperatures (400, 450, and 500 °C)

Samples	Photon Energy (eV)
TiO_2	3.24
Eggshell	3.51
TE 400°C	3.21
TE 450°C	3.13
TE 500°C	3.22

Based on **Table 2**, the band gap decreased until 450°C and increased when calcination increased. Reducing the band gap required less energy for electrons to jump from the valence band to the conduction band. This leads to an increase in the absorption spectrum correlated with results in **Table 1**. A narrower band gap allows more photons with lower energy and longer wavelengths to be absorbed. This can lead to a broader absorption spectrum because a wider range of wavelengths can now contribute to the excitation of electrons across the band gap [10]. When the band gap decreases, the absorption spectrum tends to widen because a smaller energy gap allows for the absorption of photons with a wider range of energies. This means that more photons can be absorbed across a broader range of wavelengths, resulting in a wider absorption spectrum, as shown in Fig. 2. The Decreased band gap also affected the average distance between atoms, as shown in **Table 1**. As temperature increases, the lattice vibrates more, causing the average distance between atoms to increase. This leads to a reduction in the effective potential barrier for charge carriers to overcome, effectively decreasing the band gap.

4. Conclusion

The project's outcome showed the immense potential for using TE composites using the sol-gel method. Calcination temperature at 450°C produced the lowest band gap and high absorption spectrum, which can enhance the electron injection and transportation. Therefore, TE composite can be considered used in photovoltaic devices due to narrower band gaps, which can absorb a broader spectrum of sunlight, hence increasing the efficiency of energy conversion.

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