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ENHANCED PHOTOVOLTAIC PERFORMANCE VIA $\text{CaCuSi}_4\text{O}_{10}$ DEPOSITION ON DYE-SENSITIZED TiO_2 THIN FILMS

Summary

The increased use of non-renewable energy sources has driven research into sustainable alternatives. This work investigates the use of the ceramic oxide $\text{CaCuSi}_4\text{O}_{10}$ in TiO_2 thin films sensitized by dyes, applied in dye-sensitized solar cells (DSSC). $\text{CaCuSi}_4\text{O}_{10}$ was synthesized by a solid-state route and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). The deposition onto the films was performed using the Doctor Blade method, and optical properties were analyzed by UV-Vis spectroscopy. The I-V and J-V curves showed that the addition of $\text{CaCuSi}_4\text{O}_{10}$ enhanced the efficiency of the films, with evidence of downconversion. The results indicate the material's potential in optimizing photovoltaic performance.

Keywords: $\text{CaCuSi}_4\text{O}_{10}$, TiO_2 , solar cell, DSSC, downconversion.

1. Introduction

The growing global energy demand, driven by population growth and increased industrial activities, has led to a significant rise in greenhouse gas emissions, primarily due to the burning of fossil fuels. This scenario has prompted intense efforts from the scientific community in the search for clean, renewable, and sustainable energy sources. In this context, solar energy stands out as a promising alternative, being abundant, inexhaustible, and environmentally friendly (REN21, 2023).

Dye-sensitized solar cells (DSSC), initially proposed by O'Regan and Grätzel in 1991 (O'Regan and Grätzel, 1991), represent one of the most studied emerging technologies in the photovoltaic energy field. These devices offer significant advantages over conventional silicon solar cells, such as lower production costs, ease of fabrication, and good performance under low light conditions. The basic structure of DSSCs consists of a mesoporous titanium dioxide (TiO_2) photoanode, sensitized with organic or inorganic dyes, a liquid electrolyte containing a redox couple (usually I^-/I_3^-), and a counter electrode (Grätzel, 2005).

However, the performance of these cells is still limited by several factors, such as the narrow absorption range of the dyes and the low electron mobility in TiO_2 . One of the most promising approaches to overcoming these limitations is the incorporation of luminescent materials capable of performing spectral conversion (downconversion or upconversion), thus broadening the light absorption range of the solar cell photoanode (Lin *et al.*, 2014). In this sense, luminescent ceramic materials, such as $\text{CaCuSi}_4\text{O}_{10}$ – also known as Egyptian Blue – have gained increasing interest.

$\text{CaCuSi}_4\text{O}_{10}$ is a copper silicate with a stable crystal structure, known since antiquity for its intense blue color and thermal and chemical stability. Recently, studies have shown its potential as a photoluminescent material with downconversion properties, capable of converting high-energy photons (such as UV) into lower-energy photons (visible), thereby optimizing light absorption by the photosensitive materials present in DSSCs (Accorsi *et al.*, 2009; Greco *et al.*, 2022). Furthermore, its structure is compatible with semiconductor oxides like TiO_2 , allowing for its efficient incorporation into thin films by deposition techniques such as Doctor Blade, spin-coating, and sonochemistry (Carneiro *et al.*, 2021).

This work proposes the deposition of $\text{CaCuSi}_4\text{O}_{10}$ onto TiO_2 thin films sensitized by dyes, aiming to investigate the effects of adding this material on the optical and photovoltaic properties of the devices. The central hypothesis is that the incorporation of a luminescent component like Egyptian Blue may lead to significant

improvements in the energy conversion efficiency of DSSCs, expanding their practical applicability and contributing to the advancement of low-cost solar technology.

2. Methodology

The $\text{CaCuSi}_4\text{O}_{10}$ ceramic pigment was synthesized using the conventional solid-state reaction route. Stoichiometric amounts of analytical grade precursors — calcium carbonate (CaCO_3), copper(II) oxide (CuO), and silicon dioxide (SiO_2) — were weighed and homogenized in a planetary ball mill for 2 hours. The mixture was then calcined in an alumina crucible at 900°C for 6 hours in air to promote the formation of the $\text{CaCuSi}_4\text{O}_{10}$ phase.

The obtained powder was characterized by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation to confirm phase formation and crystallinity. Scanning electron microscopy (SEM) was employed to examine the morphology of the particles, while energy-dispersive X-ray spectroscopy (EDS) was used to verify the elemental composition and uniformity of the synthesized material.

For photovoltaic application, mesoporous TiO_2 films were prepared on fluorine-doped tin oxide (FTO) glass substrates using the Doctor Blade technique. The TiO_2 pastes were deposited as uniform thin films and subsequently sintered at 450°C for 30 minutes. After cooling, the $\text{CaCuSi}_4\text{O}_{10}$ powder was dispersed in ethanol and deposited over the TiO_2 films, followed by a soft annealing step to promote adhesion and integration.

The films were then sensitized by immersion in a solution containing N719 dye for 24 hours under dark conditions. Dye-sensitized solar cells (DSSCs) were assembled in a sandwich configuration using a platinum-coated FTO counter electrode and iodide/triiodide (I^-/I_3^-) liquid electrolyte. The photovoltaic performance was evaluated under AM 1.5G illumination using a solar simulator and an Autolab PGSTAT302N potentiostat. Current-voltage (J-V) curves were recorded to assess device efficiency, and UV-Vis spectroscopy was performed to analyze optical absorption and confirm possible downconversion effects from the added ceramic material.

3. Results and Discussion

In Figure 1, the solid-state route for the synthesis of the $\text{CaCuSi}_4\text{O}_{10}$ pigment is illustrated in stages, including (a) starting oxides, (b) the final pigment after calcination, (c) the doping process of the materials, and (d) the $\text{TiO}_2 + \text{CCSO}$ composition. Each stage was carefully executed to ensure the purity and homogeneity of the material, which is essential for application in dye-sensitized solar cells.

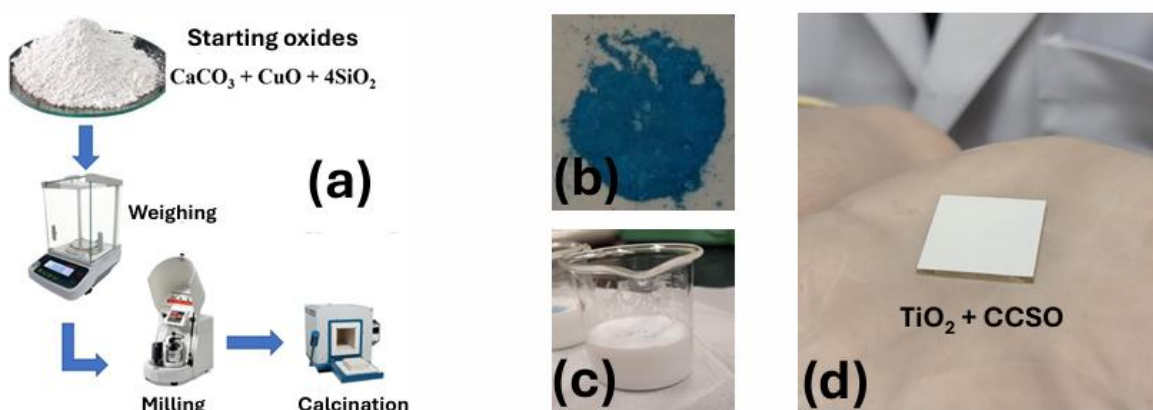


Figure 1: (a) Solid-state Route, (b) Egyptian Blue, (c) Doping of materials, (d) $\text{TiO}_2 + \text{CCSO}$.

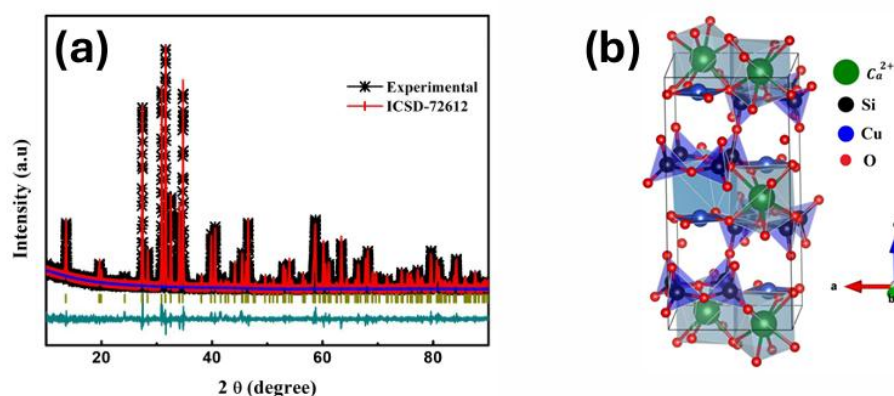
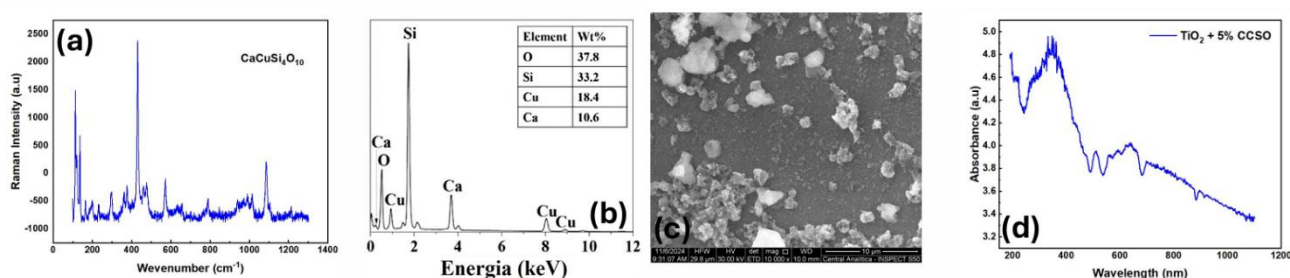


Figure 2: (a) XRD and (b) Structure of CCSO.

In Figure 2, the XRD results (a) confirm the crystalline structure of CCSO, and (b) the detailed structure of the material is presented, demonstrating its suitability for integration with TiO_2 .



Figures 3: (a) Room-temperature Raman spectroscopy, (b) EDS, (c) MEV and (d) ABS.

In Figure 3, room-temperature Raman spectroscopy (a) indicates the main vibrational characteristics, while EDS analysis (b) confirms the elemental composition of CCSO. Figure 3(c), obtained via SEM, reveals the material's morphology, and Figure 3(d) shows the optical absorption (ABS), highlighting the material's ability to capture visible light, which is essential for photovoltaic efficiency.

4. Conclusion

The deposition of $\text{CaCuSi}_4\text{O}_{10}$ pigment onto dye-sensitized TiO_2 thin films proved to be an effective strategy for photovoltaic applications. The findings suggest that the material improves energy conversion efficiency and maintains stability under operational conditions. These results underscore the potential of Egyptian Blue as a promising functional material for sustainable energy technologies.

5. References

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