

Bio-Inspired Conversion of CO₂ to Nanoscaled Hydro-Zincite Mediated via Zea Mays Saccharata

Kgotla Katlego Masibi

kkmasibi@tllabs.ac.za

iThemba Laboratory

Meisam Aligholami

University of South Africa

Hamza Mohamed

University of South Africa

Remy Bucher

iThemba Laboratory

Nolubabalo Matinise

University of South Africa

Malik Maaza

University of South Africa

Article

Keywords: CO₂ sequestration, Hydrozincite, Zea mays, Green chemistry, Nanomaterials, Electrocatalysis, Decarbonization, bio-inspired synthesis

Posted Date: February 4th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-8672754/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

BIO-INSPIRED CONVERSION OF CO₂ TO NANOSCALED HYDRO-ZINCITE MEDIATED VIA ZEA MAYS SACCHARATA

K. K. Masibi^{1-2-3*}, M. Aligholami¹⁻²⁻³, H. Mohamed¹⁻²⁻³, R. Bucher¹⁻²⁻³, N. Matinise¹⁻²⁻³,
M. Maaza^{1-2-3*}

¹ UNESCO-UNISA Africa Chair in Nanosciences and Nanotechnology, College of Graduates Studies, University of South Africa, Muckleneuk Ridge, Pretoria 392, South Africa

² iThemba Laboratory for Accelerator-Based Sciences, National Research Foundation, PO Box 722, Somerset West 7129, South Africa

³ African Centre of Competencies in Enhanced Nanosciences and Nanotechnology for SDGs, College of Graduates Studies, University of South Africa, Muckleneuk Ridge, Pretoria 392, South Africa

*Corresponding authors: Email: kkmasibi@tlabs.ac.za / Maazam@unisa.ac.za

Abstract

The potential for bio-inspired conversion of CO₂ to single phase Hydrozincite Zn₅(CO₃)₂(OH)₆ was confirmed for the first time in this contribution utilising aqueous extracts of *Zea Mays var. saccharata* (ZMS). The latter has been a successful chelating/reduction agent. Under ambient circumstances (room temperature & atmospheric pressure), this novel method produced single phase crystalline Hydrozincite Zn₅(CO₃)₂(OH)₆ with an average crystallite size of 38.5 nm. Furthermore, by including carbonate, this process provides a possible route for CO₂ capture.

The UV-VIS-DRS, PL, FT-IR, XRD, and SEM-EDS studies sustained the potential of the bio-engineered nanoscaled Hydrozincite Zn₅(CO₃)₂(OH)₆ as a high reflecting material (Diffuse reflectance >85%) & an effective blue luminescence ($\lambda^{\text{MaxEmission}} \approx 457.3$ nm). Electrochemical properties were investigated in 1 M NaOH electrolyte using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV studies demonstrated a significant increase in current response with distinct Faradaic peaks at +0.07 V, +0.18 V, and -0.16 V (vs Ag|AgCl), confirming electrocatalytic activity of the nanoparticles. This was further corroborated by EIS, which showed a substantial reduction in charge transfer resistance (R_{ct}) from 845.84 k Ω for the bare glassy carbon electrode (GCE) to 94.30 k Ω for the Zn₅(CO₃)₂(OH)₆ modified GCE, indicating significantly improved charge transfer kinetics.

These results demonstrate a scalable bio-engineering route for synthesizing single phase crystalline hydrozincite Zn₅(CO₃)₂(OH)₆ nanoparticles with favorable opto-electrochemical properties, positioning them as promising candidates for applications in CO₂ conversion, optoelectronics & catalysis.

Keywords: CO₂ sequestration, Hydrozincite, Zea mays, Green chemistry, Nanomaterials, Electrocatalysis, Decarbonization, bio-inspired synthesis

1. Introduction

Global warming, characterized by the sustained increase in Earth's temperature, is a significant global concern. This temperature rise is mainly attributed to the greenhouse effect, which is a consequence of elevated concentrations of carbon dioxide (CO₂), chlorofluorocarbons (CFCs), methane, and other atmospheric pollutants collectively denoted as greenhouse gases (GHGs).

These gases absorb the infrared radiation emitted from the Earth's surface and prevent it from being radiated back into space. As a result of such a radiation trapping, the Earth's average surface temperature continues to rise [1-3]. According to the Intergovernmental Panel on Climate Change (IPCC) Sixth Assessment Report (AR6) [4], the global temperature had already increased by 1.1 °C above pre-industrial levels by year 2020. To curb the continued rise in global temperatures and remain below 1.5 °C, GHG emissions particularly CO₂ must be halved by the year 2030. Mitigation strategies to curb atmospheric carbon dioxide include, but are not limited to CO₂ sequestration, carbon capture and storage (CCS) technologies, and broader decarbonization initiatives aimed at reducing emissions across energy, industry and transportation sectors [4-6].

CO₂ sequestration is the process of capturing and storing atmospheric CO₂ to reduce its presence or concentration [7]. This can be achieved through several pathways, primarily involving the capture of CO₂ emissions directly from industrial or energy related sources, followed by long-term or permanent storage. The first method is geological storage, where captured CO₂ is stored underground in unused oil tanks, saline aquifers, or deep into the underground rock formations [8-9]. The second method or pathway is ocean storage, in which CO₂ is injected into deep oceans waters where it dissolves and becomes trapped [10-11]. The third method is mineral carbonation, where CO₂ chemically reacts with naturally occurring minerals and metals to form long term stable carbonates & related hydrated compounds [12].

In this study, we validate the mineral carbonation as a CO₂ capture strategy by converting it to nano-scaled Hydrozincite Zn₅(CO₃)₂(OH)₆, via a bio-engineering approach. This method utilizes natural plant extracts as effective chelating agents, building upon previous demonstrations of this technique for nano-scaled carbonates [13].

The targeted compound, a hydrated form related to smithsonite (ZnCO₃), potentially exhibits broader multi-functionality. In contrast to hydrozincite Zn₅(CO₃)₂(OH)₆, smithsonite is often found as a secondary mineral in the oxidation zones of zinc ore deposits (Fig.1.a). It can also be observed in sedimentary deposits and as a direct oxidation product of sphalerite. (ZnCO₃) is an inorganic compound occurring naturally in various mineral phases, primarily as smithsonite which is the most stable crystalline form (Fig.1.b) [14-15].

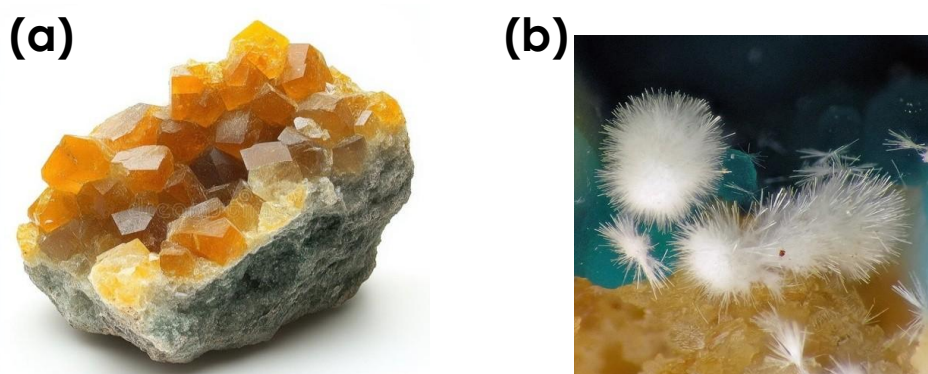


Fig.1: Typical ore crystals of bulk (a) Smithsonite (ZnCO₃) & (b) its hydrated form hydrozincite Zn₅(CO₃)₂(OH)₆ [15].

The technological applications of bulk smithsonite are relatively limited. Actually, the main technological usage of smithsonite is as a significant source of zinc, which is utilised in batteries, alloys, and galvanising. It is pivotal in the processing of minerals, especially in the flotation of zinc ores, where new methods of separation using reagents are explored [14]. These include but are not limited to collectors, depressants, and activators.

In its hydrated form, smithsonite i.e. Hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$), is likely to exhibit additional peculiar physical-chemical properties as it is demonstrated in section 2. Certainly, nanomaterials with a size range of 1-100 nm, exhibit size, shape, surface & interface effects [13, 16-19]. This includes quantum confinement, phonons confinement, breaking of the 3-D crystallographic symmetry & therefore an enhanced catalytic activity [17, 19]. Nano-scaled $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ has been identified as a promising substitute for antimony trioxide in flame retardant flexible poly(vinyl chloride) [20]. Likewise, porous $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ has shown potential as a novel anode material for advanced lithium-ion batteries [21].

While the synthesis of nano-scaled $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ is limited, nano-scaled ZnCO_3 was successfully engineered using a variety of physical & chemical methodologies [18, 20-25]. This includes hydrothermal, thermal decomposition, micro-emulsion, solid state reaction, among others.

Within this contribution, an outright green novel bio-engineering approach for the biosynthesis of single phase crystalline nano-scaled hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ is validated using H_2O as the unique solvent and natural extract of ZMS (Fig.2) as an effective chelating agent with ZnCl_2 and CO_2 as Zn & CO_3 sources respectively. Besides the major pivotal aspect of converting CO_2 to functional compound, this green bio-inspired technique has the following benefits over conventional physical and chemical approaches:

- (i) Minute energy input if, any,
- (ii) No vacuum required,
- (iii) The bio-engineering phase takes place within mild conditions (P_{atm} , $T_{\text{Room Temperature}}$),
- (iv) No catalyst required,
- (v) No harsh-reducing agents,
- (vi) green reducing agents from the Zea Mays' phyto-compounds,
- (vii) The bio-engineering is possible with Zea Mays' but not limited to as likely, any natural extract with similar phyto-compounds would be as effective,
- (viii) No harmful waste,
- (ix) No rivalry with the food industry because the phyto-compounds come from non-food sources like the cob portion that is not human consumable,
- (x) No critical or supercritical CO_2 usage conditions,

Regarding the benefit (vi), it should be noted that the Zea mays cob is the source of the natural extract used to reduce the zinc precursor in this study (Fig.2). Indeed, the Zea mays cob, often considered a by-product in maize processing, is currently underutilized. However, it has a significant concentration of bioactive substances, including but not limited to phenolic acids, anthocyanins, and bioactive oligosaccharides [26-29]. Furthermore, it has been shown that Zea mays cob can be used as a substrate to produce citric acid [30]. As in previous studies, such phyto-compounds from various plants were demonstrated to be effective chelating /reducing agents for the bio-engineering of various nanomaterials [31-41] including from Zea Mays [42].

2. Experiments, results and discussions

2.1. Synthesis & methodology

Analytical grade (purity $\geq 99\%$) chemicals and reagents were sourced from Sigma-Aldrich and used as received: carbon black, ethanol, N-methyl-2-pyrrolidone (NMP), polyvinylidene fluoride (PVDF), sodium hydroxide (NaOH), and zinc chloride (ZnCl_2). High purity ($\geq 99.99\%$) CO_2 (g) was procured from Afrox. Ultrapure water ($18.2\text{ M}\Omega\text{ cm}$) was utilized in all

experiments to uphold uniformity. The extract of ZMS was prepared following previously reported methods [42, 43], with minor modifications. The overall green synthesis process, from extract preparation to nanoparticle synthesis is schematically depicted in Fig.3. Fresh sweet corn was procured, and the husks and silk were removed. The corn cobs were thoroughly washed and cut into smaller pieces, which were then immersed in deionized water and heated at 80 °C for 1 hour. After cooling to room temperature, the mixture was filtered through Whatman No. 1 filter paper, and the resulting filtrate was collected for use as a reducing and capping agent in nanoparticle synthesis.

For the green synthesis of the targeted $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ & ZnCO_3 nanoparticles, 3g of ZnCl_2 was added to 200 mL of the prepared ZMS extract, and the mixture was vigorously stirred to ensure complete dissolution. The pH was adjusted to 7 using 1 M NaOH, and the mixture was left under continuous stirring for 24 hours at ambient temperature. Subsequently, CO_2 gas was bubbled into the solution for 30 minutes, after which stirring was continued for an additional 24 hours to allow complete reaction. The resulting precipitate was collected by centrifugation, washed sequentially with ethanol, and deionized water to remove impurities, and dried at 35°C for 12 hours to obtain a dry powder.

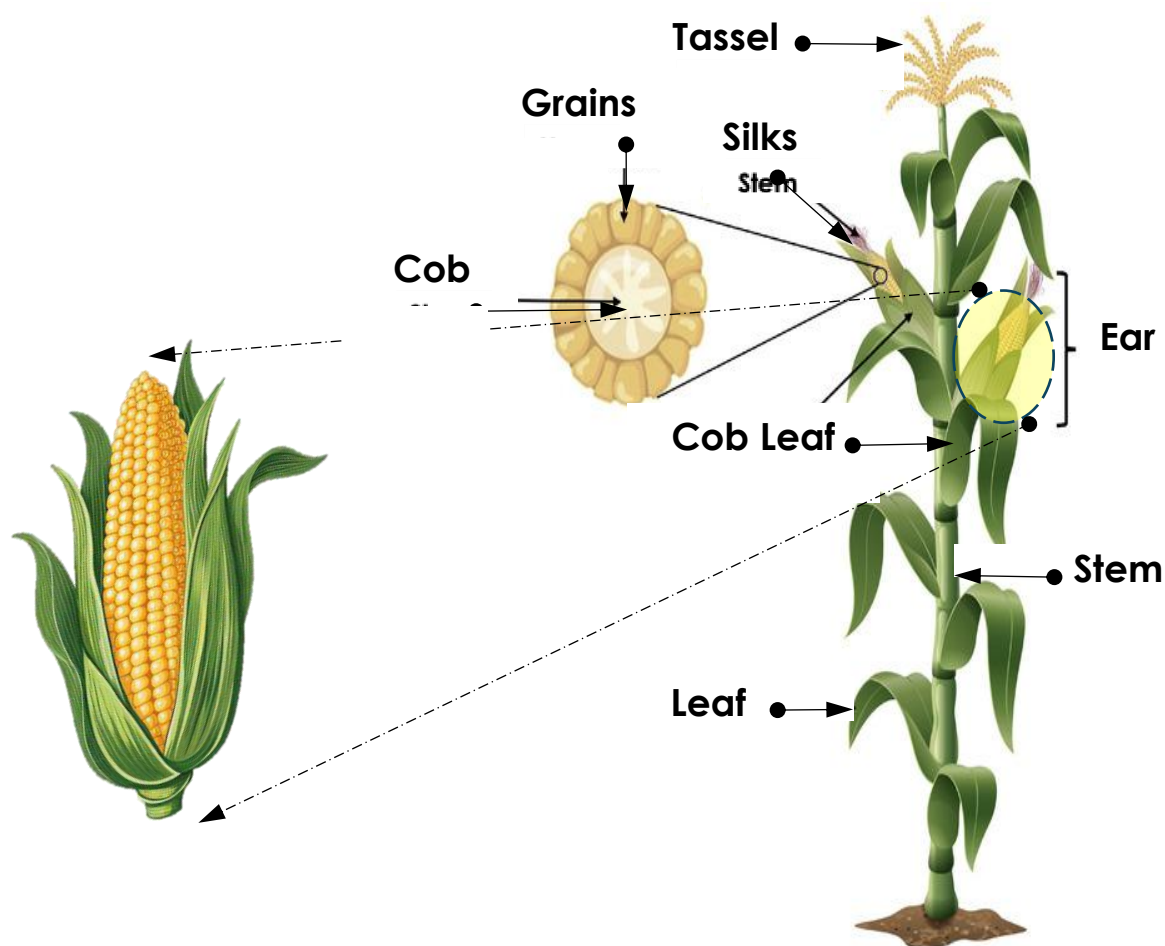


Fig.2: Schematic representation of a typical *Zea mays* plant & its major constituents [16].

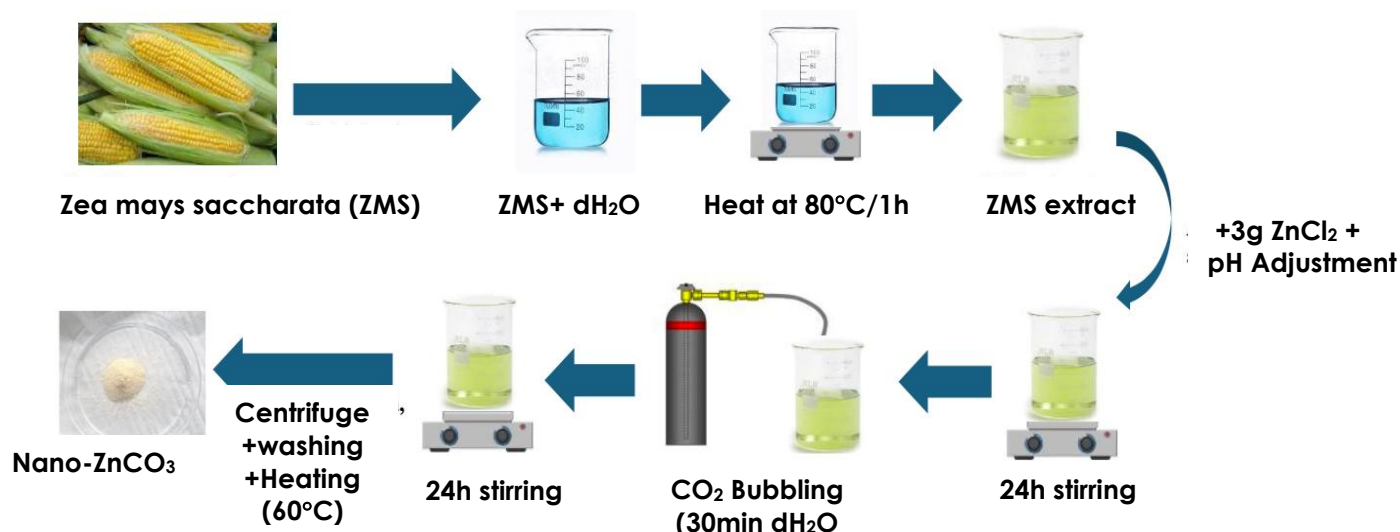


Fig.3: Schematic representation of the bio-inspired synthesis of ZnCO₃ nanoparticles using *Zea Mays saccharata* extract.

2.2: Materials and characterization:

The scanning electron microscopy (SEM) investigations were conducted on a Verios 5 XHR SEM unit. The UV–VIS–NIR diffuse reflectance studies were acquired using an Ocean Optics unit within the spectral range of 250–1100 nm. As a standard reference for reflectance measurements, - BaSO₄ standard was used. With an optical bandgap of ~ 6 eV, - BaSO₄ exhibits a low absorption extending to the UV band correlated to an elevated UV–VIS and NIR reflectance. The Luminescence measurements were recorded using a fibre-optics linked Ocean Optics system consisting of a UV light-emitting diode source coupled to a high sensitivity QE Pro-FL spectrophotometer. The excitation wavelength was fixed at 240 nm. The X-rays Diffraction measurements were carried out with a Bruker D8 equipped with a copper sealed tube x-ray source producing Cu - K_{α1} radiation at the wavelength of 1.5406 Å from a generator operating at 40 keV and 40 mA (operating in a Θ -2 Θ configuration). The scanning rate was 0.03° per minute from 20° to 85°. The Diffraction patterns were interpreted using MAUD software. The Thermal Gravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC) experiments were performed using a Mettler Toledo TGA/DSC 1 Stare System analyser with a horizontal reaction chamber. About 10–20 mg of sample were placed in a cylindrical - Al₂O₃ crucible. The TGA furnace was constantly purged with Ar gas. The samples were annealed from 25 to 900 °C at a heating rate of 10 °C/min in a stream of N₂ or Ar “reactive gas” provided directly above the sample with a flow rate of 50 mL min⁻¹. A baseline, obtained under the same conditions with an empty - Al₂O₃ crucible, was subtracted from the measured thermograms.

The electrochemical measurements were obtained from a Metrohm Autolab PGSTAT 302 Potentiostat driven by Nova 2.1 software. A three-electrode arrangement was used comprising of modified and unmodified glassy carbon electrode (GCE) as the working electrode, platinum wire counter electrode, and a reference electrode of silver-silver chloride (Ag/AgCl) in saturated potassium chloride. For the electrode preparation, the GCE was sequentially polished using 1 µm, 0.5 µm, and 0.3 µm aqueous alumina slurries on a micro-cloth pad, followed by a gentle rinse with deionized water. To ensure complete removal of surface-bound particulates, the electrode was ultrasonically cleaned in absolute ethanol for 5 minutes and then in distilled water for an additional 5 minutes. A composite consisting of 80 wt% Zn₅(CO₃)₂(OH)₆ nanoparticles, 10 wt% carbon black, and 10 wt% of PVDF was prepared by grinding the components to uniformity using a pestle and mortar. The

ground mixture was collected in a vial, and a few microliters of NMP were added. The suspension was sonicated for 2 hours to form a homogeneous paste. Finally, approximately 5 μ L of the resulting paste was drop-cast onto the electrode surface and dried at 35°C for 2 minutes to produce the modified working electrodes [44].

2.3 Elemental studies:

Fig.4 displays the Energy Dispersive X-rays Spectroscopy (EDS) of the bio-engineered particles. Besides the Zn, O, and C, likely related to the elemental composition of the hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ particles, there are several additional contaminants including Cl, P and F. While P originate prospectively from the Mays natural extract, Cl is likely to originate from the ZnCl_2 precursor with a potential F as a contaminant.

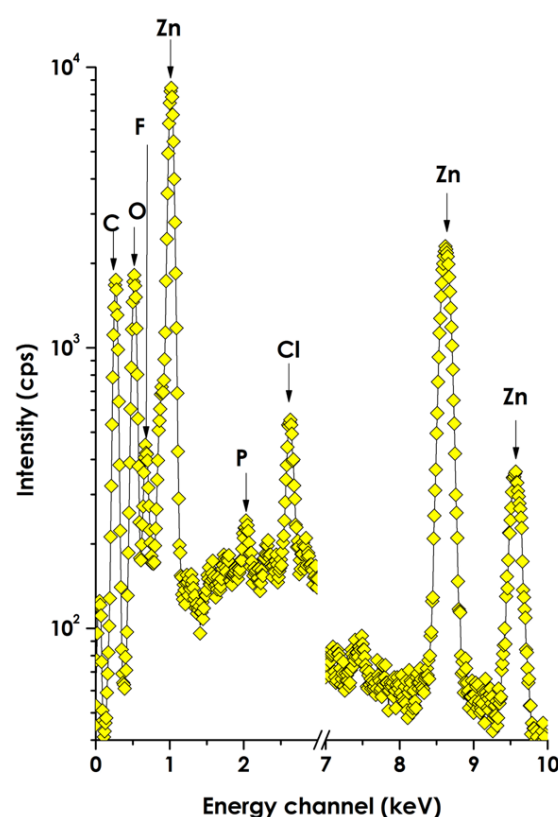


Fig.4: Typical Energy Dispersive X-rays Spectroscopy spectrum of the synthesized nanoparticles of ZnCO_3 & $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$.

2.4 Crystallographic investigations:

Fig.5 reports the Room temperature X-rays Diffraction pattern of the bio-engineered particles $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ within the angular range of 10-75 Deg. The XRD pattern is characterized by a limited number of Bragg diffraction peaks which reflects a crystallographic symmetry. The major Bragg peaks are centered at 2θ of 12.78, 28.14, 33.35, 59.20 & 69.86 Deg. This pattern is in line with highly textured (401) trigonal structure Hydrozincite $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ (JCPDS No. 01-072-1100). Hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, has a monoclinic crystal structure (C2/m space group), featuring layers built from zinc octahedra and tetrahedra, with lattice parameters of $\langle a \rangle \approx 13.6 \text{ \AA}$, $\langle b \rangle \approx 6.3 \text{ \AA}$, $\langle c \rangle \approx 5.4 \text{ \AA}$, and $\beta \approx 95.8^\circ$ [45]. Within the experimental error bar, these values are in agreement with those derived from the Rietveldt analysis of the experimental XRD pattern of Fig.5. The derived values are $\langle a \rangle = 13.64 \text{ \AA}$, $\langle b \rangle = 6.31 \text{ \AA}$, $\langle c \rangle = 5.42 \text{ \AA}$ and $\beta = 95.85^\circ$. In addition, the various Bragg peaks

are significantly broad reflecting the nano-scale size of the diffracting nano-crystals. with crystals' average size of about $\varnothing \approx 38.5$ nm. This low value is in support of the nano-scaled configuration of the bio-engineered $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ crystals ($\varnothing < 100$ nm). As a pre-conclusion within this section, it is safe concluding on the single phase Hydrozincite $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ bio-engineered particles & their nano-scale configuration.

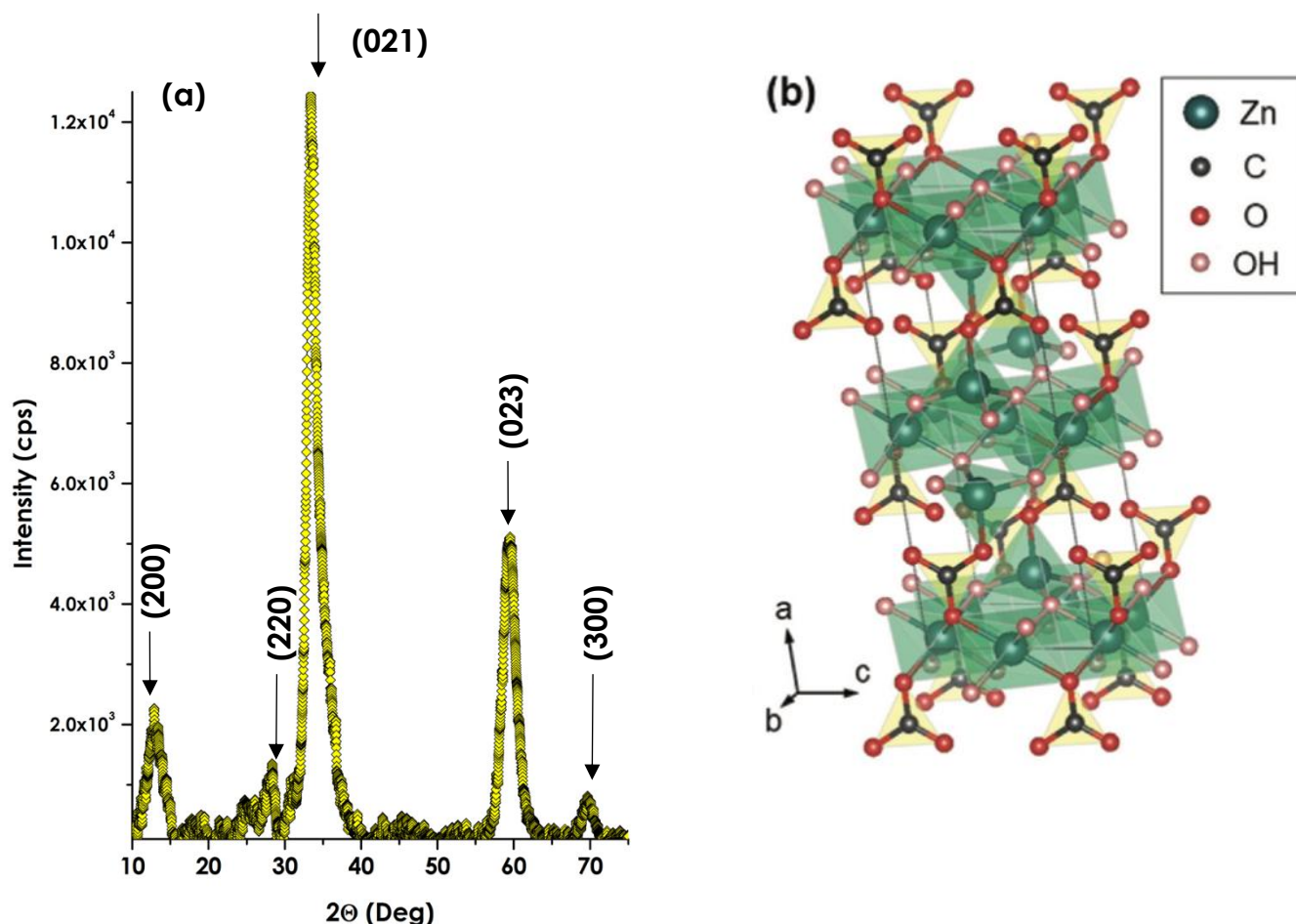


Fig.5: (a) Room temperature X-rays Diffraction pattern of the bio-engineered nanoparticles, (b) Crystallographic unit cell of hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ (JCPDS No. 01-072-1100) [46].

2.5 Vibrational (FTIR) investigations

Fig.6 displays the Fourier Transform InfraRed /Attenuated Total Reflection (FTIR-ATR) spectrum within the spectral range of 400-4000 cm^{-1} . Several vibrational modes are observed. They are centered at about 707.8, 832.2, 1024.3, 1385.6, 1360, 1495.5, 2051.4, 2287.6, and 3344.7 cm^{-1} . The vibrational modes at 1495.5, 1385.6, and 1360 cm^{-1} are ascribed to the ν_3 (CO_3)²⁻ antisymmetric stretching modes in hydrozincite. The band at 832 cm^{-1} is assigned to the ν_2 bending mode for carbonate [47, 48]. The bands are observed for the carbonate ν_4 in phase bending modes at 707 cm^{-1} [17]. The bands at 1045 and 949 cm^{-1} are assigned to the -OH bending mode [18, 49]. Once again, and as a pre-conclusion within this section, it is safe concluding on the Hydrozincite $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ nature of the bio-engineered particles.

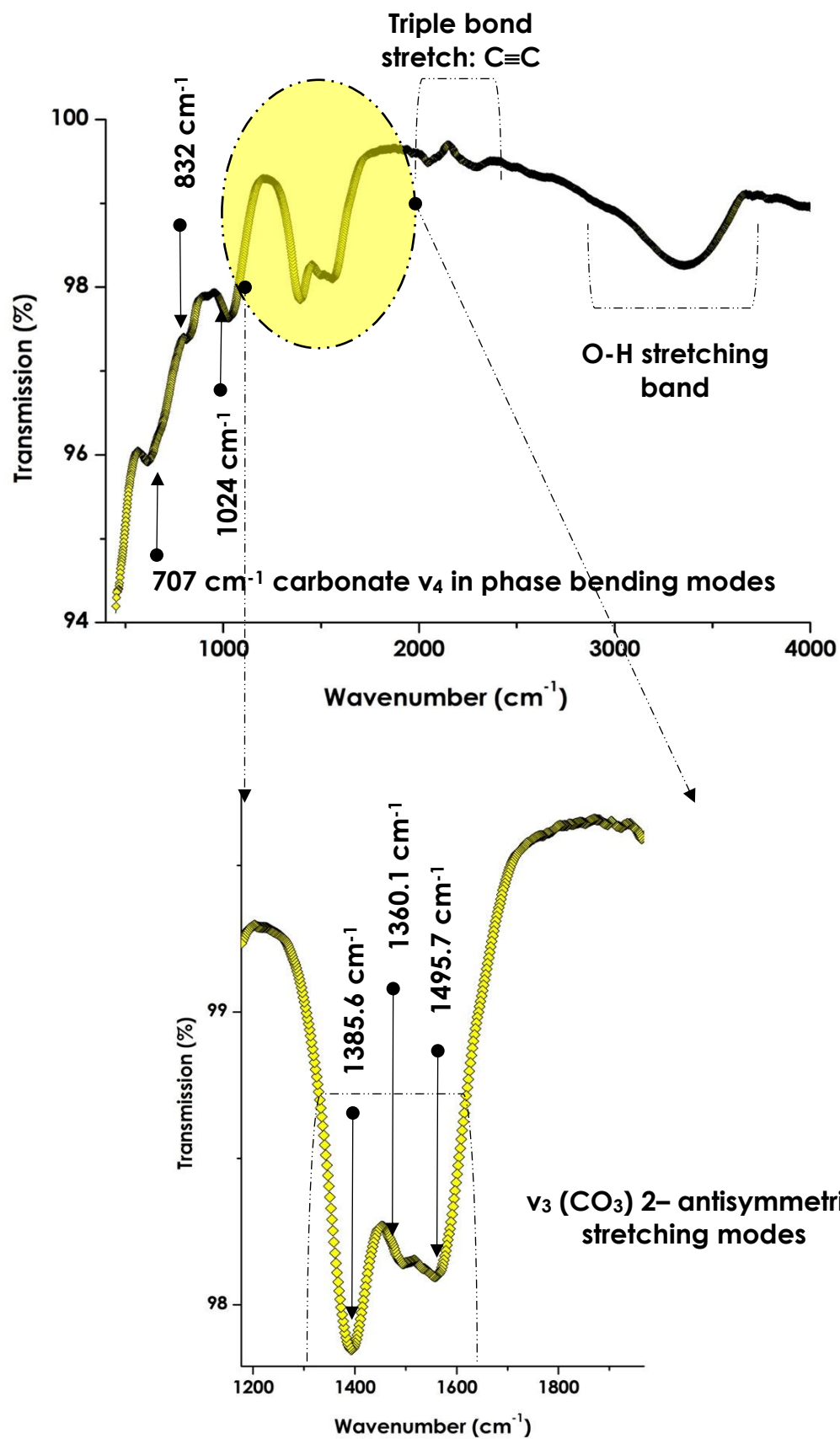


Fig.6: Room temperature ATR-FTIR spectrum of the bio-engineered nanoparticles highlighting their hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ nature.

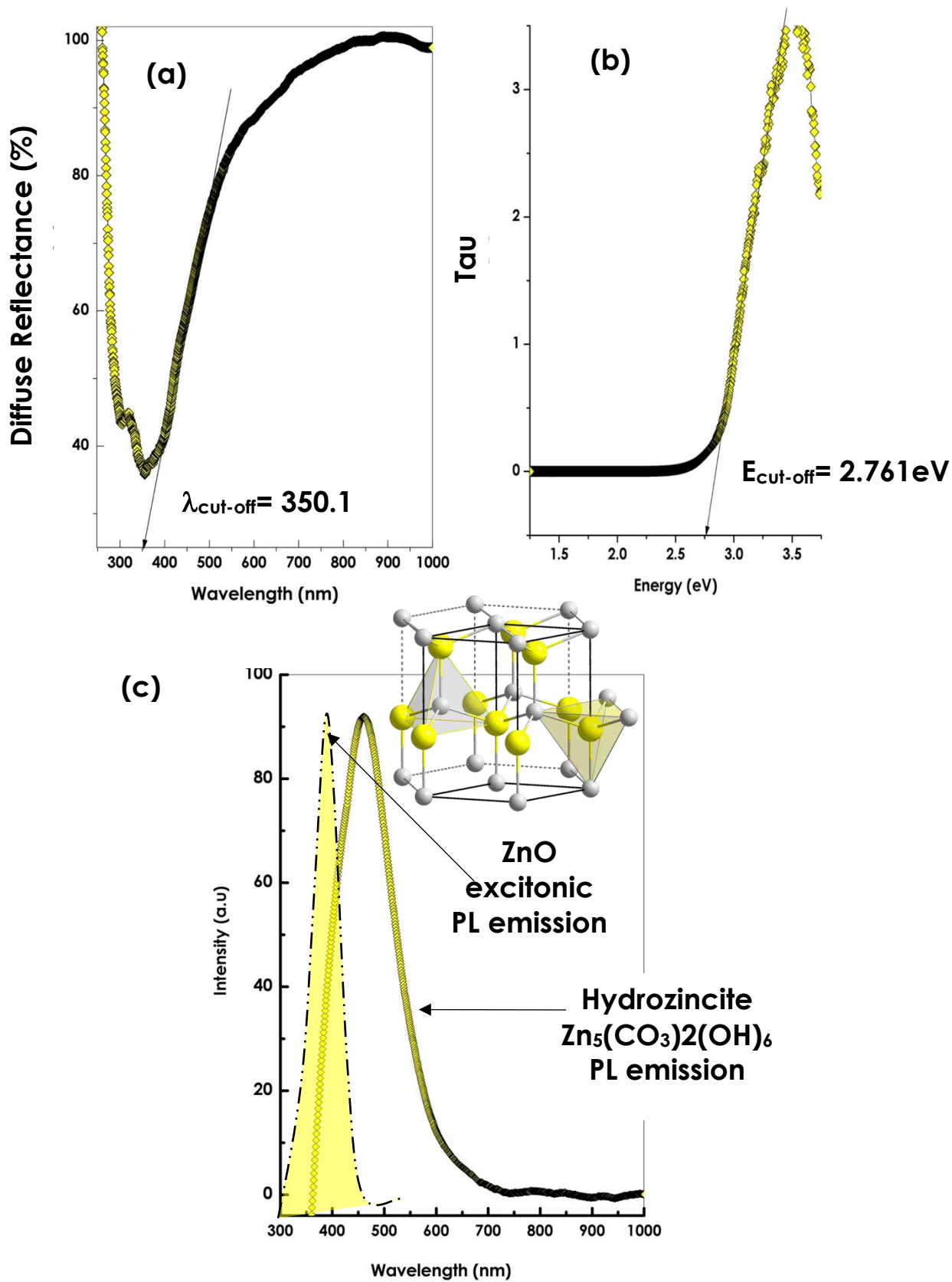


Fig.7: (a) Diffuse Reflectance, (b) its corresponding Tauc F(R) plot & (c) room temperature photoluminescence spectrum of the bio-engineered hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ nanoparticles.

2.6 Optical investigations

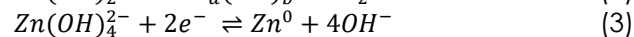
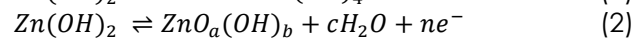
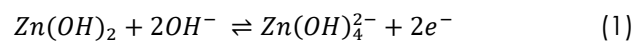
Fig.7 displays the Diffuse Reflectance Scattering (a) and the (b) Tau F(R) corresponding plot of the bio-engineered hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ nano-scaled powder. One can notice that the nanopowder is significantly reflective in the VIS, NIR & likely in the IR. The corresponding reflectivity within the NIR & IR spectral range is above 95% (Fig.7.a) which makes it a likely potential radiative cooling compound. Using the Tauc approximation, the optical band gap (E_g) was evaluated using the expression of $(\alpha h\nu)^2 = A(h\nu - E_g)$ [50], where α is the absorption coefficient, $h\nu$ is the photon energy in eV, E_g (eV) is the direct band gap and A is a constant. Yet this approximation is valid for semiconducting materials, it is used to appreciate the bandgap value & its nature (direct or indirect) for a variety of other compounds including Hydrozincite. In this case, the deduced bandgap value is about 2.761 eV (Fig.7.b). This value is far below of those reported in the literature so far. Indeed, this bandgap value which is assigned to the optical transitions of the excitonic states in hydrozincite is found to be within the range of 3.1eV-4.9eV [51, 52]. The derived value from the Tauc approximation of 2.761eV is not consistent with those reported in the literature. Henceforward, it is prudent considering the cut-off wavelength of 350.1 nm as likely to be the bandgap equivalent. The corresponding bandgap $E_g = E_{\text{cutoff}} = 1240/\lambda_{\text{cutoff}} \approx 3.542$ eV.

As a pre-conclusion, the bandgap of the bio-engineered Hydrozincite $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ is wide; 3.542eV, making it a potential candidate for UV-light applications.

In this regard, room temperature photoluminescence investigations were carried out. Fig7.c. displays such a response within the spectral range of 300-1000 nm. More accurately, the emission of the bio-engineered nano-scaled Hydrozincite exhibits a single blue emission centred at about $\lambda^{\text{MaxEmission}} \approx 457.3$ nm. Compared to the intrinsic photoluminescence of ZnO which is centred at about 380nm, this blue emission is relatively broad $\Delta\lambda \approx 125.8$ nm. This emission has been observed by Mao et al. [53]. Such an emission of the bio-engineered hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ nano-scaled powder may be attributed to native crystal defects like Oxygen vacancies (V_O) and Zinc interstitials (Zn_i). In the absence of yellow orange emissions, one could safely conclude on the absence of excess oxygen.

2.7 Electrochemistry investigations

Cyclic voltammetry (CV) studies were conducted to establish the electrochemical properties of the bio-engineered nanoparticles of hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$. The study was conducted in 1 M NaOH as supporting electrolyte at a scan rate of 25 mV/s, within a potential window of -0.4 to 0.6 V vs Ag | AgCl (in 3 M KCl). The results, presented in Fig.8.a show that bare GCE exhibited a featureless voltammogram, indicative of the absence of significant Faradaic processes. Upon modification with the bio-engineered nanoparticles of hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, an enhanced current response was observed, coupled with distinct Faradaic activity characterized by two anodic peaks at +0.07 V and +0.18 V (vs Ag | AgCl), and a cathodic peak at -0.16V (vs Ag/AgCl). Consistent with previous studies on Zn electrodes in alkaline media [54-55], the two anodic peaks may be attributed to sequential oxidation of Zn-based surface species, such as $\text{Zn}(\text{OH})_2$ to $\text{Zn}(\text{OH})_4$ (Eq. 1), followed by the possible formation of hydrated zinc oxide complexes $\text{ZnO}_a(\text{OH})_b$ as OH-species are depleted at the electrode surface (Eq. 2). The cathodic peak is then attributed to the reduction of $\text{Zn}(\text{OH})_4^{2-}$ to metallic Zn (Eq. 3).



The CV performance of the bio-engineered nanoparticles of hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ -modified electrode at varying scan rates (5 – 100 mV/s) is shown in Fig.8.b. At lower scan rates (5 – 25 mV/s), broader and less resolved anodic peaks were observed, suggesting diffusion-controlled process. At higher scan rates (50 – 100 mV/s), the peaks became sharper and shifted in potential, reflecting faster electron transfer kinetics [56]. The corresponding linear plot of anodic peak current (I_{pa}) versus the square root of scan rate (v)^{1/2} is shown in Figure 5c, confirming diffusion-controlled redox behavior in accordance with the Randles-

Sevcik model [57-58]. Electrochemical impedance spectroscopy (EIS) was used to investigate the charge transfer properties of the bio-engineered nanoparticles of hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$. The studies were conducted in 1 M NaOH supporting electrolyte over a frequency range of 0.1 – 100 kHz.

The Nyquist plots obtained are presented in Fig.8.c, with the insert representing the Randles equivalent circuit diagram used to fit the data. The circuit includes solution resistance (R_s), charge transfer resistance (R_{ct}), and a constant phase element (Q, modelled as admittance Y_0 with exponent n) representing non-ideal capacitive behavior. A summary of the fitted impedance data is shown in Table 1. Bare GCE exhibited a large semicircle with R_{ct} value of 845.84 k Ω , indicative of a likely sluggish electron transfer. After modification with the bio-engineered nanoparticles of hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, the semicircles diameters decreased significantly yielding lower R_{ct} value of 94.30 k Ω , demonstrating enhanced electron transport. These findings correlate well with the enhanced current response observed in the CV experiments. The constant phase element exponent, n , provides insights into surface characteristics values closer to 1 indicate a more ideal capacitive interface and smoother surface morphology, whereas lower n values reflect greater surface roughness and heterogeneous charge distribution.

Similarly, Y_0 is often associated with increased capacitance but must be interpreted in conjunction with n , as a high Y_0 value combined with low n may indicate surface disorder rather than efficient charge storage or charge transfer properties [59]. For the bio-engineered nanoparticles of hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ modified GCE, the admittance (Y_0) was estimated at 18.11 $\mu\Omega^{-1}\text{s}^n$ with $n = 0.83$.

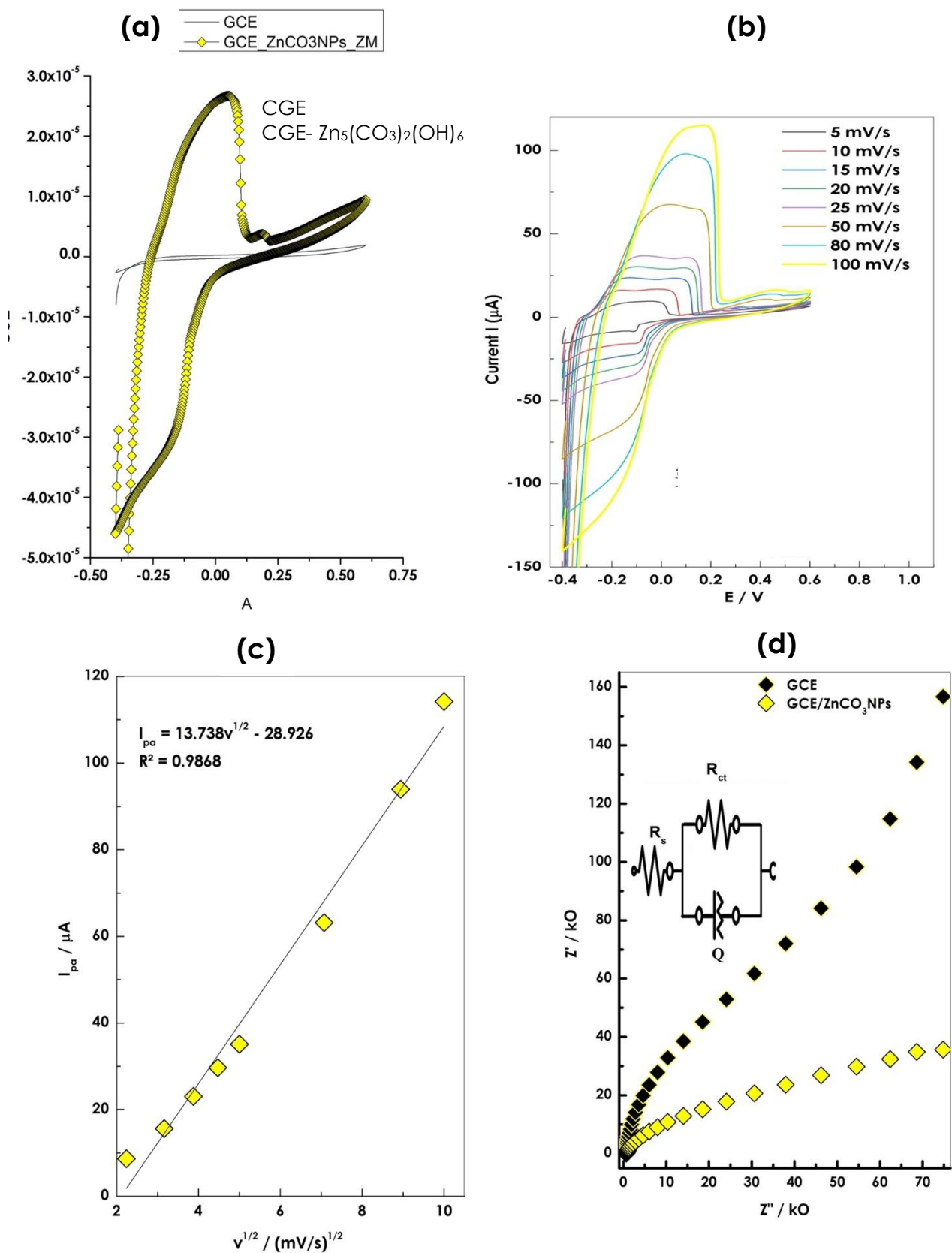


Fig.8: The C-V performance of the modified electrode of the bio-engineered nanoparticles of hydrozincite $Zn_5(CO_3)_2(OH)_6$ at varying scan rates (5 – 100 mV/s).

Table 1: Summary of the fitted impedance data for the bare GCE and ZnCO₃NPs modified GCE 1M NaOH supporting electrolyte. The values in brackets represent the percentage errors of the data fitting.

Electrode	Rs (kΩ)	Rct (kΩ)	Q		Chi-square
			Y _o (μΩ ⁻¹ s ⁿ)	n	
GCE	0.454 (0.49)	845.84 (6.16)	6.87 (0.732)	0.763	0.02752
GCE/ZnCO ₃ NPs	0.522 (0.89)	94.30 (5.04)	18.11 (1.87)	0.831	0.13216

3. Conclusion

Within this contribution, it was validated for the first time the possibility of bio-inspired conversion of CO₂ to single phase Hydrozincite Zn₅(CO₃)₂(OH)₆ using aqueous extracts of *Zea Mays var. saccharata* (ZMS). This latter has acted as an effective chelating/reduction agent. This innovative approach yielded crystalline hydrozincite Zn₅(CO₃)₂(OH)₆ with an average crystallite size of 38.5 nm under ambient conditions (Room temperature & Atmospheric pressure). Additionally, this method offers a potential pathway for CO₂ capture through carbonate incorporation. The Hydrozincite Zn₅(CO₃)₂(OH)₆ exhibited sound optical properties (High reflective response & Blue photoluminescence). Furthermore, a glassy carbon electrode (GCE) modified with the synthesized Hydrozincite Zn₅(CO₃)₂(OH)₆ demonstrated superior electrochemical properties evidenced by increased current response in CV and reduced charge transfer resistance in EIS compared to bare GCE. These findings suggest that the conversion of CO₂ to Hydrozincite Zn₅(CO₃)₂(OH)₆ synthesized by this bio-engineering approach hold strong potential for advanced electrochemical applications, including energy storage, supercapacitors, and sensors, with the added benefit of contributing to CO₂ mitigation strategies.

Competing interests

The author(s) declare no competing interests.

Contributions

K.K.M.: Conceptualization, Investigation, Data acquisition, Data Analysis, Writing – Original Draft. **M.A.:** Investigation, Data acquisition, Review & Editing. **H.M.:** Conceptualization, Data Analysis, Review & Editing. **R.B.:** Data acquisition, Review & Editing. **N.M.:** Review & Editing. **M.M.:** Conceptualization, Supervision, Writing, Data Analysis, Project administration, Review & Editing.

Acknowledgements

K.K.M., M.A., H.M., R.B., N.M., and M.M. express their gratitude to iThemba LABS, African Centre of Competencies in Enhanced Nanosciences and Nanotechnology for SDGs, and the UNESCO-UNISA Africa Chair in Nanoscience and Nanotechnology for research support and access to research facilities.

Funding

K.K.M. acknowledges the National Research Foundation (NRF) of South Africa for financial support (Grant No. PSTD240202203521).

Data availability

The data supporting the findings of this study are available from the corresponding authors upon reasonable request.

References:

- [1] E.J. Judd, J.E. Tierney, D.J. Lunt, I.P. Montañez, B.T. Huber, S.L. Wing, P.J. Valdes, A 485-million-year history of Earth's surface temperature, *Science*, 385 (2024) eadk3705 <https://doi.org/10.1126/science.adk3705>
- [2] J.S. Hoffman, P.U. Clark, A.C. Parnell, F. He, Regional and global sea-surface temperatures during the last interglaciation, *Science*, 355 (2017) 276-279 <https://doi.org/10.1126/science.aai8464>
- [3] P.J. Mayhew, M.A. Bell, T.G. Benton, A.J. McGowan, Biodiversity tracks temperature over time, *Proceedings of the National Academy of Sciences*, 109 (2012) 15141-15145 <https://doi.org/10.1073/pnas.1200844109>
- [4] IPCC, summary for policymakers, Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, IPCC, Geneva, Switzerland, 2023, pp. 1-34. <https://doi.org/10.59327/IPCC/AR6-9789291691647.001> (Accessed: 21 November 2025)
- [5] O.I. Nwali, M.A. Oladunjoye, O.A. Alao, A review of atmospheric carbon dioxide sequestration pathways; processes and current status in Nigeria, *Carbon Capture Science & Technology*, 12 (2024) 100208 <https://doi.org/10.1016/j.ccst.2024.100208>
- [6] J.C. Abanades, E.S. Rubin, M. Mazzotti, H.J. Herzog, On the climate change mitigation potential of CO₂ conversion to fuels, *Energy & Environmental Science*, 10 (2017) 2491-2499 <https://doi.org/10.1039/C7EE02819A>
- [7] M. Ahmadinia, S.M. Shariatipour, Analysing the role of caprock morphology on history matching of Sleipner CO₂ plume using an optimisation method, *Greenhouse Gases: Science and Technology*, 10 (2020) 1077-1097 <https://doi.org/10.1002/ghg.2027>
- [8] J. Xiaoyan, Z. Chen, CO₂ Storage in Deep Saline Aquifers, *Novel Materials for Carbon Dioxide Mitigation Technology*, Elsevier, 2015, (Accessed: 21 November 2025)
- [9] B. Uliasz-Misiak, J. Misiak, Underground Gas Storage in Saline Aquifers: Geological Aspects, *Energies*, 17 (2024) 1666
- [10] P. Ndlovu, R. Bulanga, L.L. Mguni, Progress in carbon dioxide capture, storage and monitoring in geological landform, *Frontiers in Energy Research*, Volume 12 - 2024 (2024) <https://doi.org/10.3389/fenrg.2024.1450991>
- [11] J.M. Matter, M. Stute, S.Ó. Snæbjörnsdóttir, E.H. Oelkers, S.R. Gislason, E.S. Aradóttir, B. Sigfusson, I. Gunnarsson, H. Sigurdardóttir, E. Gunnlaugsson, G. Axelsson, H.A. Alfredsson, D. Wolff-Boenisch, K. Mesfin, D.F.d.I.R. Taya, J. Hall, K. Dideriksen, W.S. Broecker, Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions, *Science*, 352 (2016) 1312-1314 <https://doi.org/10.1126/science.aad8132>
- [12] B.G. Miller, CO₂ Capture and Storage, *Clean Coal Engineering Technology*, Elsevier, 2010, <https://doi.org/10.1016/B978-1-85617-710-8.00010-8> (Accessed: 21 November 2025)
- [13] H. Mohamed, K. Hkiri, N. Botha, K. Cloete, S. Azizi, A.A.Q. Ahmed, R. Morad, T. Motlamane, A. Krief, A. Gibaud, M. Henini, M. Chaker, I. Ahmad, M. Maaza, Room temperature bio-engineered multifunctional carbonates for CO₂ sequestration and valorization, *Scientific Reports*, 13 (2023) 16783 <https://doi.org/10.1038/s41598-023-42905-5>
- [14] Q. Zhang, S. Wen, Z. Song, Y. Tang, Q. Feng, Advances in zinc oxide mineral flotation: Fundamentals, practices and perspectives, *Minerals Engineering*, 233 (2025) 109621 <https://doi.org/10.1016/j.mineng.2025.109621>
- [15] <https://www.le-comptoir-geologique.com/hydrozincite-encyclopedia.html> (Accessed: 25 November 2025)
- [16] R. Wahab, S.G. Ansari, Y.S. Kim, M.A. Dar, H.-S. Shin, Synthesis and characterization of hydrozincite and its conversion into zinc oxide nanoparticles, *Journal of Alloys and Compounds*, 461 (2008) 66-71 <https://doi.org/10.1016/j.jallcom.2007.07.029>
- [17] M. Maaza, M. Henini, F. Ezema, E. Manikandan, J. Kennedy, K. Bouziane, M. Chaker, A. Gibaud, A.K.F. Haque, Z. Nuru, I. Ahmad, R. Obodo, M. Akbari, Peculiar Size Effects in Nanoscaled Systems, *Nano-Horizons: Journal of Nanosciences and Nanotechnologies*, 1 (2022) 36 pages <https://doi.org/10.25159/NanoHorizons.9d53e2220e3>
- [18] M. Shamsipur, S.M. Pourmortazavi, S.S. Hajimirsadeghi, M.M. Zahedi, M. Rahimi-Nasrabadi, Facile synthesis of zinc carbonate and zinc oxide nanoparticles via direct carbonation and thermal decomposition, *Ceramics International*, 39 (2013) 819-827 <https://doi.org/10.1016/j.ceramint.2012.07.003>

- [19] B.D. Ngom, T. Mpahane, E. Manikandan, M. Maaza, ZnO nano-discs by lyophilization process: Size effects on their intrinsic luminescence, *Journal of Alloys and Compounds*, 656 (2016) 758-763 <https://doi.org/10.1016/j.jallcom.2015.09.230>
- [20] Y.-T. Pan, D.-Y. Wang, One-step hydrothermal synthesis of nano zinc carbonate and its use as a promising substitute for antimony trioxide in flame retardant flexible poly (vinyl chloride), *Rsc Advances*, 5 (2015) 27837-27843 <https://doi.org/10.1039/c5ra02987b>
- [21] R. Zhang, F. Zhang, J. Feng, Y. Qian, Green and facile synthesis of porous ZnCO₃ as a novel anode material for advanced lithium-ion batteries, *Materials Letters*, 118 (2014) 5-7 <https://doi.org/10.1016/j.matlet.2013.12.028>
- [22] T. Alhawi, M. Rehan, D. York, X. Lai, Synthesis of Zinc Carbonate Hydroxide Nanoparticles Using Microemulsion Process, *Procedia Engineering*, 102 (2015) 346-355 <https://doi.org/10.1016/j.proeng.2015.01.158>
- [23] V. Sharma, S. Basak, K. Rishabh, H. Umaria, S.W. Ali, Synthesis of zinc carbonate nanoneedles, a potential flame retardant for cotton textiles, *Cellulose*, 25 (2018) 6191-6205 <https://doi.org/10.1007/s10570-018-1962-5>
- [24] S.V. Dobrydnev, M.Y. Molodtsova, N.F. Kizim, Synthesis and study of basic zinc carbonate, *Russian Journal of Inorganic Chemistry*, 59 (2014) 798-800 <https://doi.org/10.1134/S0036023614080038>
- [25] T. Alhawi, M. Rehan, D. York, X. Lai, Hydrothermal Synthesis of Zinc Carbonate Hydroxide Nanoparticles, *Procedia Engineering*, 102 (2015) 356-361 <https://doi.org/10.1016/j.proeng.2015.01.161>
- [26] Z. Yang, W. Zhai, Identification and antioxidant activity of anthocyanins extracted from the seed and cob of purple corn (*Zea mays* L.), *Innovative Food Science & Emerging Technologies*, 11 (2010) 169-176 <https://doi.org/10.1016/j.ifset.2009.08.012>
- [27] P. Thiraphatthanavong, J. Wattanathorn, S. Muchimapura, W. Thukham-mee, P. Wannanon, T. Tong-un, B. Suriarn, K. Lertrat, Preventive Effect of *Zea mays* L. (Purple Waxy Corn) on Experimental Diabetic Cataract, *BioMed Research International*, 2014 (2014) 507435 <https://doi.org/10.1155/2014/507435>
- [28] P. Gullón, G. Eibes, J.M. Lorenzo, N. Pérez-Rodríguez, T.A. Lú-Chau, B. Gullón, Green sustainable process to revalorize purple corn cobs within a biorefinery frame: Co-production of bioactive extracts, *Science of The Total Environment*, 709 (2020) 136236 <https://doi.org/10.1016/j.scitotenv.2019.136236>
- [29] P. De Nisi, G. Borlini, P.A. Parizad, A. Scarafoni, P. Sandroni, E. Cassani, F. Adani, R. Pilu, Biorefinery Approach Applied to the Valorization of Purple Corn Cobs, *ACS Sustainable Chemistry & Engineering*, 9 (2021) 3781-3791 <https://doi.org/10.1021/acssuschemeng.0c08717>
- [30] A. Ashour, S. El-Sharkawy, M. Amer, A. Marzouk, A. Zaki, A. Kishikawa, M. Ohzono, R. Kondo, K. Shimizu, Production of Citric Acid from Corncobs with Its Biological Evaluation, *Journal of Cosmetics, Dermatological Sciences and Applications*, 4 (2014) 141-149 <https://doi.org/10.4236/jcdsa.2014.43020>
- [31] F.T. Thema, E. Manikandan, M.S. Dhlamini, M. Maaza, Green synthesis of ZnO nanoparticles via *Agathosma betulina* natural extract, *Materials Letters*, 161 (2015) 124-127 <https://doi.org/10.1016/j.matlet.2015.08.052>
- [32] N. Thovhogi, E. Park, E. Manikandan, M. Maaza, A. Gurib-Fakim, Physical properties of CdO nanoparticles synthesized by green chemistry via *Hibiscus Sabdariffa* flower extract, *Journal of Alloys and Compounds*, 655 (2016) 314-320 <https://doi.org/10.1016/j.jallcom.2015.09.063>
- [33] B.T. Sone, E. Manikandan, A. Gurib-Fakim, M. Maaza, Sm₂O₃ nanoparticles green synthesis via *Callistemon viminalis* extract, *Journal of Alloys and Compounds*, 650 (2015) 357-362 <https://doi.org/10.1016/j.jallcom.2015.07.272>
- [34] I.S. Okeke, K.K. Agwu, A.A. Ubachukwu, I.G. Madiba, M. Maaza, G.M. Whyte, F.I. Ezema, Impact of particle size and surface defects on antibacterial and photocatalytic activities of undoped and Mg-doped ZnO nanoparticles, biosynthesized using one-step simple process, *Vacuum*, 187 (2021) 110110 <https://doi.org/10.1016/j.vacuum.2021.110110>
- [35] K. Ssekatawa, D.K. Byarugaba, M.K. Angwe, E.M. Wampande, F. Ejobi, E. Nxumalo, M. Maaza, J. Sackey, J.B. Kirabira, Phyto-Mediated Copper Oxide Nanoparticles for Antibacterial, Antioxidant and Photocatalytic Performances, *Frontiers in Bioengineering and Biotechnology*, Volume 10 - 2022 (2022) <https://doi.org/10.3389/fbioe.2022.820218>

- [36] P.B.E. Kedi, F.E.a. Meva, L. Kotsedi, E.L. Nguemfo, C.B. Zangueu, A.A. Ntoumba, H.E.A. Mohamed, A.B. Dongmo, M. Maaza, Eco-friendly synthesis, characterization, in vitro and in vivo anti-inflammatory activity of silver nanoparticle-mediated *Selaginella myosurus* aqueous extract, *International Journal of Nanomedicine*, 13 (2018) 8537-8548 <https://doi.org/10.2147/IJN.S174530>
- [37] K.K. Masibi, O.E. Fayemi, A.S. Adekunle, E.-S.M. Sherif, E.E. Ebenso, Electrochemical Determination of Caffeine Using Bimetallic Au–Ag Nanoparticles Obtained from Low-cost Green Synthesis, *Electroanalysis*, 32 (2020) 2745-2755 <https://doi.org/10.1002/elan.202060198>
- [38] E. Ismail, M. Khenfouch, M. Dhlamini, S. Dube, M. Maaza, Green palladium and palladium oxide nanoparticles synthesized via *Aspalathus linearis* natural extract, *Journal of Alloys and Compounds*, 695 (2017) 3632-3638 <https://doi.org/10.1016/j.jallcom.2016.11.390>
- [39] A.T. Khalil, M. Ovais, I. Ullah, M. Ali, Z.K. Shinwari, S. Khamlich, M. Maaza, Sageretia Thea (Osbeck.) Mediated Synthesis of Zinc Oxide Nanoparticles and Its Biological Applications, *Nanomedicine*, 12 (2017) 1767-1789 <https://doi.org/10.2217/nnm-2017-0124>
- [40] A.K.H. Bashir, L.C. Razanamahandry, A.C. Nwanya, K. Kaviyarasu, W. Saban, H.E.A. Mohamed, S.K.O. Ntwampe, F.I. Ezema, M. Maaza, Biosynthesis of NiO nanoparticles for photodegradation of free cyanide solutions under ultraviolet light, *Journal of Physics and Chemistry of Solids*, 134 (2019) 133-140 <https://doi.org/10.1016/j.jpcs.2019.05.048>
- [41] S. Hameed, A.T. Khalil, M. Ali, M. Numan, S. Khamlich, Z.K. Shinwari, M. Maaza, Greener Synthesis of ZnO and Ag–ZnO Nanoparticles Using *Silybum Marianum* for Diverse Biomedical Applications, *Nanomedicine*, 14 (2019) 655-673 <https://doi.org/10.2217/nnm-2018-0279>
- [42] A.C. Nwanya, M.M. Ndipingwi, N. Mayedwa, L.C. Razanamahandry, C.O. Ikpo, T. Waryo, S.K.O. Ntwampe, E. Malenga, E. Fosso-Kankeu, F.I. Ezema, E.I. Iwuoha, M. Maaza, Maize (*Zea mays* L.) fresh husk mediated biosynthesis of copper oxides: Potentials for pseudo capacitive energy storage, *Electrochimica Acta*, 301 (2019) 436-448 <https://doi.org/10.1016/j.electacta.2019.01.186>
- [43] T. Motlhalamme, H. Mohamed, A.G. Kaningini, G.K. More, F.T. Thema, K.C. Mohale, M. Maaza, Bio-synthesized calcium carbonate (CaCO₃) nanoparticles: Their anti-fungal properties and application as nanofertilizer on *Lycopersicon esculentum* growth and gas exchange measurements, *Plant Nano Biology*, 6 (2023) 100050 <https://doi.org/10.1016/j.plana.2023.100050>
- [44] N. Matinise, A. Fall, Electrochemical and physical properties of magnesioferrite nanomaterial and photocatalytic degradation of methylene blue, *Scientific Reports*, 15 (2025) 2164 <https://doi.org/10.1038/s41598-025-85510-4>
- [45] S. Ghose, The crystal structure of hydrozincite, Zn₅(OH)₆(CO₃)₂, *Acta Crystallographica*, 17 (1964) 1051-1057 <https://doi.org/10.1107/S0365110X64002651>
- [46] K. Suzuki, H. Miyamura, J. Balachandran, One-pot hydrothermal synthesis of carbon dots-immobilized hydrozincite for ZnO-based nanocomposite lighting applications, *Journal of Asian Ceramic Societies*, 9 (2021) 1473-1480 <https://doi.org/10.1080/21870764.2021.1995939>
- [47] O. Długosz, Z. Chlebowska, M. Banach, Preparation of Materials Based on Metal Carbonate Nanoparticles for Photodegradation of Organic Pollutants, *Journal of Cluster Science*, 36 (2025) 55 <https://doi.org/10.1007/s10876-025-02773-7>
- [48] R.L. Frost, W.N. Martens, D.L. Wain, M.C. Hales, Infrared and infrared emission spectroscopy of the zinc carbonate mineral smithsonite, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 70 (2008) 1120-1126 <https://doi.org/10.1016/j.saa.2007.10.027>
- [49] R. S, S. Joghee, E. Alves, G. Bannimath, A. Susil, H. Harindaranath, A. Pilli, B.R.P. Kumar, A.S. Biswas, P.G. Achar, *Zea mays* L.: Nature's Pharmacy hidden in a cereal crop, *Pharmacological Research - Natural Products*, 8 (2025) 100351 <https://doi.org/10.1016/j.prenap.2025.100351>
- [50] J. Pankove, Optical processes in semiconducting thin films, *Thin Solid Films*, 90 (1982)
- [51] E. Turianicová, M. Kaňuchová, A. Zorkovská, M. Holub, Z. Bujňáková, E. Dutková, M. Baláž, L. Findoráková, M. Balintová, A. Obut, CO₂ utilization for fast preparation of nanocrystalline hydrozincite, *Journal of CO₂ Utilization*, 16 (2016) 328-335 <https://doi.org/10.1016/j.jcou.2016.08.007>

- [52] I. Yanase, S. Konno, Photoluminescence of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ nanoparticles synthesized by utilizing CO_2 and ZnO water slurry, *Journal of Luminescence*, 213 (2019) 326-333 <https://doi.org/10.1016/j.jlumin.2019.05.030>
- [53] J. Mao, X. Chen, T. Ling, X. Du, Strong blue emission from zinc hydroxide carbonate nanosheets, *Journal of Luminescence*, 177 (2016) 242-248 <https://doi.org/10.1016/j.jlumin.2016.05.006>
- [54] M. Cai, S.M. Park, Spectroelectrochemical Studies on Dissolution and Passivation of Zinc Electrodes in Alkaline Solutions, *Journal of The Electrochemical Society*, 143 (1996) 2125 <https://doi.org/10.1149/1.1836970>
- [55] S.E. Berrabah, A. Benchettara, F. Smaili, S. Tabti, A. Benchettara, Electrochemical investigation of ZnNPs and $\text{Zn}(\text{OH})_2$ NPs thin films behaviour grown on graphite rod by a two-step electrochemical conversion process, *Bulletin of Materials Science*, 47 (2024) 96 <https://doi.org/10.1007/s12034-024-03149-9>
- [56] A.J. Bard, L.R. Faulkner, H.S. White, *Electrochemical methods: fundamentals and applications*, John Wiley & Sons, 2022
- [57] Z. Masood, H. Muhammad, I.A. Tahiri, Comparison of Different Electrochemical Methodologies for Electrode Reactions: A Case Study of Paracetamol, *Electrochem*, 5 (2024) 57-69 <https://doi.org/10.3390/electrochem5010004>
- [58] N. Elgrishi, K.J. Rountree, B.D. McCarthy, E.S. Rountree, T.T. Eisenhart, J.L. Dempsey, A practical beginner's guide to cyclic voltammetry, *Journal of chemical education*, 95 (2018) 197-206 <https://doi.org/10.1021/acs.jchemed.7b00361>
- [59] F.A. Adesanya, O.E. Fayemi, Impedimetric pyrene determination at fMWCNTs/CuO-ZnO modified glassy carbon electrode, *Discover Applied Sciences*, 7 (2025) 396 <https://doi.org/10.1007/s42452-025-06822-8>