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Electrochemical preparation of nanostructure zinc oxide in emulsion deep eutectic solvents mixtures

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ABSTRACT

Deep eutectic solvents (DESs) offer important advantages over classical nano-metal oxides based on eutectic systems as a result of important characteristics based on forming significant molecular design and appropriate diminution molecules; they can be candidates as fundamental materials in electrochemistry applications, such as batteries, nanogenerators, and solar cells. In this study, an ethaline: oxaline 1:1 M ratio was successfully applied to synthesize uniform nano zinc oxide using polyaniline polymer molecules as an additive. The deep eutectic solvent system exhibited new and novel active media for synthesising ZnO nanoparticles. The addition of aniline and water molecules to DES media significantly supported the formation of zinc oxide nanoparticles. Nano zinc oxide was synthesised from extracted olive leaves. The olive leaves were extracted using digestion systems in aniline: ethaline: oxaline deep eutectic solvent systems. Deep eutectic solvent emulsions have been assessed as effective synthesis media in current electrochemical processes because they are inexpensive and environmentally friendly. They produce ZnO nanocrystals with 37 nm diameters dispersed in homogeneous reagents, whereas the morphology of ZnO nanocomposites prepared in a microemulsion exhibits significant structure and 50–100 nm ZnO nanoparticles. In electrochemical synthesis conditions, when using the electrochemical method, microemulsion systems were found to serve as enhancement media for forming special structures of ZnO nanocomposite cooperate together with aniline, exhibiting excellent electrochemical activity.

1. Introduction

Microemulsion deep eutectic solvents (MDESs) have emerged as a new type of liquid that can efficiently improve the functional features of nanoparticle dimensions with polymeric matrices.[1] The presence of deep eutectic solvents (DESs) in polymer systems facilitates the modification of different polymers' conductive properties (such as surface modifications), and the properties of the fabrication of the polymer matrix in the presence of semiconductor nanocrystal metals.[2-4] These nanocomposite systems were shown to be useful for many purposes; DESs contribute as highly effective solvents to the control of the electrical conductivity in a wide range of chemical applications in electronic devices.[5,6] Semiconductors with polymer matrices have performed well in multiple capacities, including medical applications[7] and solar cell systems.[8].

Although the literature includes many scientific efforts to improve ZnO nanoparticle synthesis methods,[9-11] there have been difficulties recovering sedimentation outcomes during the agglomeration of ZnO precipitates, as well as issues associated with the size distribution of nanoparticles. In contrast, microemulsion deep eutectic solvent systems offer potential as new-generation media capable of providing large interfacial surfaces and more spherical particle sizes with highly conductive surfaces and good stability compared with other traditional methods.[12] Although many studies have reported the creation of new nanocomposite compounds in aqueous systems, few studies have focused on synthesizing nano ZnO using microemulsion systems.[13-15] Rao et al. developed a method for creating ZnO, RuO2, and Ag nanowire composites mixed in polyaniline and polypyrrole polymer. The key limitation of their research was that they performed nanocomposite film production using vacuum-dried materials for two days at temperatures greater than 90 °C; such high temperatures probably changed the polymer molecules or decreased electrical conductivity.[16-18].

This study attempted to formulate ZnO nanoparticles in microemulsion deep eutectic solvents at room temperature using extracted olive leaves. The olive plant was extracted through digestion in emulsion (ethaline: oxaline: aniline) deep eutectic solvent systems. Emulsion deep

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eutectic solvents have been applied as green synthesis media in many electrochemical processes because they are inexpensive and environmentally friendly. This study also investigated the characterisation of ZnO particles with respect to DES mixtures.

2. Materials and methods

2.1. Preparation of samples

A mixture of 1 ethaline: 1 oxaline was prepared at room temperature using 0.05 mg of water.[19] The aniline (99.6 %, Fisher Scientific) and concentrated anhydrase oxalic acid, $C_2H_2O_4$, used were analytical grade (99.5 % Sigma Aldrich). The electrochemical experiments were performed at room temperature (25 °C). The microemulsion solvents were formed by mixing 0.05 mg of H_2O with DES mixtures [20].

2.2. Electrochemical cell set up

Classic reference electrodes were prepared for use in this study's electrochemical experiments. Constructed Ag/AgCl was prepared for use as an appropriate DES reference electrode.[22] A silver wire was immersed in a concentrated hydrochloric acid solution for approximately 20 min; then, the wire was placed in a 4 M AgCl solution in DESs. A Pt flag acted as a counter electrode; the working electrode was a Pt disc (homemade) type electrode with a surface area of approximately 1.882×10^{-3} cm^2, which was used in all the electrochemistry laboratory experiments. Cyclic voltammograms were produced for the electropolymerisation of ZnO added to 0.1 M aniline in oxaline: ethaline with a scan rate of 20 mV/s at 25 °C.

Deep eutectic solvents (DESs) were synthesized by combining an anion and a cation to form DESs. For oxaline, the quaternary ammonium salt choline chloride (ChCl) was mixed with oxalic acid as a hydrogen-bond donor (HBD). Ethaline was produced during the mixing of choline chloride as the anion and ethylene glycol (HBD) in a 1:2 M ratio.

The sample was then stirred in a 400 mL beaker and heated on a hot plate for approximately 2 h at 50 °C until a homogeneous liquid formed. Oxaline solvent was prepared using the same method, but changing the cation to oxalic acid, in a 1:1 M ratio to form a 1:1 (ChCl: oxalic acid) mixture. The ethaline and oxaline mixture was formed by adding equal quantities of ethaline to oxaline liquid in a beaker; this was then stored in sealed containers and left overnight in an oven at 40 °C. Several electrochemical instruments were used to analyse the nano ZnO manufactured using a DES mixture as the base solvent. First, the SIRION SEM scanning electron microscope was used to characterise the ZnO in the emulsion mixture. Next, an FTIR device (BRUKER–TENSOR–27) was used to determine the ZnO nanocomposite. The spectrum wave number ranged from 500 to 3900 Cm^{-1}.

2.3. Preparation of polyaniline

Electrochemical experiments were used to prepare aniline solvent as an additive material to support the emulsion content using a potential applied via a power supply. The electrochemical cell was arranged using three (working, reference, and counter) electrodes. The polymer was achieved in 0.1 M aniline in 1 ethaline: 1 oxaline using a 12% water solution at room temperature (25 °C).

2.4. Preparation of samples for extracting zn from olive leaves

Olive leaves were collected, washed with water, left until dried, and then ground in a mechanical blender for 15 min. The sample was left in DESs for 24 h. After the digestion process in DESs, approximately 25 g was dissolved in a 400 mL beaker in DESs. The mixture was stirred using a magnetic stirrer until a homogeneous solution formed. Electricity was applied to the mixture using a power supply with a potential of 5.0 V for approximately 2 h to produce ZnO.

3. Results and discussion

3.1. Cyclic voltammetry of nano ZnO with aniline polymer composite in different DESs

It was previously known that inorganic metal–polymer matrix nanoparticles could contribute to the realization of advanced and efficient conductive properties in non-aqueous systems. In this field, it has been reported that polymeris not essential for producing ZnO nanoparticles in protonation electrolytes [19,21].

The preparation of polymer nano ZnO in relatively deep eutectic solvents produces morphology phases in a manner dependent on a high proton concentration, i.e., strong acidity. The Abbott study emphasised that a polymer nanocomposite could only be prepared in systems when aniline was used in an emulsion system.[14] This important finding helped form other emulsion systems using water/ionic liquid mixtures to enhance particles' properties, such as their size, shape, and conductive properties, for a wide range of electrochemical applications. It was evident that ethaline mixed with oxaline produces a different current than ethaline: water mixtures do, as shown in Fig. 1 for the formation of nano ZnO in polyaniline in different DESs.

In addition, three anodic peaks were observed during the positive potential scan, whereas two cathodic peaks were observed during the negative potential scan. These peaks were attributed to the formation of polyaniline. After the third cycle, a composite of PANI with nano ZnO particles was formed in the DES mixtures, as shown in Fig. 1 a and b. Furthermore, a decrease in the current intensity of the redox peak was observed, which indicated dispersion of ZnO nanoparticles in the polymer matrix due to decreases in the electrolyte surface activity.

Comparing two DESs showed that adding oxaline to ethaline could dramatically increase polymer growth due to increasing emulsion systems; the polymer/ZnO oxidation peak at 0.5 V was related to the oxidation of ZnO nanoparticles in DESs.[21].

3.2. Characterisation of nano ZnO preparation

3.2.1. Morphology of ZnO in different aniline: DES mixtures

The morphology and images of manufactured ZnO nanoparticles are related to their electrochemical activities.[16,22,23] Fig. 2 (a) and (b) show SEM images of nano ZnO produced in two DESs (ethaline: aniline: water and ethaline: oxaline: aniline), which show an increase in the formation of ZnO particles compared to the images of DES systems without the addition of aniline and oxaline. The literature includes numerous verified methods regarding the importance of the additive polymer matrix in nanocomposites.[24] Previous studies reported that adding aniline molecules to the mixture tended to boost the emulsion function, which is primarily responsible for the similarity in the ZnO particles' structure in the polyaniline matrix due to aniline's structural direction in a doped state. However, ZnO's texture and porosity became more obvious in the presence of aniline. The diameter range for nano ZnO particles in polymer additives was approximately 27 to 52 nm for both DES mixtures, as shown in Fig. 2.

The influences of nanostructures were evidenced by differences in the nano ZnO morphology, which depends on how solvent molecules adhere onto the crystallites faces that developed in the crystal-growing direction of the nanoparticle unit cell. Surface energy is also controlled by solvent properties, such as morphology. For example, Fig. 2 illustrates obvious differences in surface energy in system solvents a and b; significantly more rapid growth was induced in the upper surface energy planes than in the lower growth planes.

3.2.2. FTIR spectra properties of nano ZnO

To fully understand the influences of aniline molecules in the formation of ZnO particles, FTIR was used to determine the appearance of interactions between zinc and polyaniline molecules. It was evident that polyaniline molecules' stretching and vibration peaks in bands C = N

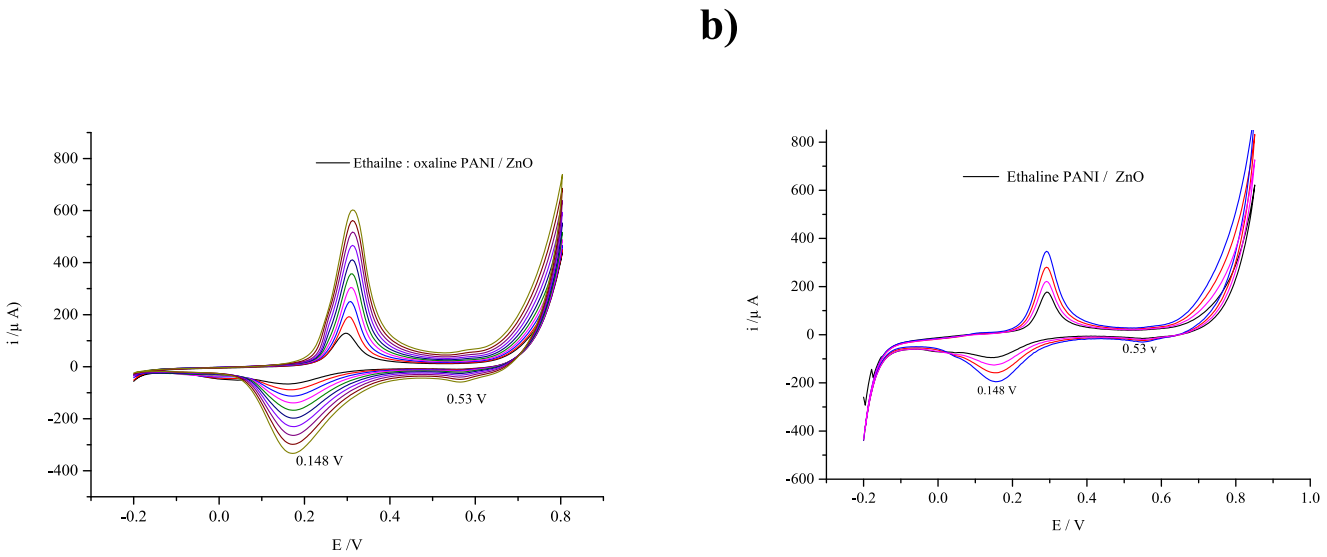


Fig. 1. Cyclic voltammograms for electropolymerisation of ZnO nanocomposite: **(a)** 0.1 M aniline in oxaline: ethaline and **(b)** 0.1 M aniline solutions in ethaline media, with a scan rate of 20 mV/s.

and C = C at wave numbers between 1683 and 1425 cm^{-1} referred to the benzenoid form. However, C-N stretching was the benzenoid circlet type, and wasindicated at 1244 cm^{-1}.

The C-H bond documented in the chart at 807.9 cm^{-1} and 872.1 corresponded to the monosubstituted aromatic group present in the aniline monomer for conductive polymer molecules.[24] However, Fig. 3 a) shows that the absorption peaks for the band between 1205 and 1900 occurred at the same time as the interaction between ZnO particles and polyaniline molecules, which formed a bonding N-H group of ZnO and polyaniline. The existence of the wave numbers from 515 to 808 cm^{-1} was based on the formation of ZnO. Previous studies reported the same interaction behaviours between ZnO nanocomposite and polyaniline structure.[25].

3.2.3. AFM measurements

The formation of ZnO nanoparticles was investigated to study the sizes of the nanostructures corresponding to ionic liquid categories; these were characterised by determining the structure properties and particles grown size in solvent systems. Notably, the nature of the DES system in each reaction combination was controlled by its chemical and physical properties. In many cases, the nanostructure changed even when pure deep eutectic solvents were applied as a base solvent. For example, oxaline and reline water mixtures, which have long hydrophobic tails, classically offer high active properties similar to those in surfactant systems. The two DES types had obviously different patterns in the highly resolved AFM images recorded at room temperature, as shown in Fig. 4; nano ZnO synthesis in ethaline: oxaline increased more than it did in ethaline: water mixtures in the presence of the same polymer molecules.

3.2.4. X-ray diffraction analysis

The XRD technique was used to explore the crystalline structure properties for various nano ZnO crystallite sizes. The X-ray diffraction data for the electrochemical current method revealed nano zinc oxide, as shown in Fig. 5. The x-axis represented peaks at 2θ in different places (31.29137°, 34.0888°, 36.0505°, 47.0899°, 56.4611°, 62.6105°, 66.0751°, 67.7059°, 68.9442°, and 76.5282°) associated with relative crystal planes, as shown in Fig. 5. The Scherrer equation was applied to calculate the obtained nano ZnO's average particle size, as follows:[26].

$$D = \frac{0.94\lambda}{\beta(hkl)cos\theta(hkl),} \quad \ldots\ldots\ldots\ldots\ldots (1).$$

where D is the size of crystal growth, θ acts as the angle of reflection, K refers to the Scherrer constant = 0.94, β represents the full width at half maximum of the diffraction peak, and λ refers to the wavelength of lights to the diffraction at (λ = 1.54 Å).[22].

3.2.5. Characterization for ZnO/polymer using transmission electron microscopy

TEM was applied to examine the shape and particle size distribution of ZnO. Fig. 6 shows the TEM images at resolutions of 100, 200, and 500 nm. All the photos illustrate organized development with spherical particle sizes. The particle distribution was estimated, and the results corresponded with those of the XRD data.

3.3. Ultraviolet-Vis spectroscopy measurements (UV–Vis)

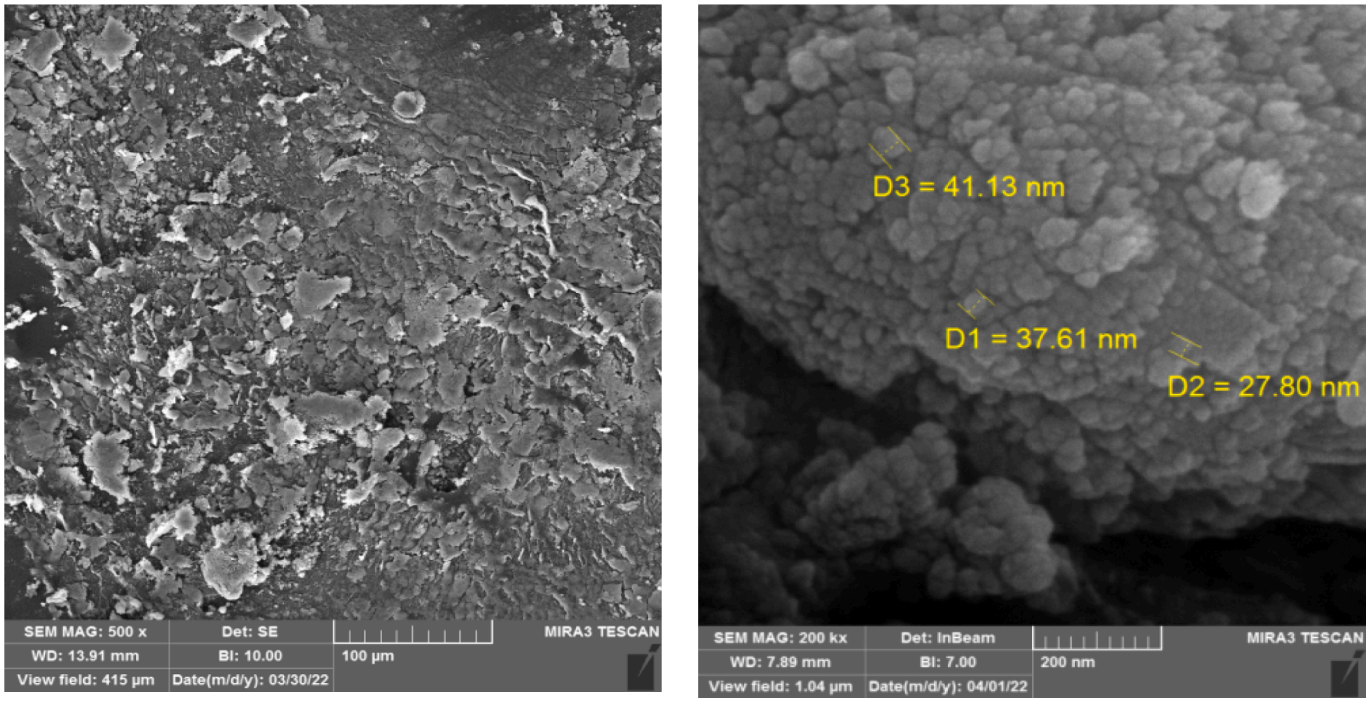
The reaction species for ZnO and polyaniline was examined using UV–Vis spectroscopy. The absorption wavelengths for ZnO nanoparticles were observed to be 343 nm. However, wavelengths of 290, 605, and 670 nm were observed in aniline solution in polymer form. [24,25] Fig. 7 a) clearly shows the interfaces of the aniline polymer molecules with nano ZnO nanoparticles; the diagram illustrates a shift from polyaniline with ZnO compared with the absorbance of pure polyaniline solutions. The observed polaron absorption region's intensity indicated minimization of the doping level regions; this was a result of increasing radical cation sizes for particles in the polymer matrix. [24,25] The same context revealed a decrease in the intensity of the π-polaron absorption band at 670 nm due to nano ZnO's contribution to doping development [26–32].

The prepared nano ZnO samples' band gaps were measured using a Tauc plot; the diffraction of band gaps to relative ZnO nanoparticles synthesized for each DES were calculated. The absorbance scan for photo-absorption energy (hv) showed a maximum absorbance from 2.98 to 3.06 eV, comparable to the ZnO nanoscales produced in DES systems. Table 1 shows the comparison values for the band gaps and energy absorption maxima for ZnO in DESs using previously reported data. ZnO nanoparticles formed in ethaline: oxaline: aniline systems had higher absorption energies than those formed in ethaline: water: aniline at approximately 3.06 eV.

4. Conclusion

This study focused on microemulsion DESs and their application as alternative solvents for synthesising nano ZnO, a new electrochemical method for producing nano ZnO from olive oil. Using DESs as creative

a) Ethaline: oxaline: aniline



b) Ethaline: water :aniline

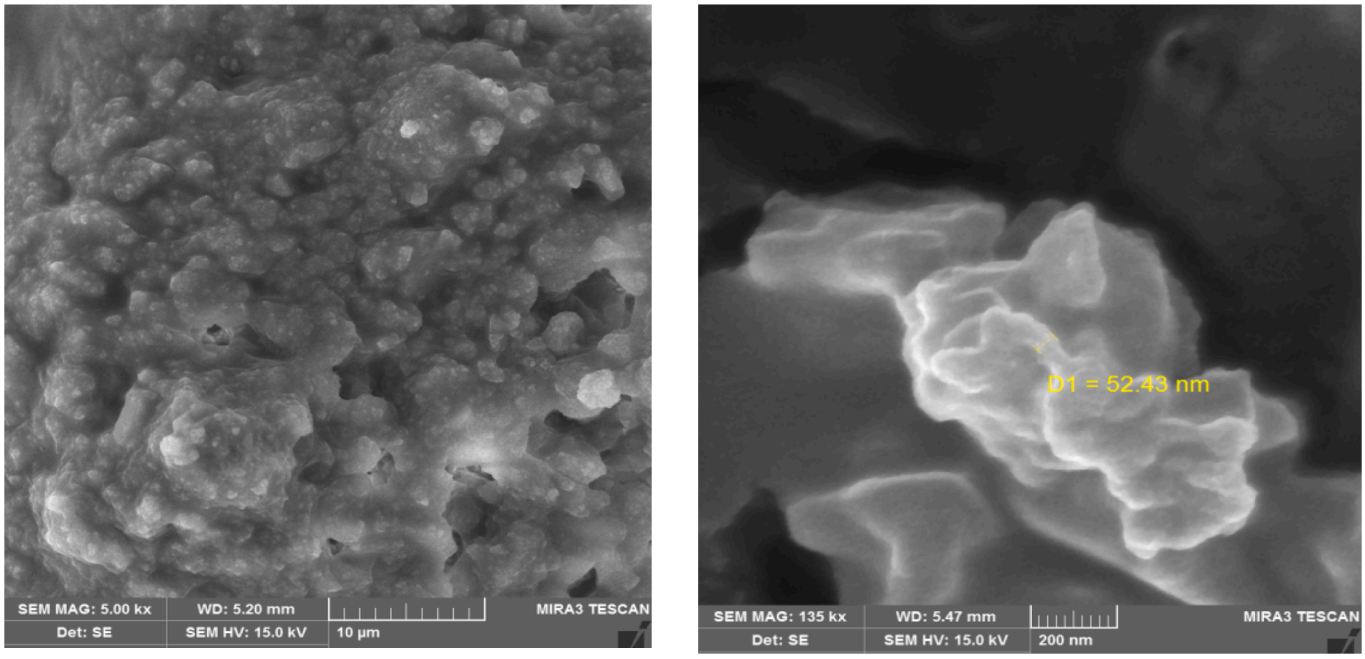


Fig. 2. SEM images showing the morphology of ZnO nanostructures with 0.1 M aniline in two DESs: **a)** ethaline: oxaline: aniline and **b)** ethaline: water: aniline.

solvents for this type of nano-metal oxide can reveal new methods for forming nano-metal oxides in emulsion DES systems for use in different applications. This is because nano-metal oxide DESs fundamentally do not evaporate (and are therefore thermally stable up to 700 °C) and also because many DESs operate as unique nano ZnO media, as shown in this study. TEM and AFM data confirmed a uniform matrix. The electrochemical process indicated the presence of nano ZnO in polymer using SEM and XRD, and the particle nature of the produced nanocomposites was described. A new ZnO generation based on polyaniline formed an exemplary composite with an improved electric band gap in DES media; this is significant for a wide range of electrochemical applications. Ethaline: oxaline: aniline was found to be a better medium for forming nano ZnO particles than ethaline: water: aniline mixtures. SEM and XRD demonstrated that the ZnO nanoparticles prepared in polymer yielded a crystalline nature in the polymer nanocomposite, which was also indicated by the electrochemical results. An improved electric band gap using DES media was achieved using nanostructured ZnO based on conductive polyaniline; this significant finding can be easily applied in a

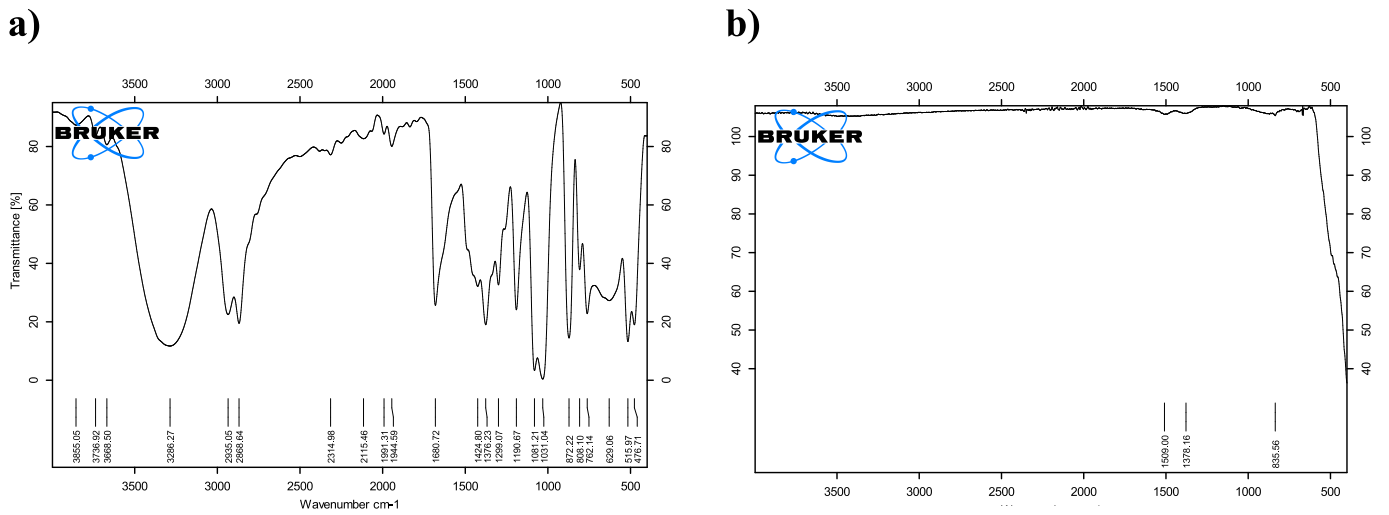


Fig. 3. FT-IR spectra in ethaline: oxaline for (a) addition of emulsion polymer aniline-ZnO in ethaline: oxaline and (b) crystal production of nano ZnO particles at room temperature.

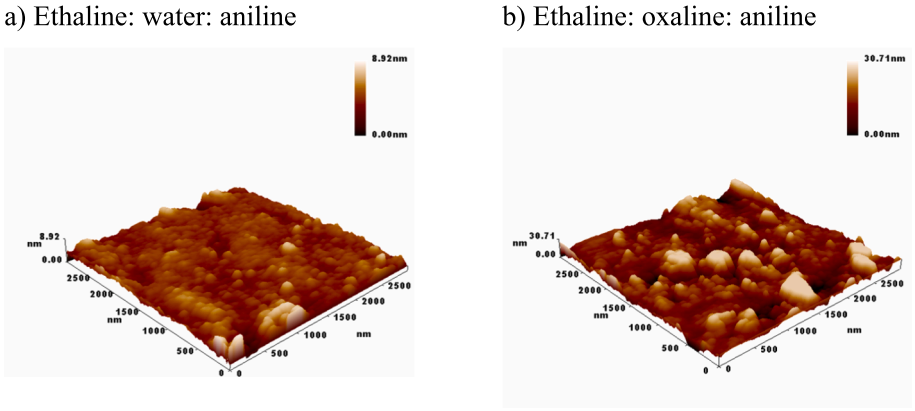


Fig. 4. AFM images for different nano ZnO/PANI in DESs: a) ethaline: water: aniline and b) in ethaline: oxaline: aniline mixtures.

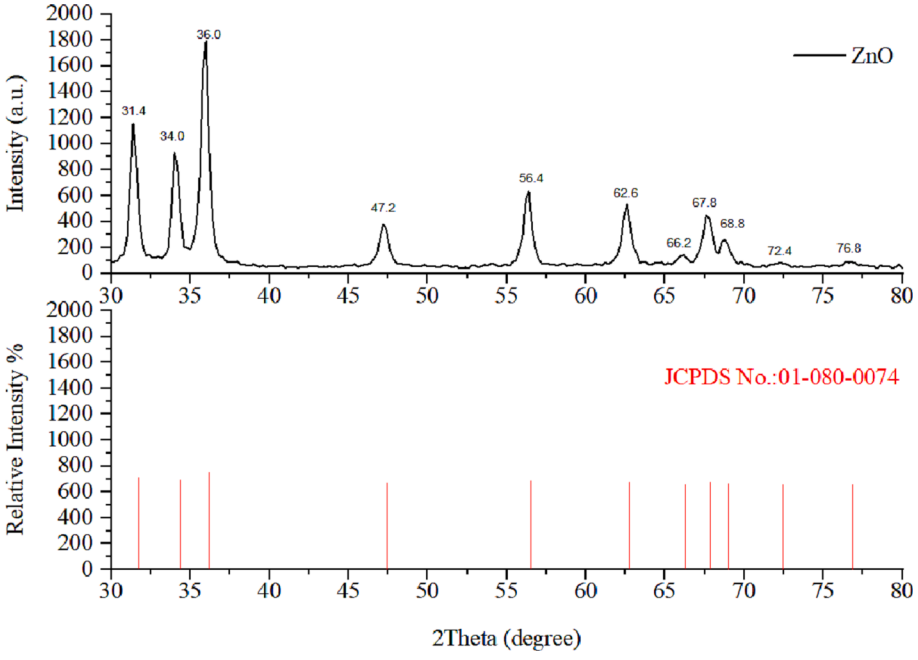


Fig. 5. X-ray diffraction pattern of nano ZnO in ethaline: oxaline at 25 °C produced using 0.1 M polymer molecule (aniline).

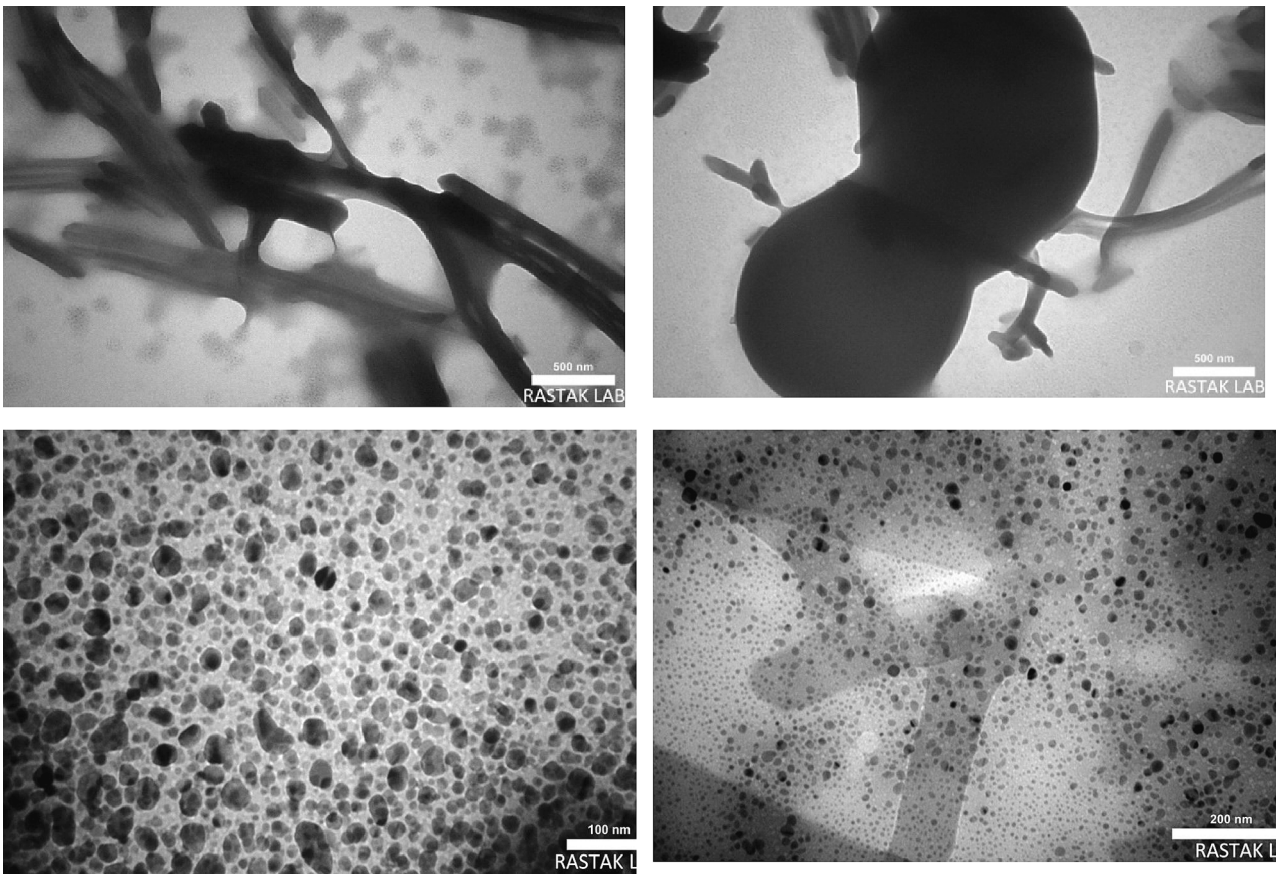


Fig. 6. TEM morphology and particle size for nano ZnO in 0.1 M aniline in ethaline: oxaline mixture.

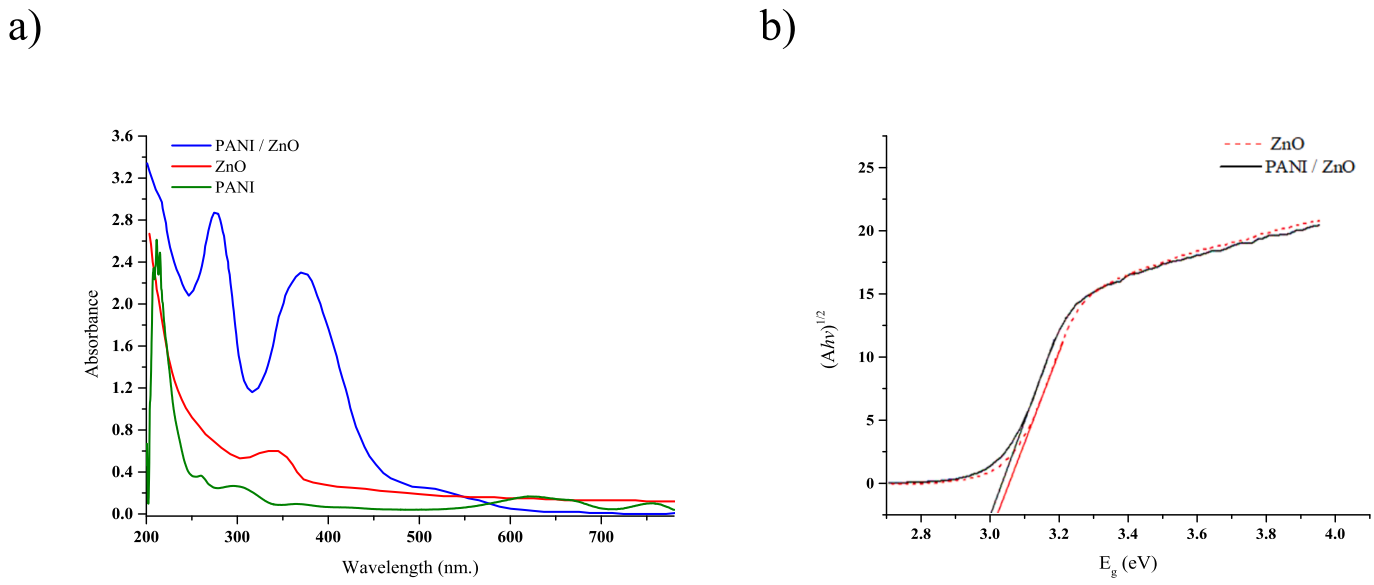


Fig. 7. A) spectra uv–Vis measurements for polymer nano ZnO in DES mixtures and b) ZnO's optical band gap in the presence of 0.1 M aniline in ethaline: oxaline at room temperature.

wide range of electrochemical applications, such as solar systems and microchemical sensors.

CRediT authorship contribution statement

Ahmed Z.M. Al-Bassam: Funding acquisition, Writing – original draft, Investigation, Validation, Software, Conceptualization, Methodology. **Sahar S.M. Alabdullah:** Supervision, Writing – review & editing, Data curation, Investigation, Resources, Formal analysis, Validation, Software, Conceptualization. **Dhuha H. Fadhil:** Funding acquisition, Project administration, Visualization, Resources, Investigation, Validation, Conceptualization.

Table 1
Comparison of nano ZnO band gap measurements using verity DESs and other methods.

Solvent type	Optical band gap	Energy (*hv*) at maximum absorption (eV)	References
Ethaline: Oxaline	3.06 ± 0.04	3.03 ± 0.03	Current work
Ethaline: Water	3.00 ± 0.04	3.06 ± 0.04	Current work
Toluene: Water	3.33 ± 0.03	3.33 ± 0.03	[27]
DMF: Water	3.40 ± 0.04	3.20 ± 0.04	[27]

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. no financial interests.

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