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Green Synthesis of ZnO/CuO Nanocomposite Using *Punica granatum* for the Enhanced Photocatalytic Performance

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Abstract

Zinc oxide nanoparticles (ZnO NPs) and zinc oxide/copper oxide (ZnO/CuO) nanocomposites were constructed via green-synthesis route involving the use of *Punica granatum* seed extracts through microwave method. The as-synthesized samples were investigated for their catalytic activities. The fabricated nanomaterials were characterized using UV-visible spectroscopy (UV-vis), X-ray diffraction (XRD), Energy dispersive spectroscopy (EDS), Dynamic light scattering (DLS) spectroscopy, Field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). The peak observed at 385 nm in the surface plasmon resonance of ZnO NPs suggests the formation of nanoparticles of different sizes. The successful synthesis of composite was inferred from the shifting of UV-vis absorbance peak. Furthermore, the band gap energy of ZnO/CuO (with 10 wt.% of CuO precursor) was obtained to be 2.52 eV which was found lesser than that of nanoparticles. Phase morphology studied *via* XRD revealed the nanoparticles of crystalline nature. The mean crystallite size of extract mediated ZnO NPs and ZnO/CuO nanocomposites were found to be 61.5 and 53 nm, correspondingly. Similarly, morphological analysis of as-synthesized nanoparticles *via* HR-TEM showed the irregular to roughly spherical shape with size 100-200 nm. Nanomaterials generated in this manner were employed for the catalytic reduction of toxic 4-nitrophenol. The ZnO/CuO (with 10 wt.% of CuO) nanocomposites showed the higher degradation efficiency towards reduction of 4-nitrophenol compared to ZnO/CuO (5 wt.%) nanocomposites.

Keywords: *Dynamic light scattering, ZnO/CuO, Punica granatum, nanocomposites, 4-nitrophenol*

1. Introduction

Researchers are being fascinated by the synthesis of metallic nanomaterials such as silver, gold, copper, zinc, titanium, and oxides such as TiO_2, ZnO, CuO, and SnO_2 for their redox active and semiconducting characteristics (Hashemi, 2016; Elena Sanchez-Lopez, 2020; Shume, 2020). Among these, ZnO is regarded as one of the most versatile nanoparticles for easy availability, chemical stability, environmentally benign nature, crystalline nature, optical activeness, catalytic propensity and many other properties (Zanni *et al.,* 2016; Sapkota *et al.,* 2019; Matsubura *et al.,* 2003; Hochepied *et al.,* 2004). Specifically, ZnO is an n-type semiconductor exhibiting wide bandgap of 3.37 eV and large exciton binding energy 60 meV along with interstitial oxygen vacancies in its crystalline state of ZnO (Yulizar *et al.,* 2018; Li 2020). Owing to the unique properties, ZnO and its composites are turned to be the materials of choice for optoelectronic devices (Sapkota *et al*., 2020).

Metal oxide nanocomposites have emerged as the materials of choice for materials with superior physicochemical properties, both in the industrial and academic sectors (Osman & Mustafa 2015). Among the various kinds of nanocomposites, ZnO/CuO nanocomposites have great potential in advancement of photonic, electronic devices, photovoltaic, light emitting diode (LED) lasers, UV detectors, solar cells, transistors, cosmetics, and textile industries (Li 2020; Arujo Junior 2017; Mirzaei *et al.,* 2009). Similarly, the nanocomposites have displayed antimicrobial activity as well as great biomedical significance (Shehu *et al*., 2020; Widiarti *et al*., 2017); Bairamy *et al.,* 2020). Overviewing literatures available, catalytic efficiency of nanocomposites have been remained as the preferred topic of research for removal of heavy metal ions, organic, and inorganic pollutants (Sakib *et al*., 2019).

In general, numerous physical and chemical procedures such as precipitation, sol-gel, sonochemical, solvothermal, hydrothermal, polyol, and so on are widely used in synthesis of the nanocomposites (Buzar *et al.,* 2019). Basically, physical and chemical methods mainly involve the use of high temperature, pressure and toxic chemicals. High temperature and pressure are difficult to handle and the toxic chemicals may coat over the synthesized nanomaterials. As a consequence, such methods are producing some toxic nanomaterials which thus have very limited applications. Hence, the fabrication of nanomaterials needs environmentally clean and cost-effective green approach. Accordingly, the method of synthesis of nanomaterials has shifted to green synthesis. The green synthesis process is essentially carried in the presence of non-toxic chemicals as solvent and precursors for the synthesis of nanomaterials. Regarding green synthesis, variety of naturally available benign materials such as extracts from fruits, tree bark, stem, leaves, flowers, fruit peel, seed rhizomes and even microorganisms are commonly used for the synthesis of nanomaterials (Aboud 2014; Mohammadian *et al.,* 2018).

Although the literature contains enough reports on green synthesis and their different applications, synthesis of ZnO/CuO nanocomposites using pomegranate seed extracts and microwave technique has rarely been found. Moreover, the available reports do not provide in-depth details of the synthesis and application. Therefore, we used pomegranate seed extract as the

mediator of microwave assisted synthesis of ZnO/CuO nanocomposites. Pomegranate belongs to the family *Lythraceae*. The genus *Punica* of this family contains fruit bearing trees, which can possess sugar, tannins, gallic acid, ellagic acid, flavonoids, etc in their fruits (Topalovic *et al.,* 2021). Thus, assuming pomegranate seeds to be good reducing and stabilizing agents, they were selected for the synthesis of ZnO nanomaterials and ZnO/CuO nanocomposites.

People of the current era are well acquainted with the problem of polluted water which is due the release of toxic effluents from various chemical industries like textile, cosmetic, pharmaceutical, paper, food, pesticides etc. A phenolic pollutant, 4-nitrophenol is one of the hazardous chemicals that is commonly present in the waste water from pharmaceutical and pesticide industries. Degrading such harmful carcinogenic and mutagenic organic pollutants from wastewater seems to be one of the urgent tasks these days (He *et al.,* 2019; Almeida *et al.*, 2020).

Present research work mainly emphasizes the synthesis of ZnO/CuO nanocomposite using pomegranate seed extract assisted by microwave technique to explore the catalytic activity of the nanocomposites on degrading 4-nitrophenol.

2. Materials and methods

2.1 Chemicals

Zinc(II) nitrate and copper(II) acetate monohydrate were used as purchased without the further purification as the precursors for ZnO and CuO, respectively. Distilled water (DW) was employed to work out all solutions.

2.2 Green synthesis of zinc oxide nanoparticles (ZnO NPs)

Pomegranate (*Punica granatum*) fruit was purchased from a local fruit shop. Its juice extract was prepared simply by crushing the fresh pomegranate seeds with the help of a mortar and removing the unnecessary solid residue through filtration. ZnO NPs were synthesized adding (5M) NaOH dropwise to the mixture of precursor (3.47g of zinc nitrate in 100 mL DW) solution till the pH was set between 9-10. The resulting mixture was mixed with the extract prepared by mixing DW and juice (DW: juice = 80:20 v/v) under stirring condition. Then, the mixture was subjected to microwave system in the household microwave oven (2.45 GHz and 1000 W), and the sample so formed was collected after purification using centrifugation at 3,500 rpm and drying at 60 ºC for 24 h. Similarly, zinc oxide nanoparticles were synthesized by chemical precipitation using microwave irradiation following the previous protocol with slight modification (Mohammadi-Aloucheh *et al.,* 2018).

2.3 Synthesis of zinc oxide/copper oxide (ZnO/CuO) nanocomposites

ZnO/CuO composites of varied concentration (5 and 10% CuO precursor by weight) were prepared using the green synthesis method as described in section 2.2. The pH of the solution was adjusted between 9 and 10 by adding aqueous solution of NaOH (5M) dropwise and then the solution was exposed to microwave irradiation for 10 min. The as-synthesized precipitate was subjected to repeated washing and centrifugation process and finally allowed to dry at 60 ºC for 24 h. The composition of all the samples so prepared is presented in table 1.

Table 1: Composition of nanoparticles

Sample	$Zn(NO_3)_2$ (g)	$Cu(CH_3COO)_2$ (g)	% wt. of CuO precursor in ZnO/CuO	DW/Ext (mL)
a	3.47	-	-	100/0
b	3.47	-	-	80/20
c	3.127	0.347	10	80/20
d	3.297	0.173	5	80/20

Samples 'c' and 'd' are designated as ZnO/CuO (5%) and ZnO/CuO (10%), respectively.

2.3 Characterization techniques

As-synthesized nanomaterials were characterized utilizing a double-beamed UV-vis spectrophotometer (Model LT-2802) in wavelength range of 200-700 nm, X- ray Diffraction (XRD, Rigaku Smart Lab) having Cukα (λ = 1.54 Å) radiation at Bragg's angle (2θ) = 5 ° to 90°. The crystallite size (D) of the nanomaterials was computed by using Scherrer equation (Equation 1) (Pradhan et al., 2020).

$$D = 0.94\lambda/\beta\cos\theta \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

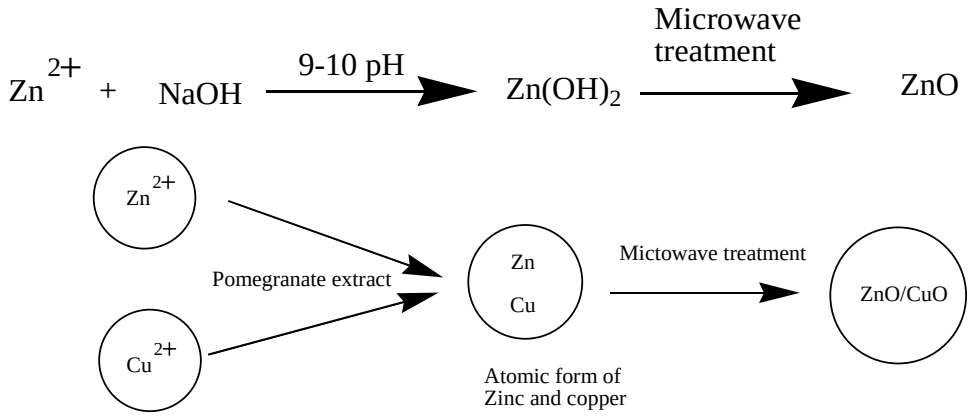
Where, λ = wavelength (CuKα) of X-ray, β = full-width at half maximum (FWHM) and θ = Bragg's angle. Similarly, elemental composition and size of the samples was determined via Energy Dispersive X-ray Spectroscopy (EDS, Hitachi SD-8230) and dynamic light scattering (DLS) (HORIBA SZ-100) was used. The surface morphology of the nanocomposites was investigated by Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi SD-8230 and High-Resolution Transmission Electron Microscopy (HR-TEM, JEM-2010, JEOL, Japan). Catalytic activity was studied by reacting 2 mL of aqueous 4-nitrophenol (1 mM) and 4 mL of freshly prepared $NaBH_4$ (0.33 mM) in the presence and absence of nanomaterials under UV light. Degradation reaction of 4-nitrophenol was studied via UV-vis spectrophotometer at room temperature at regular interval of time (1 minute).

3. Results and discussion

3.1 Visual observation

Preliminarily, the solutions of ZnO NPs without extract were appeared to be clearly white when observed through naked eye. Similarly, other samples ZnO/Ext NPs, ZnO/CuO 5 % and 10 % appeared to be of purple, blackish green. In general, change in colouration of the reacting solution indicates the bio-reduction of the precursor salt solution which indicates the formation of nanomaterial *via* biosynthesis (Barzinjy 2020). The literature revealed that naturally available phytochemicals occurring in the plant extract act as the benign reductant and stabilizing agent for

the nanomaterials. Thus, the phenols, flavonoids and ellagic acids present in pomegranate extract play the role of reducing agent and the higher temperature offered by microwave help for forming ZnO NPs. Similarly composites of ZnO/CuO are formed by green method and possible reactions are depicted in the scheme 1. First reaction shows the formation of ZnO NPs *via* chemical method and second reaction glimpses the green synthesis of ZnO/CuO nanocomposites.



Scheme 1: Schematic representation of ZnO NPs and ZnO/CuO nanocomposites formed via microwave technique in the absence and in presence of pomegranate extract.

3.2 UV-visible spectroscopic analysis

The UV-vis spectra of as-synthesized samples (ZnO with, without extract and its CuO nanocomposites of varied 5% and 10% are presented in **Fig. 1.**

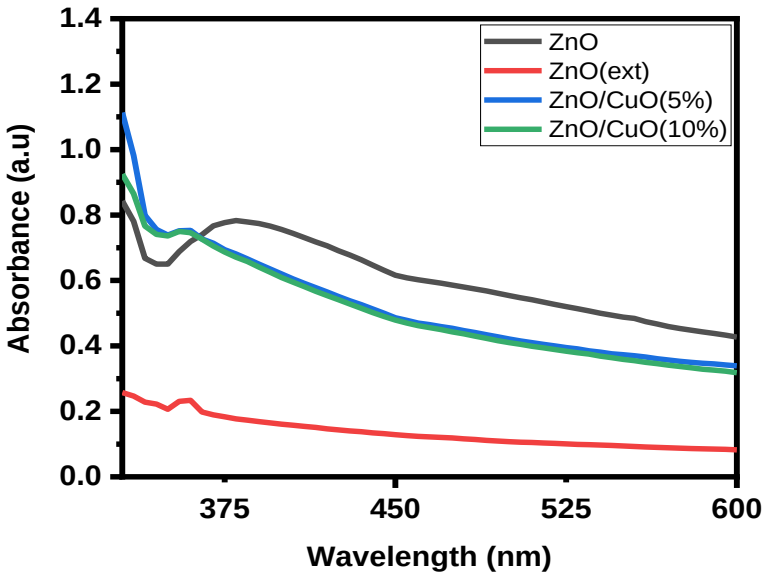


Fig. 1: UV- vis spectra of the ZnO, ZnO (Ext), ZnO/CuO (5%) and ZnO/CuO (10%).

The UV-vis spectra of ZnO NPs without extract (**Fig**. **1**), shows broad absorption peak at 385 nm suggesting the formation of ZnO NPs of different size. It has been known that surface plasmon resonance observed attributes for transition of electrons present in the surface of ZnO NPs (Balaraj *et al.,* 2017). Similarly, the UV-vis absorption peak of ZnO/Ext is observed at 360 nm, showing blue shift with respect to ZnO NPs without extract. The blue shift suggested for quantum confinement effect due to smaller sized nanoparticles (Chen *et al.,* 2019; Elumalai *et al.,* 2015).

UV-vis spectra of extract mediated ZnO/CuO nanocomposites of 5 and 10 wt.-% show absorption peaks at around 353 nm revealing blue shift with respect to pure ZnO with and without extract. The shifting of UV-vis absorption peak infers for the formation of nano-composites of smaller size. The result shown here is in agreement with that of the literature (Mohammadi-Aloucheh *et al.,* 2018). At the same time, in the spectra of nanocomposites, the intensity of the peak is increased with increase in wt.% of CuO due to formation of greater number of NPs (Mohammadi-Aloucheh *et al.,* 2018). Hence the results conclude that the pomegranate extract acts the vital role for forming ZnO NPs and the nanocomposites as well. Furthermore, the UV-vis spectroscopic result of all the one-week aged samples showed no significant change in intensity and absorption peak positions concluding that the extract mediated ZnO NPs and the nanocomposites are quite stable in nature. The pomegranate seed extract also played as the stabilizing agent.

The band gap energy (E_g) of the as-prepared ZnO NPs and its nanocomposites were also calculated using Tauc's equation (Equation 2) (Alkter *et al.,* 2021).

$$(\alpha h\nu)^{\gamma} = \text{A}\ (\text{h}\nu - E_g) \quad \ldots\ldots(2)$$

Where, α is the absorption coefficient, h is Planck's constant, ν is the photon's frequency, A is a proportionality constant, E_g is the bandgap energy, γ denoted the nature of the electronic transition. Band gap energy (E_g) of all samples is calculated from the graph plotted between the $(\alpha h\nu)^2$ *vs* energy (**Fig. 2**). The calculated band gap energy is presented in the Table (2).

Table 2: Calculated value of band gap energy of ZnO NPs with, without extract and its ZnO/CuO nanocomposites.

S. N.	Nanoparticles/ Nanocomposites	Band gap (E_g) (eV)
1.	(a) ZnO	3.21
2.	(b) ZnO/Ext	3.10
3.	(c) ZnO/CuO (5%)	2.80
4.	(d) ZnO/CuO (10%)	2.52

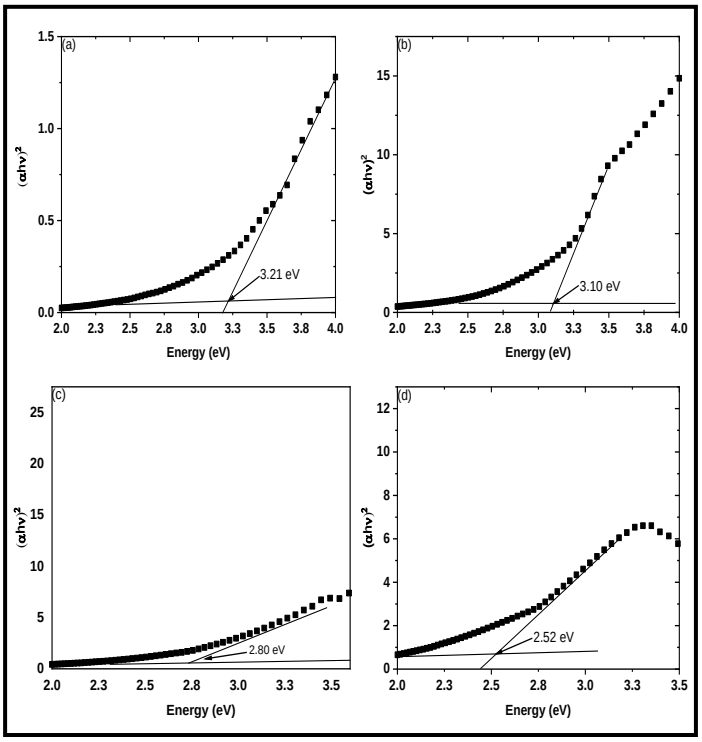


Fig. 2: Band gap energy of (a) ZnO (b) ZnO (Ext) (c) ZnO/CuO (5%) and (d) ZnO/CuO (10%).

The band gap energy of ZnO NPs with and without pomegranate extract is just matched with the reported value of 3.37 eV (Tidjani *et al.,* 2014). The band gap energy of ZnO/CuO nanocomposites is relatively lesser than that of ZnO NPs. It provides a good support for formation of nanocomposites as the band gap of composites is lower than that of ZnO NPs (Das *et al.,* 2017).

3.3 X-ray diffraction spectroscopic analysis

Diffraction pattern of the ZnO NPs with extract, and ZnO/CuO nanocomposites of 5 wt.% CuO is presented in **Fig**. **3**. The diffraction pattern comprises chief crystal planes of ZnO NPs such as (100), (002), (101), (111), (102), (110), (103), (202) corresponding to diffraction angles 31.92°, 34.45°, 36.26°, 38.9°, 47°, 56°, 62°, 69°, respectively. The XRD result confirmed the generation of hexagonal wurtzite of ZnO with reference to JCPDS No. 36-1451 (Sapkota *et al*., 2019; Sakib *et al.,* 2019; Shrestha *et al*., 2022). Likely, the presence of additional crystal lattice, ($1\bar{1}1$), ($\bar{2}02$), (113) and (200) (marked with asterisk) present in ZnO/CuO nanocomposites suggests for the formation of monoclinic type of CuO crystal structure (Sapkota *et al*., 2021, Mohammadi-Aloucheh *et al.,* 2018; Widiarti *et al.,* 2017). The average crystallite size of ZnO/Ext NPs and ZnO/CuO NPs calculated as 61.4 nm (with reference to most intense peak 31.82°) and 53 nm with base peak (31.92°).

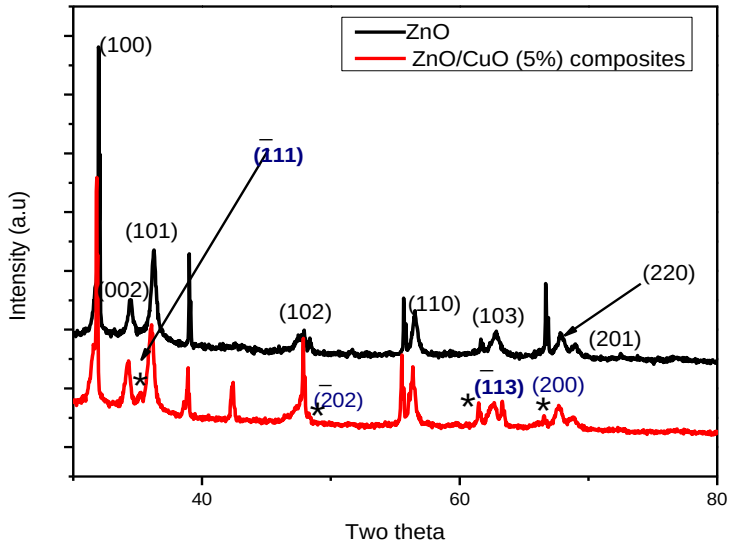


Fig. 3: Diffraction patterns of ZnO/Ext nanoparticles and ZnO/CuO (5 wt.%) nanocomposites.

3.4 Energy dispersive spectroscopic analysis

Energy dispersive spectroscopic images (**Fig. 4**) of ZnO/Ext and ZnO/CuO (5 wt.%) nanocomposite exhibits the characteristic energy absorption bands of desired elements such as Zn, O, Cu etc. at 1.5 keV, 0.5 keV, 8.5, and 8.9 eV, respectively which well supports the formation of ZnO/CuO nanocomposites. Additional energy absorption bands of C, and Si assumed to be arisen from sampling process. The elemental composition of the ZnO/Ext nanoparticles and ZnO/CuO (5 wt.%) nanocomposite are presented in **Table 3**.

Table 3: Elemental composition of ZnO /(ext) and ZnO/CuO (5 wt.-%) nanocomposites achieved from Energy Dispersive Spectroscopic (EDS) analysis

Elements	**Wt. %**		**Atomic %**	
	ZnO/Ext	ZnO/CuO (5%)	ZnO/Ext	ZnO/CuO (5%)
C	12.00	42.04	16.00	64.55
O	55.44	21.90	30.48	25.25
Cu	0.00	1.17	0.00	0.34
Zn	32.44	34.84	53 .46	9.83
Si	0.12	0.05	0.06	0.03

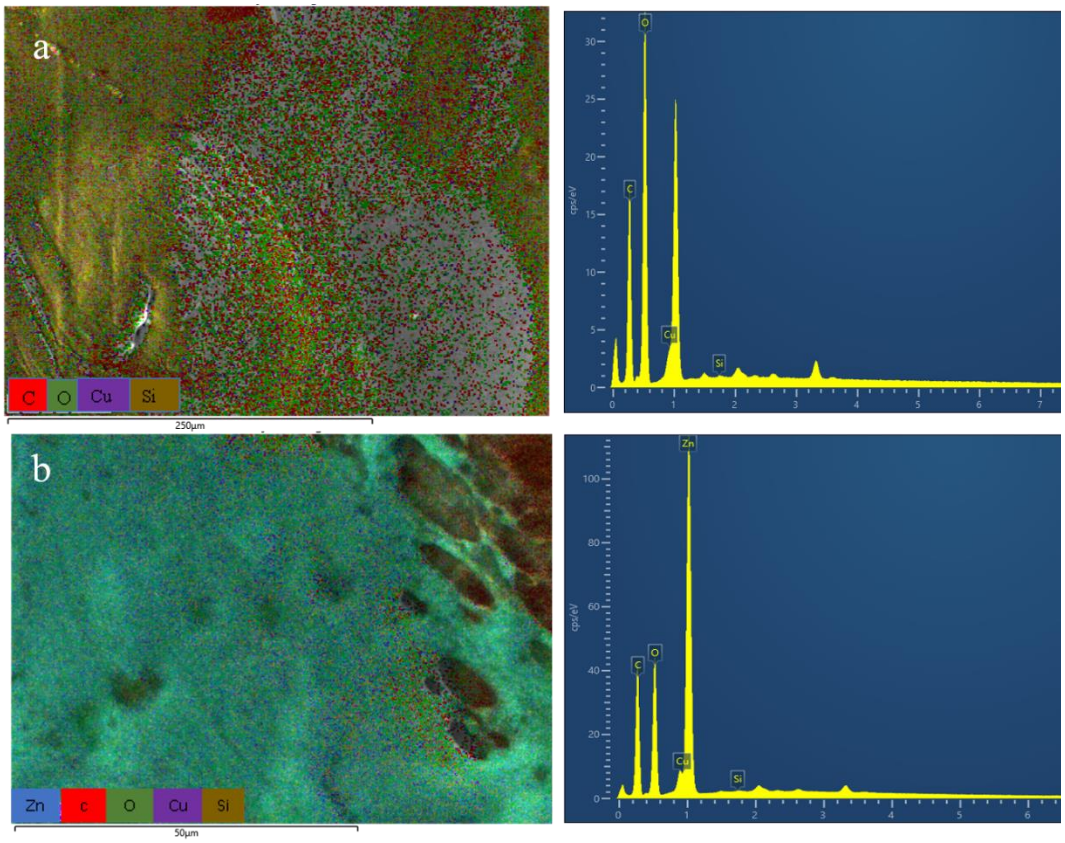


Fig. 4: Energy Dispersive Spectra (EDS) of: a) ZnO (Ext) nanoparticles, and b) ZnO/CuO (5 wt.%) nanocomposites.

3.5 Dynamic light scattering analysis

Generally, dynamic light scattering (DLS) is regarded as one of the reliable tools for calculating the size variation of as synthesized nanoparticles in suspension or in emulsion. Main principle of DLS lies on the Brownian motion of the particles. It states that smaller the particle, more will be the speed, and hence, moves faster. The bigger particles move slower in a liquid medium. The light scattered by particles provides information about diffusion speed and size distribution. The particle size is calculated using Stokes- Einstein relationship (Equation 3) (Babick *et al.,* 2020). The diffusion coefficients (D) of the particles are inversely proportional to the size (dp, hydrodynamic diameter) of the particles according to the Stokes- Einstein relationship.

$$D = \frac{kT}{3\pi\eta dp} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where, k = Boltzmann constant
T = temperature
η = viscosity
dp = hydrodynamic diameter

The size of as-synthesized nanoparticles (ZnO, ZnO/Ext NPs and ZnO/CuO (5wt.%) and ZnO/CuO (10 wt.%) nanocomposites estimated from DLS measurement is compared and the values are tabulated in the **Table 4**.

Table 4: Size of ZnO NPs and ZnO/CuO nanocomposites calculated from Dynamic Light Scattering

Nanoparticle	**Size (nm)**
ZnO	87
ZnO/Ext	268.2
ZnO/CuO (5%)	195
ZnO/CuO (10%)	55

It shows that the average size of nanoparticles is bigger compared with that calculated from XRD. Comparatively, the size of nanoparticles calculated from DLS are bigger with respective to that of XRD method due to hydrodynamic nature.

3.6 Field emission scanning electron microscopic studies (FE-SEM)

The FE-SEM image, **Fig. 5a** reveals presence of irregular spherical shaped ZnO NPs formed due to microwave treatment in the presence of pomegranate extract. Similarly, **Fig. 5b** depicts compact irregular spherical particles of whitish grey colour suggesting the formation of nanocomposites. Furthermore, the detail morphology of ZnO/Ext NPs and ZnO/CuO (5 wt.%) nanocomposites were clarified from HR-TEM.

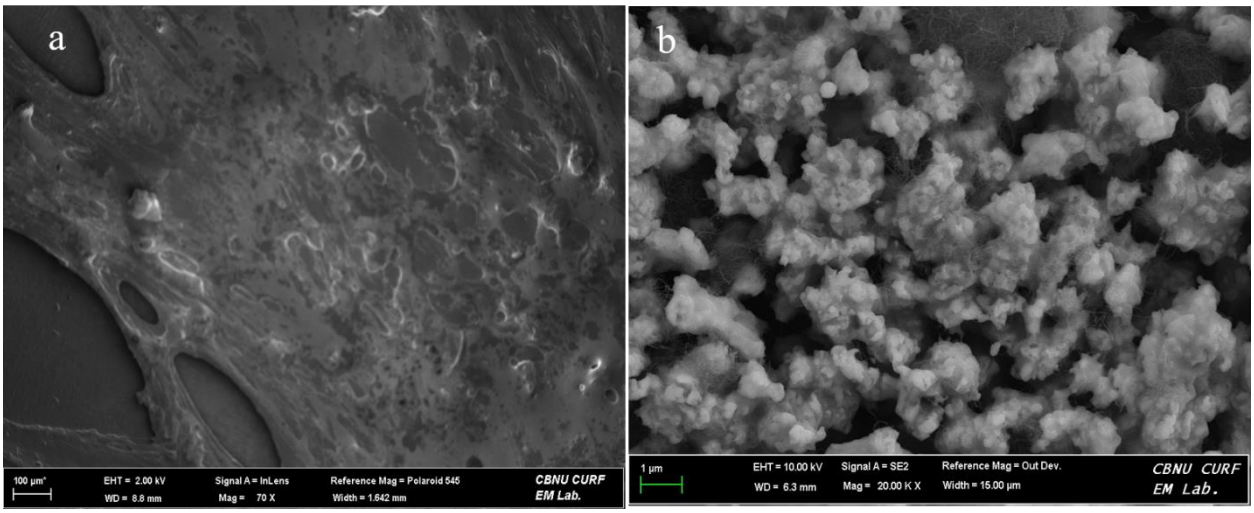


Fig. 5: Field Emission Electron Micrographs: a) Extract mediated ZnO NPs, b) ZnO/CuO (5%) Nanocomposites

3.7 High resolution transmission electron microscopy (HR-TEM)

High resolution transmission electron micrographs (**Fig. 6a**) confirmed for forming spherical ZnO(ext) nanoparticles as indicated by SEM image. The histogram presented in **Fig. 6a** shows that the size of ZnO/ext NPs is in the range 100-200 nm. Similarly, HR-TEM image (**Fig. 6b**) of ZnO/CuO (5%) nanocomposite consists of particles with spherical morphology of 20-200 nm size in histogram.

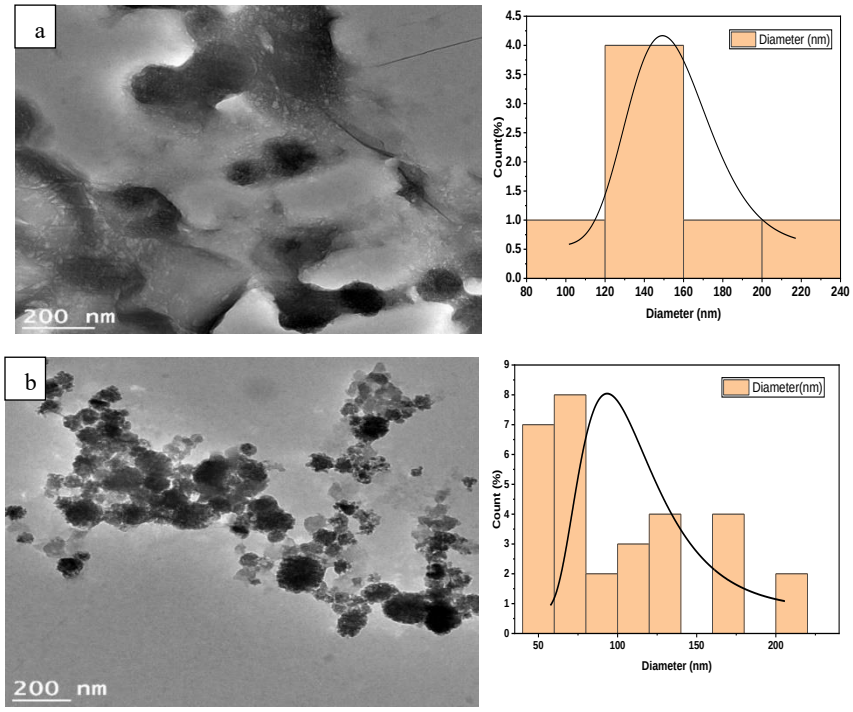


Fig. 6: HR-TEM images (a) ZnO(ext) nanoparticles and (b) ZnO/CuO (5%) nanocomposite

3.8 Catalytic activity of nanoparticles

The catalytic activity of the as-prepared nanomaterials was explored using UV-vis spectrophotometer. At first, the reaction between 4-nitrophenol (4-NP) and $NaBH_4$ at ordinary condition was examined as a blank test. The degradation effect was monitored at 1 minute's interval. The results showed that there is almost no change in the peak (UV-vis) intensity of 4-NP with time for solution mixture without catalyst and ZnO NPs (**Fig. 7a & b**). It suggests that reduction of 4-NP could not happen in blank as reported elsewhere (Sharma *et al.,* 2014). Similarly, the catalytic activity test result of ZnO/Ext NPs and ZnO/CuO nanocomposites of two different wt.% revealed that the green synthesized nanomaterials exhibit potential degrading behavior. The results mentioned were justified from the gradual decrease of UV-vis absorbance peak intensity of 4- nitrophenol when monitored at regular interval of time up to 9 minutes. At the same time, the formation of shoulder peak of aminophenol (350 nm) also supported for efficient catalytic

reduction of the as synthesized nanomaterials (**Fig. 7c, d & e).** The potential catalytic activity of ZnO /Ext and extract mediated ZnO/CuO nanocomposites attributes for exhibiting stabilizing effect endorsed by various secondary metabolites of the *Punica granatum.*

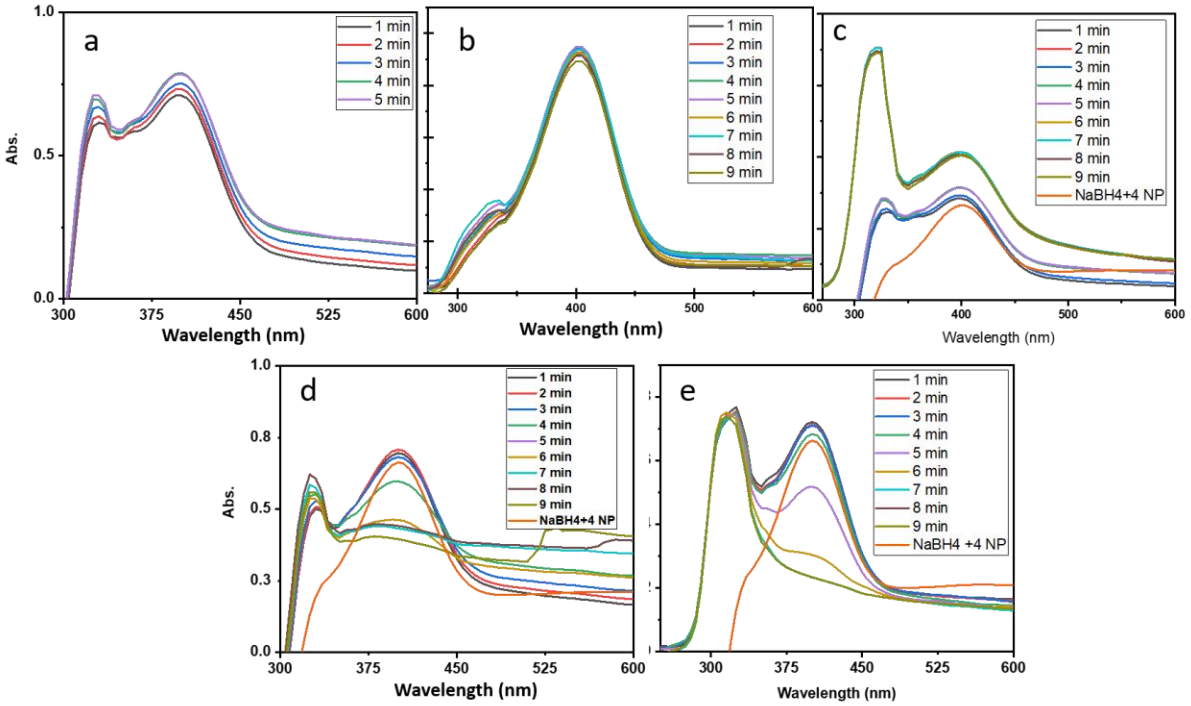


Fig. 7: Catalytic activity of as-synthesized nanoparticles: a) $NaBH_4$, b) ZnO NPs c) ZnO/Ext, d) ZnO/CuO (5%), and, e) ZnO/CuO (10%).

The results shown are in agreement with those reported by Berku *et al*., (2022). The completion of the reduction reaction was observed from the flat curve achieved after nine minutes of irradiation. Furthermore, the catalytic efficiency of nanocomposite (10 wt.%) was greater (65.92%) than that of 5 wt.% nanocomposite (42.7%) calculated from the equation (4), (Sharma *et al.,* 2014), (Hasan *et al.*, 2020).

$$\%\ 4-NP\ Degradation = \frac{c_0 - c_t}{c_0} * 100 \qquad \text{..... (4)}$$

Where, c_o and c_t are concentrations of the 4-NP before and after degradation.

The catalytic mechanism was accomplished via two important steps: adsorption of NP on catalyst surface and electron transfer of BH_4^- to $-NO_2$ group. Thus, the UV-vis spectra infer us that the as-synthesized nanoparticles could be used as effective photocatalyst.

4. Conclusions

Green synthesis of ZnO NPs and ZnO/CuO nanocomposites using Pomegranate (*P. granatum)* extract was successfully carried out. The process is purely economical, environmentally benign, efficient and safe method. Bio-synthesized ZnO NPs were confirmed from the sharp UV-

vis absorption peak at 385 nm. Similarly, formation of the ZnO/CuO nanocomposite was confirmed by shifting of UV-vis absorption peak. The as-synthesized nanoparticles exhibited crystalline morphology. The mean crystallite size of ZnO/CuO nanocomposite was computed to be 61 nm from XRD analysis. Additionally, the sizes of the NPs were calculated from DLS. The chief elements present in ZnO/CuO nanocomposites were confirmed by EDS spectra. Morphological structure of ZnO (Ext) and composite studied via HR-TEM revealed to be of irregular spherical type. The HR-TEM also indicated the formation of ZnO/(Ext) NPs and ZnO/CuO (5%) nanocomposite having 100 -200 nm and 20 - 200 nm size, respectively. Finally, the green synthesized ZnO and ZnO/CuO nanocomposite were found to possess better catalytic efficiency towards the reduction of 4-nitrophenol. Hence, the extract mediated ZnO NPs and ZnO/CuO could be used as effective photocatalyst for degrading hazardous water pollutants. Photocatalytic degradation of large number of organic pollutants using green synthesized metal oxide nanomaterials could be interesting topic for future.

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