Prayogik Rasayan

Green synthesis of zinc oxide nanoparticles, their characterization and utilization for photocatalytic removal of methylene blue

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Abstract

In this study we report a facile synthesis of zinc oxide nanoparticles by green chemistry utilizing fresh lemon juice, zinc acetate and ethylene glycol. The prepared ZnO NPs were characterized using the analytical techniques viz. FTIR spectroscopy, X-ray diffraction analysis, DLS, FESEM and EDAX. The particles were found to be hexagonal wurtzite form having average particle size ~250 nm. The developed ZnO-NPs were checked for the photocatalytic degradation of artificial dye Methylene Blue under UV light irradiation at 365 nm and found to have photocatalytic degradation activity. A 25% reduction in intensity was observed by just 30 mins of exposure.

Keywords: *zinc oxide, dyes, photocatalysis, degradation, UV*

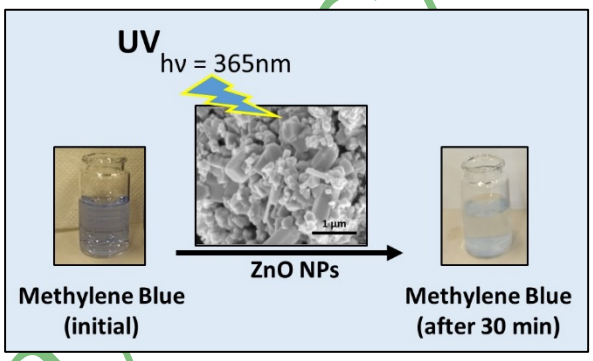
1. Introduction

Zinc oxide (ZnO) nanomaterials have been the most widely utilized n-type semiconductor ingredient having a wide band gap (3.37 eV) and large excitation energy.[1] ZnO is a low-cost, non-toxic, shemically resistant material having wide variety of applications in sensors, solar devices, drug delivery, catalysis, etc.[1] ZnO nanoparticles have been synthesized by various physical and chemical routes which for industrial applications are not viable both commercially and environmental point of view. Therefore, use of natural eco-friendly materials as templates, stabilizers and functionalization are gaining accepatance.[2]

Currently, artificial dyes are being used in almost all major industries such as textile, leather, food, etc. They are highly toxic, cancerous and severly affect marine life if expulled out into the effluent stream without effective treatment. The dye molecules inhibit the penetration of sun rays into the water bodies thus impedes the process of photosynthesis.[3] To overcome this issue various strategies have been applied such as adsorption, photocatalysis, membrane sparation, coagulation, biosorption, etc.[4]

Photocatalysis is an efficient and eco-friendly process where industrial effluents such as dyes, organic molecules, etc. can be treated by generation of highly reactive hydroxyl radical. ZnO NPs has been used for photocatalytic degradation of various kinds of artificial dyes such as methylene blue, direct blue, etc.[1-2]

This study reports the facile preparation of ZnO-NPs utilizing fresh lemon juice containing citric acid which forms soluble complex with zinc present in zinc acetate and ethylene glycol. The synthesized nanoparticles were analyzed using XRD, FTIR, DLS, SEM and EDAX. The

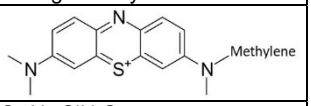


results corroborate towards formation ofZnO NPs with hexagonal wurtzite morphology. Photocatalytic activity was assessed using methylene blue (MB) as representative dye molecule under UV light irradiation at 365 nm.

2. Experimental

Zinc acetate, ethylene glycol were purhcased from Sigma Aldrich, Prague, Czech republic. Fresh lemons were obtained from the local supermarket. The methylene blue dye was kindly donated by a lab member, the molecular structure, formula and characteristic λ_{max} are mentioned in Table 1.

Table 1: Physical characteristics of methylene blue (MB).

Appearance	Dark green crystals
Molecular structure	
Molecular formula	$C_{16}H_{18}ClN_3S$
maximum wavelength (λ_{max})	668 nm
Molecular weight	373.5 (g/g mol)
Common name	Basic blue 9; Swiss Blue
Water solubility	40 g/L at 20 °C

2.1. Synthesis of ZnO NPs

5 g of zinc acetate (Sigma Aldrich, Prague, Czech Republic) was dissolved in 40ml of ethylene glycol (Sigma Aldrich, Prague, Czech Republic). Fresh lemon fruits obtained from local market were squeezed, sieved and filtered to remove the solid particles. 40ml of clear lemon extract was added dropwise into the precursor solution for 1 h under vigorous stirring. The reaction was further continued for 3h maintained at 90 °C. Resultant yellow gel was dried

overnight in oven at 110 °C and subsequently calcined at 700 °C for 90min to obtain white ZnO powder. Figure 1 shows a flowchart of sol-gel process for preparation of ZnO nanoparticles.

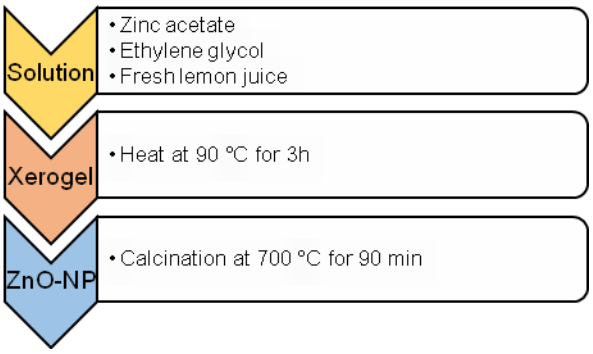


Fig. 1: ZnO nanoparticles preparation using sol-gel method

2.2. Material characterization

The sample was characterized by different analytical techniques. FTIR spectra on Nicolet–320 Fourier transformed infrared (FTIR) spectrophotometer (ThermoScientific, NH, USA). X-ray diffraction pattern of the material was recorded by using MiniFlex-600 X-ray diffractometer (XRD) (Rigaku, Tokyo, Japan): 2θ=5–75°, Co-Kα radiation. The surface morphology of the material was analyzed from the micrographs obtained with a Nova-450 field emission scanning electron microscope (FE-SEM) (FEI, OR, USA) equipped with Octane plus energy dispersive X-ray (EDX) spectroscopy (EDAX, Ametek Inc., PA, USA). The particle size distribution was determined using Zetasizer Nano ZS(Malvern Instruments, Malvern, UK). The dye concentrtion was recorded on a ES-290 UV–vis spectrophotometer (Esse3 SRL, Rettore, Italy).

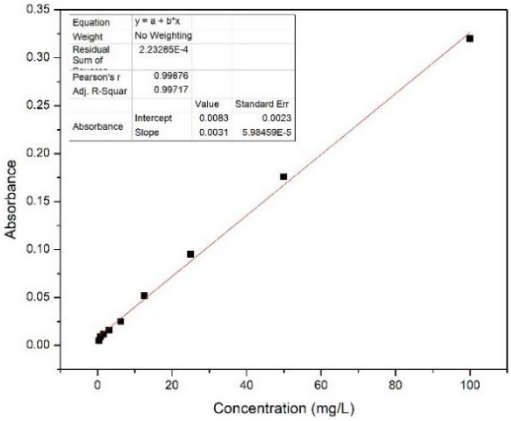


Fig 2: Calibration curve of methylene blue at λ_{max} = 668 nm.

2.3. Photocatalytic study of ZnO-NPs

The photocatalytic dye degradation was performed with the synthesized ZnO nanogranules(100mg) and methylene blue dye solutions (44.87mg/L) under UV lamp irradiation at 365 nm under continuous stirring at 100 rpm. After 30 min sample was drawn from the solution and the catalyst was removed by centrifugation at 14000 rpm and the concentration of dyes in the rest solution was monitored using UV–vis spectroscopy. The degradation efficiency can be defined by the equation 1.[1]

$$\%Degradation = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

Where, A_0 is the initial and A is the final absorbance at λ_{max} of MB dye. Calibration curve of MB dye was plotted using solutions ranging from 100-0.4 mg/L and is shown in Figure 2.

3. Result and discussion

3.1. Mechanism of synthesized ZnO NPs

The esterification of citric acid present in lemon juice takes place upon mixing with ethylene gylcol at moderate temperatures (90 °C). Zinc forms a stable chelate complex in ethylene glycol which is soluble. Over the period as the solvent evaporates, a randomly branched polymeric precursor resin is formed with Zn^{2+} ions uniformly attached throughout the binding sites. This polymeric precursor breaks down upon calcination at 700 °C resulting in formation of ZnO NPs.The reaction mechanism is shown in Figure. 3.

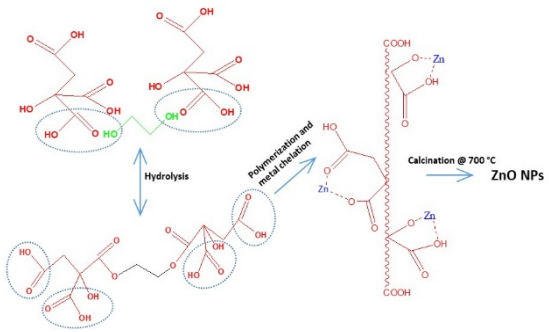


Fig. 3: mechanism of reaction of synthesis of ZnO-NPs

3.2. XRD analysis

Figure 4 displays X-ray diffractograms of synthesized ZnO. Sharp intense peaks at 2θ values 31.6 (100), 34.6 (002), 36.3 (101), etc. along with other characteristic peaks matched with hexagonal ZnO structure.

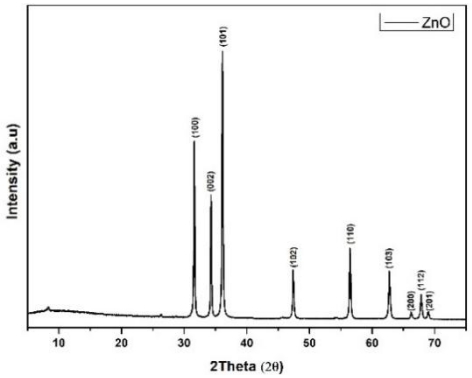


Fig. 4: X-ray diffraction pattern of synthesized ZnO nanoparticles.

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3.3. Morphology and composition

The size, morphology and composition were determined from FESEM and EDAX analysis. As can be seen from SEM micrograph in Figure 5a, there are distinctively two types of particles viz. hexagonal rods (dia. ~250 nm and length ~1000 nm) and cubes with size ~250 nm. The elemental analysis of synthesized ZnO shown in Figure 5b, displayed peaks located around 0.55, 1.0 and 8.6 KeV which are characteristic peaks for O (Ka), Zn (Ka) and Zn (La), repectively.[1] The dynamic light scattering analysis of ZnO-NPs shown in Figure 5c, the results corroborated with the FESEM findings. The PSD was bimodal with two peaks at 280 and 969 nm, respectively indicating towards rod shaped particles.

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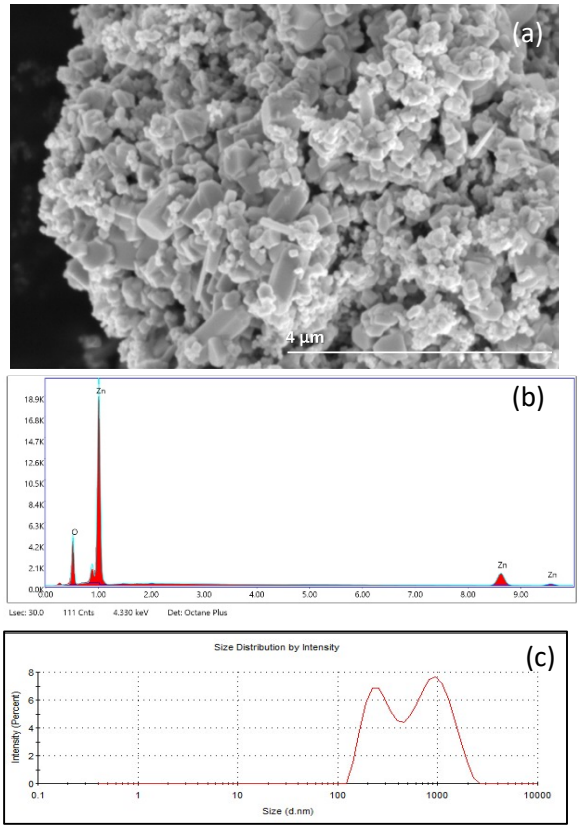

Figure 5: (a) FESEM micrograph, (b) EDAX spectrum and (c) particle size analysis by DLS of synthesized ZnO.

3.4. FTIR analysis

Structure and physico-chemical properties of ZnO was analyzed by FTIR and shown in Figure 6. Weak absorption bands at 1460, 840 and 1040 cm^{-1} result from organic traces which remained during formation of ZnO. ATR spectra does not show peak at 400-500 cm^{-1}, however, the upward shift of spectra near the range shows presence of such absorption band which is characteristic of pure ZnO-NPs.

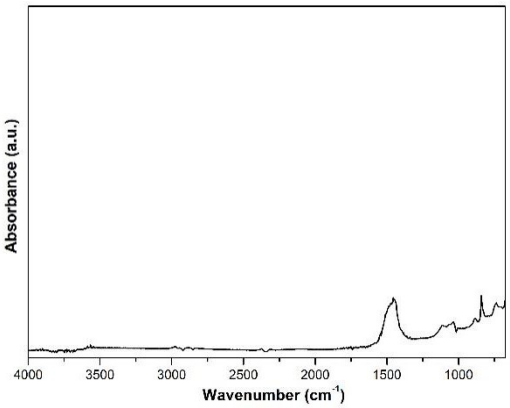

Figure 6: ATR-FTIR spectra of synthesized ZnO.

3.5. Photocatalytic degradation of MB dye

Photo degradation of methylene blue dye using synthesized ZnO-NPs was carried out under the presence of UV light at 365nm. The MB (44 mg/L) dye was exposed to UV light for 30 minutes under constant stirring and intensity was observed again after this time period at λ_{max} = 668 nm. As can be seen in Figure 7, It was found that ~25% dye degradation was achieved with just 30 min of exposure. The photo degradation of MB dye was achieved by hydroxy and hydroperoxy radicals formed by combination of excited electron-hole pairs diffused from catalyst surface with water oxygen and hydroxide species of under the presence of UV light.[5] The dye degradation was still less than reported by Prasad et. al. the plausible reason could be high amount of catalyst dosage which led to high turbidity. Another reason could be sample not properly exposed to UV lamp.

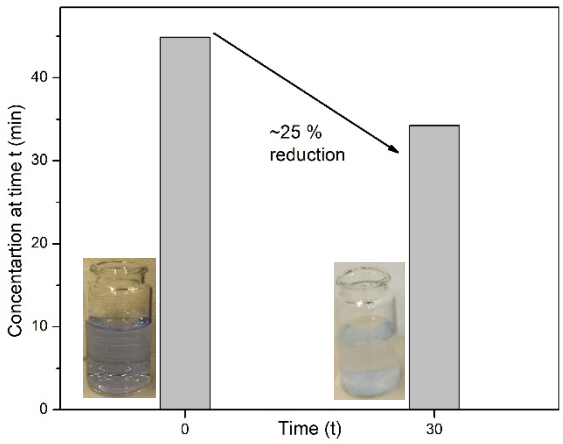

Figure 7: Photocatalytic activity of ZnO-NPs under UV illumination after 30 minutes for degradation of MB dye.

4. Conclusions

To summarize, hexagonally wurtzite ZnO-NPs were synthesized using facile green route using fresh lemon juice and ethylene glycol. The nanoparticles had a uniform particle size of ~250 nm with rod shaped with hexagonal face. The elemental analysis by EDAX and X-ray diffractograms confirm the purity of the material. The FTIR analysis showed traces of organic residues from synthesis

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stage. The photolytic activity was found to be ~25% reduction in intensity with just 30 minutes of UV exposure. In future, the experiments shall be carried out in UV reactor with lesser catalyst dosage to reduce the turbidity so that UV light can penetrate easily. Similarly, these ZnO NPs can be used to photocatalytic degradation of other artificial dyes as well which will be studied in future.

5. Acknowledgements

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6. Notes and References

1. Prasad, A. R., Ammal, P. R. & Joseph, A. Effective photocatalytic removal of different dye stuffs using green synthesized zinc oxide nanogranules. Materials Research Bulletin 102, 116-121 (2018).

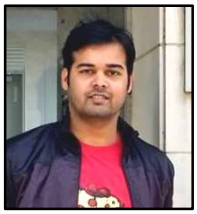
2. Taghavi Fardood, S., Ramazani, A., Moradi, S. & Azimzadeh Asiabi, P. Green synthesis of zinc oxide nanoparticles using arabic gum and photocatalytic degradation of direct blue 129 dye under visible light. Journal of Materials Science: Materials in Electronics 28, 13596-13601, doi:10.1007/s10854-017-7199-5 (2017).

3. Sun, H., Cao, L. & Lu, L. Magnetite/reduced graphene oxide nanocomposites: One step solvothermal synthesis and use as a novel platform for removal of dye pollutants. Nano Research 4, 550-562, doi:10.1007/s12274-011-0111-3 (2011).

4. Dalvand, A. et al. Modeling of Reactive Blue 19 azo dye removal from colored textile wastewater using L-arginine-functionalized Fe3O4 nanoparticles: Optimization, reusability, kinetic and equilibrium studies. Journal of Magnetism and Magnetic Materials 404, 179-189, doi:https://doi.org/10.1016/j.jmmm.2015.12.040 (2016).

5. Kim, J., Choi, W. & Park, H. Effects of TiO_2 surface fluorination on photocatalytic degradation of methylene blue and humic acid. Research on Chemical Intermediates 36, 127-140, doi:10.1007/s11164-010-0123-8 (2010).

7. About the author(s)



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