

# ZnO Doped Lanthanide Oxide Nanomaterials as Photocatalysts for Selective Organic Transformation Reactions: Synthesis of N-Phenyl-P-Benzoquinonimine

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## Abstract

Heterogeneous semiconductor nanomaterials are widely employed nowadays as efficient photocatalysts for selective organic transformation reactions. A co-precipitation technique was employed for the preparation of ZnO doped dysprosium oxide from the respective metal nitrates and characterization studies were conducted by FT-IR, X-Ray Diffraction, UV-Visible-DRS and FE-SEM analysis. XRD showed the prepared nanomaterial to be in a nano range with high crystallinity. The particles possessed a spherical morphology and of the order of 40-50 nm (particle size) as evidenced from FE-SEM analysis. From the UV-Visible-DRS analysis the band gap energy was calculated as 3.15 eV. The synthesized ZnO doped dysprosium oxide was employed as a photocatalyst under UV light irradiation for selective organic transformation reaction. Quinones especially benzoquinones are a class of compounds which forms a basic structural skeleton for various natural compounds. They are widely employed as a precursor for natural products synthesis. Herein we report the synthesis of N-phenyl-p-benzoquinonimine from diphenylamine by employing ZnO doped dysprosium oxide as a photocatalyst under UV light irradiation in ethanol. Thin Layer Chromatography was used to check the progress of the reaction. Optimization studies for the reaction parameters were conducted systematically. Copyright © VBRI Press.

**Keywords:** Diphenylamine, lanthanide oxide, n-phenyl-p-benzoquinonimine, photocatalysis, selective organic transformation UV irradiation, zinc oxide.

## Introduction

Heterogeneous semiconductor photocatalysis has been widely employed as a promising strategy for selective organic transformation reactions [1]. Since, TiO<sub>2</sub> based nanomaterials were discovered as photocatalytic materials for water splitting applications by Fujishima and Honda, [2] many researchers have been working on the development of modified semiconductor materials for various photocatalytic applications [3-5]. The search for an alternative metal oxides to TiO<sub>2</sub> has been widely attempted by various research groups and oxides such as ZnO, Bi<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, WO<sub>3</sub> have been identified as they possess similar properties [6-8]. Though these pristine metal oxides are comparatively cheap, the main demerit of these oxides are their inefficiency for preventing the recombination of electron-hole pairs [9]. Therefore, to prevent the easy recombination of electron-hole pairs, the pristine metal oxides are modified by various techniques. They include coating of pristine oxides on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> [10], supported on graphene based materials [11] and carbon nanotubes [12], preparation of composites [13] and core-shell materials [14] and also by metal-doping [15], non-metal-doping [16] and

lanthanide material doping [17]. Among these materials, doping with rare earth metals was found to result in highly promising photocatalyst. Since rare earth materials possess *f-subshells* which are capable of trapping the electrons excited to the conduction band (CB) from the valance band (VB), such that the holes in the VB could react freely and prevent the recombination process [17].

Various research groups are widely working on the photocatalytic properties of heterogenous semiconductor for the degradation of dyes, phenolics, and phthalates and endocrine disruptors by advanced oxidation process [18]. There are very few reports on the employment of heterogenous semiconductors for selective organic transformation reaction. Rare-earth based ZnO has been studied as an efficient photocatalyst for dye degradation reaction [17]. Hence, it is worthy to investigate rare-earth based ZnO for its selective organic transformation capability. It would also be a promising catalyst for the oxidation of organics. Benzophenones are classified under simple quinones and are distributed widely in the plants and animal kingdom. It forms the structural skeleton for

various natural products found widely in natural [19]. Since, benzophenones are multi-functional, it would exhibit both the properties of alkenes and ketones to undergo addition reactions. Also it is capable for exhibiting nucleophilic addition reactions and be used as a dienophile in the Diels Alder reaction [20]. Hence the synthesis of materials of the benzophenone family would provide way for the preparation of nature identical organics by total synthesis from simple starting materials. Diphenylamine (DPA) is a simple aromatic amine and its photoconversion to N-phenyl-p-benzoquinonimine (NPBQ) is very slow [21]. Very few report on its photocatalytic conversion have been studied employing pristine oxides such as ZnO, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, CeO<sub>2</sub> etc. [22]. Recently our research group worked on ZnO doped Lanthanide oxide (ZLO) and it was found to posses interesting photocatalytic dye degradation properties. Herein, we report for the first time a diphenylamine oxidation employing ZLO. The nanomaterial was prepared by a co-precipitation technique and characterization were conducted by FT-IR, XRD, UV-Visible-DRS and FE-SEM analysis. The prepared material was employed for the selective organic transformation of diphenylamine. The reaction progress was monitored by thin layer chromatography (TLC). The product was analyzed by UV-Visible absorbance analysis.

## Experimental section

### Materials

Zinc nitrate hexahydrate (98%, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and Dysprosium Nitrate (99.9%, Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) and Diphenylamine (99.9%) were purchased from Sigma–Aldrich, India. Ethanol and sodium carbonate were procured from Merck, Mumbai, India.

### Synthesis

ZLO was prepared by a co-precipitation technique as reported earlier [17]. Aqueous solutions of precursors of the lanthanide oxide (dysprosium oxide, Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), Zinc oxide (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and Na<sub>2</sub>CO<sub>3</sub> were prepared in milli-Q water. The precursors of metal oxides and sodium carbonate were in a 1:1 molar ratio. 25 ml of 0.1M dysprosium nitrate was vigorously stirred and 25 ml of 0.1M Na<sub>2</sub>CO<sub>3</sub> was added slowly and a white precipitate was formed. This was followed by serial addition of 25 ml of 0.1M zinc nitrate and 25 ml 0.1M Na<sub>2</sub>CO<sub>3</sub> into the same. The formed precipitates were further stirred for 30 min and centrifuged. The resulting precipitate was thoroughly washed with H<sub>2</sub>O followed by ethanol. Then the white substance was dried (100°C) for 12 h and calcined at 700°C (2 h) in a muffle furnace.

### Characterizations of the prepared ZLO

Various techniques were employed for characterizing the prepared semiconductor nanomaterials. The functional group analysis were carried out in a FT-IR

spectrometer (Perkin Elmer) were potassium bromide was used as a standard. The crystallinity was studied by a X-ray diffractometer (PAN analytical), (Germany) with 2θ scan range of 10° - 70°C employing Cu Kα radiation and 40 kV accelerating voltage and 25 mA emission current. The UV-Visible DRS spectrum was analysed in a UV 2600 spectrometer, Model-Shimadzu (Japan) in a scan range of 200-1400 nm and 200 nm/min scan speed respectively. The particle size, morphology and doping percentage was analyzed by FE-SEM and EDX in a Supra 55 - Carl Zeiss, (Germany).

### Photoreactor setup

Selective organic transformation reactions were studied in a batch type annular UV photo reactor supplied by Heber (India) which consisted of 8 W lamps (8 No) as an irradiation source. The lamps emitted UV light of 254 nm, the reactor had provisions for either 6 smaller reactor tubes 1.5 × 30 cm (inner diameter × height) or 1 large reactor tube 3.5 × 30 cm made of quartz. The reactor was equipped with cooling fans for removing the heat generated during the irradiation process. The required amount of catalyst was added to the required molar concentration of DPA in ethanol and irradiated under UV light with air bubbling. The reaction was monitored by TLC and eluted in a 10% Ethyl acetate 90% Hexane mixture. Aliquots of the samples was also withdrawn periodically, diluted accordingly and the spectrum was recorded in a UV-Visible absorbance spectrophotometer.

## Results and discussion section

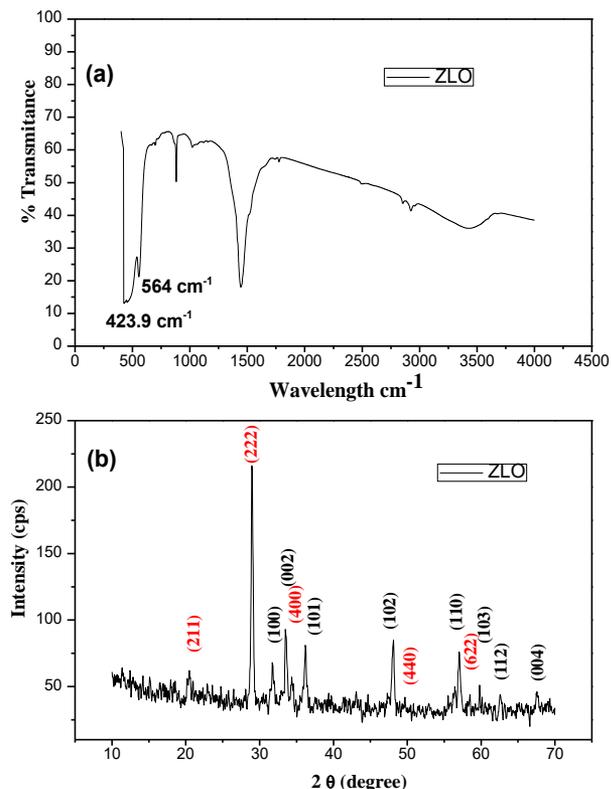
### Analysis of ZLO by FT-IR and XRD

The functional group analysis of the prepared ZLO were conducted by FTIR spectroscopy, (Fig. 1(a)). The bands at 423 cm<sup>-1</sup> and 564 cm<sup>-1</sup> confirm the presence of metal oxide stretching vibrations in the prepared ZLO, which are attributed to the Zn-O and Dy-O bonds and were corroborated with literature [23, 24]. The broad band at 3450 cm<sup>-1</sup> are attributed to the surface hydroxyl groups on the sample. The crystallite size and crystallinity of the prepared ZLO were analysed from the XRD analysis. The results in Fig. 1(b) shows patterns at (211), (222), (100) (002), (400), (101), (102), (440), (110), (622), (103), (112) and (004) are attributed to the presence of ZnO and Dy<sub>2</sub>O<sub>3</sub> in the prepared ZLO and corroborated with literature (JCPDS No.36-451 for ZnO and JCPDS 01-079-1722 for Dy<sub>2</sub>O<sub>3</sub>) [25]. The XRD patterns show the prepared particles to be crystalline and nanosized.

The average particle size were calculated as 40-50 nm by Scherer equation (1),

$$D = k\lambda / (B \cos \theta) \quad (1)$$

where, k is 0.94 (assuming as spheres), λ is 0.154 nm (wavelength) and B is FWHM and θ half angle diffraction.



**Fig. 1.** (a) FT-IR spectrum and (b) XRD patterns of the prepared ZLO. In figure (b) the peaks shown in black represent zinc oxide and red represent dysprosium oxide.

### UV-vis-DRS analysis

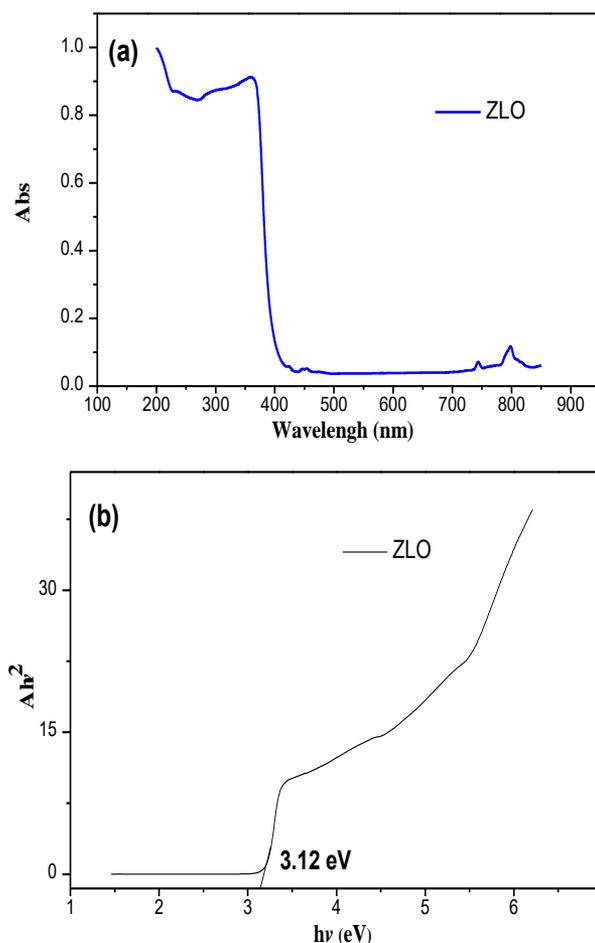
The UV-Visible DRS analysis of the as-prepared ZLO was conducted and the results are portrayed in **Fig. 2(a)**. The maximum absorbance was found to be at 400 nm and extends into the UV region. Hence, the prepared ZLO would be active in UV and Visible light. It could also be noticed that a small peak is present between 700–800 nm which is attributed to the presence of *f-f transitions* which is a characteristic feature of lanthanide elements. The band gap energy of the prepared ZLO was calculated, as the band gap energy is the deciding factor for the nanomaterial to act as a photocatalyst. Only if the band gap energy is within the permissible limit, the material could take the incident irradiation and get excited from VB to CB. The band gap energy of the prepared ZLO could be calculated by using Equation (2)

$$A = [K \cdot h\nu - E_g^{1/2}] / h\nu \quad (2)$$

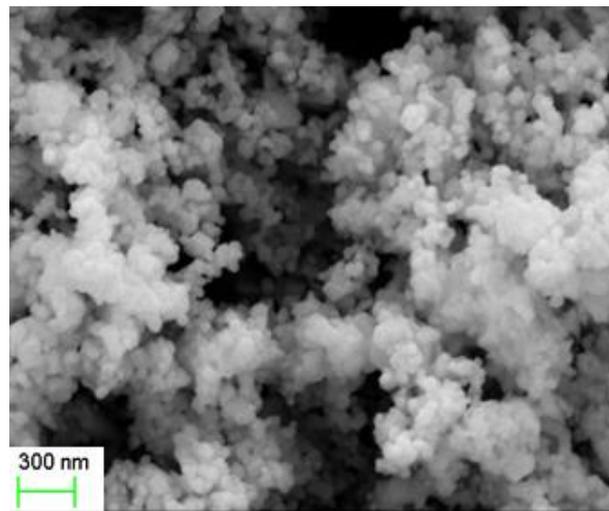
where,  $h$  and  $k$  are constants and  $\nu$  is the frequency of irradiation. Calculation of band gap was by plotting  $(Ah\nu)^2$  in the y-axis and  $h\nu$  in the x-axis. **Fig. 2(b)**.

### FE-SEM analysis of ZLO

The morphology and size of particles of ZLO were determined from FE-SEM images. The shape of the prepared ZLO was observed to be irregular spheres with a particle size of 40 to 50 nm, (**Fig. 3**).



**Fig. 2.** (a) shows the UV-Visible DRS spectrum and (b) plot of band gap energy of the synthesized ZLO.



**Fig. 3.** FE-SEM image of the prepared ZLO nanomaterial.

## Photocatalytic organic transformation reaction

### Preliminary studies

The reaction was conducted in a quartz tube with 10 ml volume of sample. The catalyst amount was varied from 2.5 to 400 mg (2.5, 5, 10, 25, 50, 100, 200, 300 and

400 mg) for a 5 mM concentration of DPA in ethanol. The reaction progress was monitored by TLC analysis. On increasing the time of irradiation, the product spot appeared in the developed TLC after light irradiation of 30 min for 5 to 25 mg of catalyst and a visible colour change was observed, whereas for 50 and 100 mg of catalyst dosage the visible colour change and spot in TLC appeared after 60 min. For 200 to 400 mg, the visible colour change appeared after prolonged irradiation of 120 min. This may be attributed to the fact that, as the amount of catalyst is increased in the reaction system, scattering of light occurs which leads to decreased penetration of light and hence lowered activity [26]. 2.5 mg of catalyst showed the product spot after 60 min of irradiation. Hence, 5 mg/10 mL of 5 mM DPA in ethanol was fixed as the optimized condition for conducting the reaction.

The amount of catalyst employed for effective organic transformation is very less when compared to literature (1g for 25 ml of 5mM DPA in ethanol). The increase in activity for the prepared ZLO when compared to other pristine oxides in literature is due to the doping of rare earth oxides in ZnO. As the material with f-orbitals are present in the prepared catalyst, the light falls on the nanomaterial and the electron excites from VB to CB, but before it could recombine, the electrons that excited gets trapped in the f-subshells and this delays the recombination process. Meanwhile the separated holes in the VB oxidize the DPA molecule in the presence of dissolved O<sub>2</sub>. Hence, the reaction occurs fast in the current reaction system. The mechanism is shown in Fig. 4.

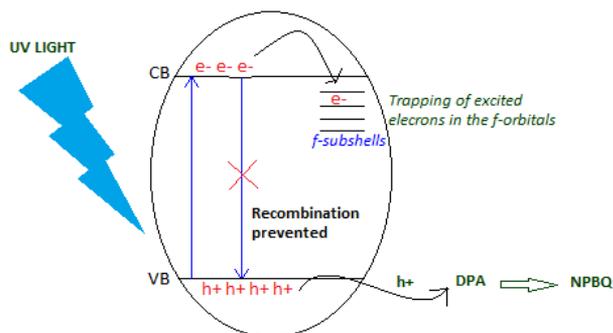


Fig. 4. Shows the photocatalytic mechanism.

### Selective organic transformation of DPA to NPBQ

With the optimized the reaction parameters the organic transformation reaction was conducted. To 200 mL of 5mM DPA in ethanol, 100 mg of the prepared ZLO was added and irradiated under UV light with constant air bubbling. The reaction progress was continuously monitored by TLC analysis and showed the selective formation of a single product spot and no other side products. Small amount of the reaction mixture were withdrawn periodically and diluted accordingly and the UV-Visible absorbance analysis was performed, (Fig. 5 (a)). The increase in intensity of peak upon increase in

reaction time at around 400 – 500nm confirms the formation of NPBQ in the reaction mixture [22]. Fig. 5(b) shows the increase in colour of the reaction mixture upon increasing the time of irradiation. The increase in colour showed the visible formation of NPBQ in the reaction mixture.

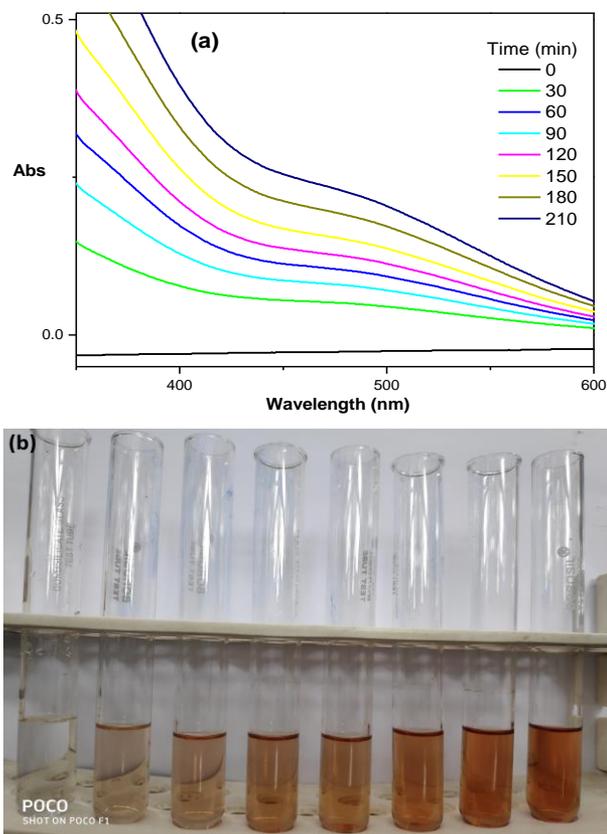


Fig. 5. (a) Spectrum of UV-Visible absorbance for the formation of NPBQ and (b) Visible colour change for the formation of NPBQ.

### Summary

ZnO doped lanthanide oxide (ZLO) was successfully prepared from its nitrate precursors by a co-precipitation method using sodium carbonate as the precipitating agent. The synthesized ZLO was further studied by FT-IR, XRD, UV-DRS and FE-SEM analysis. The FT-IR suggested the formation of metal-oxygen bond in ZLO which are attributed to Zn-O and Dy-O bonds. XRD proved that highly crystalline particles were formed and the peaks of both ZnO and Dy<sub>2</sub>O<sub>3</sub> were present in the prepared ZLO. The particle sizes of ZLO were in the range of 40-50 nm and were found to be in an irregular morphology. The nanocrystalline ZLO particles were employed as efficient photocatalysts for the selective organic transformation of DPA to NPBQ as confirmed from UV-Visible absorbance analysis. Also, the amount of catalyst required for conducting the transformation is many fold decreased when compared to literature. Hence, ZLO is an efficient catalyst for selective organic transformation reaction and it may be employed as

photocatalyst for other organic transformation reactions under Visible and UV light irradiation. Hence, the organic transformation reactions could be made cost efficient by conducting the reactions under solar light irradiation.

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