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# A facile and green strategy for the synthesis of 1-dimensional luminescent ZnO nanorods and its reduction behavior for aromatic nitro-compounds

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#### Abstract:

This article illustrates a facile microwave assisted synthesis of 1D ZnO nanorods using lauric acid. The fatty acid acts as complexing and capping agent in the synthesis of ZnO nanorods. The average diameter of ZnO nanorods was ~5.5-10.0nm. The ZnO nanorods were characterized using TEM, SAED, XRD, FTIR, UV and PL spectra. The synthesized ZnO nanorods showed unusual luminescence properties. For the first time, the reduction of toxic aromatic nitro compounds, such as para-nitrophenol, para-nitroaniline and 2,4,6-trinitrophenol were carried out using synthesized ZnO nanorods as a catalyst in presence of NaBH<sub>4</sub> in aqueous medium.

#### Keywords: ZnO nanorods, lauric acid, PL, catalyst, reduction, aromatic nitro compounds.

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#### 1. INTRODUCTION

Aromatic nitro-compounds are the most toxic organic compounds. Para-nitrophenol is one of the hazardous nitro-compounds and it causes severe health hazards which impose threat to human, animal and aquatic lives. The nitro compounds bearing more than one nitro group were generally used as an explosive such as, 2,4,6-trinitrophenol, which was widely used as an explosive in wars and industries. The presence of strong electron withdrawing nitro-group in aromatic compounds makes it an explosophore, which is capable of inducing explosive properties into a compound [1]. Hence, their disposal into the nearby water sources from industries causes serious environmental pollution and harms the ecosystem. Various effective means were developed for the treatment of such toxic compounds. The reduction of nitro compounds into their amino

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analogue is one of the most effective means for the treatment of such toxic compounds. The amino derivatives were non-toxic and they were used as an important intermediate in the synthesis of various analgesic, antipyretic drugs and in the synthesis of various dyes, as a photographic-developer, corrosion inhibitor [2]. Therefore, it is more suitable to develop an effective method to convert the nitro compounds into their amino derivatives. The conventional methods of hydrogenation of nitro compound were associated with serious environmental problems. In recent years, much attention was devoted towards the catalytic reduction of aromatic nitro compounds by NaBH<sub>4</sub> in presence of noble metal nanoparticles as a catalyst [3]. However, there is much less reports regarding the catalytic activity of metal oxide nanoparticles in the reduction of aromatic nitro-compounds. Therefore, in this paper, for the first time, we reported the catalytic reduction of aromatic nitro-compounds, such as para-nitrophenol (PNP), para-nitroaniline (PNA) and 2,4,6-trinitrophenol (TNP) by NaBH<sub>4</sub> in presence of ZnO nanorods as catalyst, in aqueous medium.

ZnO, a II-VI semiconductor having a wide band gap of 3.37eV, has gained a lot of interest in recent years because of its fascinating luminescence, optical, electrical, chemical and biological properties. ZnO nanoparticles have wide range of promising applications in catalysis, antibacterial treatment, fabrication of sensors and solar cells, optoelectronic devices namely LED and lasers, etc. [4-6]. Numerous methods and techniques were employed for the synthesis of varied morphology of ZnO nanoparticles [5-7]. However, most of the synthetic methods were associated with high temperature, expensive reagents, typical reaction conditions, sophisticated instrument and tedious reaction strategies. In this paper, we report a facile microwave heating method for the synthesis of 1D ZnO nanorods (NRs). This communication describes a lauric acid mediated synthesis of ZnO NRs in ethanol. The synthesized ZnO NRs show enhanced luminescence properties. Many researchers have reported ZnO nanoparticles having blue and green emission bands [7]. However, this paper reports the yellow emission observed in case of synthesized ZnO NRs which is very rare along with negligible blue and green emission.

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#### 2. EXPERIMENTAL

#### Materials and Method:

All the reagents, zinc nitrate hexahydrate ( $Zn(NO_3)_2$ .  $6H_2O$ ), methylamine, lauric acid, NaBH<sub>4</sub>, pnitrophenol, p-nitroaniline and 2,4,6- trinitrophenol were procured from Merck and were of analytical grade (AR). The reaction was carried out in a domestic microwave oven.

ZnO NRs were synthesized using zinc nitrate hexahydrate, lauric acid and methyl amine. A total of 0.01M zinc nitrate hexahydrate was dissolved in 20ml ethanol and was treated with 20ml of 0.01M ethanolic solution of lauric acid and 10ml of 40% methyl amine aqueous solution with constant stirring. The pH of the reaction was maintained at 11. The reaction mixture was then irradiated with microwave waves for 180s. This leads to the formation of white precipitate which was centrifuged and washed with alcohol and distilled water several times. The precipitate was finally calcined at 120°C and collected for characterization.

ZnO NRs were characterized by powder X-ray diffraction (XRD) method using Phillips X'Pert PRO diffractometer with CuKα radiation of wavelength 1.5418Å. The size, morphology and diffracted ring pattern of ZnO NRs were determined by JEM-2100 Transmission Electron Microscope. Infrared spectrum was recorded by Bruker Hyperion 3000 FTIR spectrometer. Absorption spectra were recorded on Cary 100 BIO UV-visible spectrophotometer.

#### Catalytic reduction of toxic aromatic nitro compounds:

For the reduction of aromatic nitro compounds, 6mM solution of aromatic nitro compound (p-nitrophenol, p-nitroaniline and 2,4,6- trinitrophenol) and 0.1 M solution of NaBH<sub>4</sub> were prepared. All the reactions were carried out in a quartz cuvette and the absorbance was recorded in order to investigate the reduction process. In the cuvette, 2ml of water was taken and then 60µl of nitro compound and 350µl of NaBH<sub>4</sub> solution were added and the absorption was recorded. To the above solution, 300µl solution of ZnO NRs (0.005g) was

added to initiate the reduction process. The absorbance was recorded immediately and at a regular interval of time to study the reduction of the aromatic nitro-compounds.

#### 3. RESULTS AND DISCUSSION

The FTIR spectrum was recorded in order to investigate the formation of ZnO and the role of lauric acid in the synthetic pathway. Fig. 1(a) represents the FTIR spectrum of synthesized ZnO NRs. The band observed at 497 cm<sup>-1</sup> was attributed to the characteristic vibration of Zn-O bond [8]. This peak confirmed the formation of Zn-O bond. The appearance of broad band around 3515cm<sup>-1</sup> corresponds to OH group of lauric acid. The presence of lauric acid was also confirmed by the occurrence of sharp peaks at 2925 and 2854cm<sup>-1</sup> due to C-H asymmetric and symmetric stretching vibration. Therefore, the lauric acid gets adsorbed on the surface of ZnO NRs. It was also evident that the band around 1710cm<sup>-1</sup> observed in case of lauric acid was absent. The existence of bands around 1570 and 1415cm<sup>-1</sup> correspond to carboxylate asymmetric and symmetric stretch. This confirmed the existence of lauric acid as laurate anion absorbed on the surface of ZnO. Therefore, analysis of FTIR suggested that lauric acid act as a capping agent in the synthesis of ZnO NRs.

Fig. 1(b) represents the XRD pattern of synthesized ZnO NRs. The crystalline structure, nature and purity of a compound were investigated using XRD pattern. The occurrence of peaks at 2θ values of 31.86, 34.55, 36.33, 47.65, 56.69, 62.89, 66.33, 68.1, 69.13, 72.9, 77.14 and 89.71°C clearly reflects (100), (002), (101), (102), (110), (103), (200), (112) (201), (004), (202) and (203) planes, respectively. The diffraction pattern was well indexed to the hexagonal crystal structure of ZnO and also in good agreement with JCPDS card No. 89-0511. The appearance of sharp peaks depict that the synthesized material is well crystallized. The diffraction pattern did not show any peak for the precursor molecules or impurity which indicated the purity and complete conversion of starting material into products. The average crystalline size of ZnO NRs obtained using De-bye Scherrer equation [6] was 18.08nm.

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The optical properties of ZnO NRs were investigated using UV and PL spectra. The UV-visible spectrum (Fig. 1c) showed a broad absorption band around 379 nm which confirms the formation of ZnO nanoparticles and is associated with the transfer of electrons from valence band to conduction band [8]. The optical band gap energy can be obtained from the absorption onset using Tauc's plot [6]. The band gap energy of synthesized ZnO nanoparticles can be obtained from the following equation [16]:

$$\alpha h v = K (h v - E_g)^n - \dots - (1)$$

where *K* is a constant,  $E_g$  is the band gap energy and the exponent '*n*' depends on the type of transition whose value is <sup>1</sup>/<sub>2</sub> for allowed direct transition. Therefore, by plotting  $(\alpha hv)^2$  versus incident photon energy (hv) and by extrapolating the linear portion of the curve to zero absorption coefficient, the band gap energy can be estimated. The inset of Fig. 1(c) showed the plot of  $(\alpha hv)^2$  versus (hv) for the synthesized ZnO nanorods. The band gap energy of ZnO NRs was calculated from the plot of  $(\alpha hv)^2$  versus photon energy (hv) (inset of Fig. 1c) by extrapolating the linear region of the curve to zero absorption coefficient and was found to be 3.28 eV [6].

The PL spectrum gives brief information regarding the purity and quality of the synthesized material. The room temperature PL spectrum (Fig. 1d) of ZnO NRs showed a strong UV emission band centered at 387nm and an emission band at 583nm when  $\lambda_{ex}$ =300nm. The UV emission at 387nm is the band-edge emission arises due to the recombination of free excitons between the valence and conduction bands [6]. The yellow emission band at 583nm occurs due to native deep level defects mainly attributed to oxygen interstitials (O<sub>i</sub><sup>-</sup>) [9]. Blue and green emission bands of very negligible intensity were also observed around 450 and 550 nm, respectively. The occurrence of blue and green emission peak was due to the radiative transition from the extended Zn<sub>i</sub> to valence band and from the conduction band to deep oxygen vacancies level, respectively [7]. The intensity of UV emission reveals the crystallinity of the sample and the intensity of the bands in the visible region reflects the concentration of defects in the sample [10]. Hence, the PL spectrum indicates the

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highly crystalline nature of synthesized ZnO NRs and the presence of defects also indicates an increase in the optical and electrical properties of synthesized material. The synthesized ZnO nanorods showed unusual luminescence properties, thereby showing a prominent yellow emission band. Roy et al. synthesized ZnO nanorods with average length and diameter of 100–150 nm and 10–20 nm, respectively (aspect ratio=10), showed blue and green emission bands [7]. The dependence of luminescence properties on the change in size of ZnO nanoparticles were studied by Raoufi and in that case, he concluded that with an increase in particle size, the intensity of visible deep level emission increases [11]. Wang et al. also showed that the photoluminescence property of ZnO nanoparticles is size-dependent [12]. Herein, we reported the synthesis of ZnO nanorods with a lower aspect ratio (length:diameter) of 1.3-1.8 and showed unusual yellow emission band may be attributed to the lower aspect ratio of the synthesized ZnO nanorods. Hence, the incorporation of lauric acid leads to a decrease in the length and diameter of ZnO nanorods thereby decreasing the aspect ratio which play an important role in determining the luminescence properties of ZnO nanoparticles.

The energy band diagram shown in Scheme 1 explains the probable mechanism of blue, green and yellow emission in ZnO nanorods. The mechanism of blue, green and yellow emission bands were related with the coexistence of  $Zn_i$  interstitials, oxygen vacancies and  $O_i$  interstitials in the synthesized ZnO nanorods. The electrons from the valence band get excited to the conduction band only when the energy of incident photon is greater than the band gap of the synthesized ZnO nanorods. The synthesized ZnO NRs showed a blue emission having energy of 2.75 eV which was due to the transition from extended  $Zn_i$  to valance band. The calculated energy gap between the conduction band and  $Zn_i$  was found to be 0.53 eV. The electrons excited from valence band to the conduction band undergo non-radiative transition to the extended  $Zn_i$ , wherein further transition occurs directly to the valence band giving rise to the blue emission band at 450 nm. The

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electrons that were forced into the conduction band de-excite to the deep levels of oxygen vacancies and this give rise to green emission band at 550 nm. The calculated energy for green emission was 2.25 eV. The synthesized ZnO nanorods showed unusual luminescence properties by giving rise to a prominent yellow emission band along with negligible blue and green emission bands. The origin of yellow emission is attributed to oxygen interstitials, O<sub>i</sub>. The calculated yellow emission energy for the synthesized ZnO NRs was 2.11 eV. The mechanism of yellow emission proceeds through the non-radiative transition of excited electrons from conduction band to the extended oxygen interstitial O<sub>i</sub>, with energy difference of 1.17 eV. From O<sub>i</sub>, the electrons undergo further transition to the valence band thereby giving rise to an intense yellow emission band at 583 nm. The intensity of blue and green emission bands are negligible in comparison to the yellow emission band which indicate that most of the excited electrons from conduction band undergo non-radiative transition to the extended oxygen interstitials, O<sub>i</sub> and then further undergoes transition to the valence band thereby giving rise to a prominent high intensity yellow emission band.



Scheme 1. Schematic diagram for the probable mechanism of blue, green and yellow transitions

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The morphology and particle size distribution of synthesized ZnO nanoparticles were elucidated by Electron Microscopic analysis. The TEM image (Fig. 2a) showed the formation of rod-like ZnO nanoparticles with diameter and length of 5.5-10.0 and 10-13 nm, respectively. The microstructure of ZnO nanorods were analyzed by HRTEM image (Fig. 2b). The spacing between adjacent lattice planes obtained from HRTEM image (Fig. 2b) was 0.122 and 0.165nm which corresponded to (202) and (110) lattice planes, respectively. The SAED pattern (Fig. 2c) revealed the hexagonal crystal structure of ZnO NRs which was in resemblance with the XRD pattern. The SAED pattern also reflects that ZnO NRs were well crystallized in nature.

In the synthesis of ZnO NRs, lauric acid plays the role of complexing as well as capping agent. Being basic in nature, methyl amine is supporting the deprotonation of lauric acid thereby enhancing the formation of ZnO NRs. However, for further confirmation of the role of lauric acid as capping agent in the synthesis of ZnO NRs, a control experiment was carried out for the synthesis of ZnO nanoparticles in the absence of lauric acid and the corresponding TEM image and FTIR spectrum was recorded (Fig. S1(a, b)<sup>+</sup>). The TEM image (Fig. S1a<sup>+</sup>) showed the formation of ZnO nanorods with average diameter and length of 130 nm and 415 nm, respectively. This clearly indicates that the involvement of lauric acid in the synthesis of ZnO nanoparticles leads to the formation of small sized ZnO nanorods. The adsorption of laurate anion on the surface of ZnO nanorods terminate the growth of ZnO nanoparticles and prevent agglomeration by giving rise to small sized ZnO nanorods with diameter and length 5.5-10 nm and 10-13 nm, respectively. The FTIR spectrum (Fig. S1b<sup>+</sup>) of ZnO nanoparticles synthesized in the absence of lauric acid was also recorded and the spectrum showed a band around 491 cm<sup>-1</sup>. The appearance of this band confirmed the formation of Zn-O bond. No bands were observed in the region 1700-1500 cm<sup>-1</sup> which clearly depicts the absence of laurate anion on the surface of ZnO nanorods which inhibit the growth of ZnO nanorods thereby acting as a good capping agent.

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#### Reduction of toxic aromatic nitro compounds using ZnO NRs as heterogeneous catalyst:

The catalytic reduction of aromatic nitro-compounds by  $NaBH_4$  was taken as a model reaction to evaluate the catalytic activity of ZnO nanorods. Fig. 3(a) represented the absorption spectra which indicate the change of concentration of p-nitrophenol (PNP) with time in aqueous medium in presence of NaBH<sub>4</sub> acting as a reducing agent and ZnO NRs as a heterogeneous catalyst. It was evident that the absorption maximum of PNP was centered at 317nm and after the addition of NaBH<sub>4</sub> the absorption maximum was shifted to 403nm due to the formation of p-nitrophenolate ions (Fig. S2<sup>+</sup>). The color of the solution also changes to intense yellow after the addition of NaBH<sub>4</sub> due to the formation of p-nitrophenolate ions under alkaline condition. The peak at 403nm remains unaltered after a couple of days in absence of any catalyst. It is a kinetically restricted reaction in the absence of any catalyst. Therefore, PNP reduction doesn't take place using only the reducing agent NaBH<sub>4</sub> in the absence of any catalyst [2]. However, after the addition of ZnO NRs the absorption maximum at 403nm gradually decreases with time which indicates the reduction of PNP and the color of the solution also fades away. A new peak centered at 300nm started generating with an increase in reduction time. This peak arises due to the formation of p-aminophenol which is the final reduced product [2, 3]. The complete reduction takes place within 120min. The rate of the reaction was studied using first order kinetics by plotting  $\ln A_t$  versus time (Fig. 3b) and was found to be 0.026min<sup>-1</sup>.

The absorption spectrum for the reduction of p-nitroaniline (PNA) using NaBH<sub>4</sub> in presence of ZnO NRs as heterogeneous catalyst is represented in Fig. 4(a). The disappearance of peak at 380nm and appearance of a new peak centered at 300nm indicates the complete reduction of PNA to p-phenylenediamine [3]. The rate of the reaction was obtained using first order kinetics (Fig. 4b) and rate constant was found to be 0.044 min<sup>-1</sup>. Similarly, the reduction of 2,4,6-trinitrophenol (TNP) was carried out using NaBH<sub>4</sub> as a reducing agent in presence of ZnO NRs acting as a catalyst. From the UV-visible spectrum (Fig. 5a), it was evident that TNP showed an absorption maximum at 358 nm. The disappearance of the band around 357nm and the

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appearance of a new peak at 300nm showed the complete reduction of the nitro compound into their corresponding amino derivative [3]. This reaction also followed first order kinetics. The rate of the reaction obtained from the linear plot of  $\ln A_t$  versus time (Fig. 5b) was 0.141min<sup>-1</sup>.

Moreover, to verify the role of ZnO NRs and NaBH<sub>4</sub>, control experiments were also performed for the reduction of PNP, PNA and TNP using only NaBH<sub>4</sub> in the absence of ZnO NRs. It was found that all the aromatic nitro-compounds were not reduced even after a couple of days. The reduction took place only when ZnO NRs were added. Moreover, the reduction of nitro compounds carried out using ZnO NRs in the absence of NaBH<sub>4</sub> doesn't take place successfully which further conferred that ZnO NRs cannot act as a reducing agent. These control experiments confirmed the role of NaBH<sub>4</sub> as a reducing agent and ZnO NRs as a catalyst in the effective reduction of aromatic nitro compounds.

Therefore, ZnO NRs act as an effective catalyst in the reduction of p-nitrophenol, p-nitroaniline and 2,4,6trinitrophenol to their corresponding amino derivates. Table 1 represented the overall study for the reduction of toxic aromatic nitro compounds in aqueous medium using ZnO NRs as a catalyst.

#### 4. CONCLUSION

A facile microwave assisted route was developed for the synthesis of 1D ZnO NRs using lauric acid as complexing and capping agent in ethanol medium. The ZnO NRs having an average diameter of 5.5-10.0nm possesses hexagonal crystal structure and is well crystalline in nature. ZnO NRs showed unusual luminescence properties wherein, high intensity UV and yellow emission bands were observed along with negligible blue and green emission bands. The toxic nitro-compounds, such as, PNP, PNA and TNP were completely reduced into amino derivatives by NaBH<sub>4</sub> in presence of ZnO NRs as a catalyst in aqueous medium within 120, 45, and 18 min, respectively.

**†Supplementary Information:** TEM image and FTIR spectrum of ZnO nanoparticles synthesized in the absence of lauric acid, absorption spectrum of PNP and absorption spectrum of PNP after addition of NaBH<sub>4</sub> were available in Supplementary Information

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#### **Figure:**

**1.Figure 1.** (a) FT-IR spectrum of synthesized ZnO NRs showing the formation of ZnO and analyzing the role of lauric acid as capping agent in the synthesis of ZnO NRs; (b) XRD pattern of as-prepared ZnO NRs predicting a hexagonal crystalline stucture; (c) Absorption spectrum of synthesized ZnO NRs

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showing a broad absorption band around 379 nm (upper right inset represents the corresponding plot of  $(\alpha hv)^2$  versus photon energy, hv); (d) PL spectrum of ZnO NRs ( $\lambda_{ex}$ = 300nm).

- **2.Figure 2.** (a) TEM microphotograph of synthesized ZnO NRs having average diameter and length of 5.5-10.0 nm and 10-13 nm respectively, (b) HRTEM image of as-prepared ZnO NRs, (c) SAED pattern of synthesized ZnO NRs having a hexagonal crystal structure.
- **3.Figure 3.** (a) Absorption spectrum for conversion of PNP to PAP using ZnO NRs as catalyst in presence of NaBH<sub>4</sub> in aqueous medium, (b) Plot of ln[A<sub>t</sub>] versus reduction time.
- **4.Figure 4.** (a) UV-spectrum for reduction of PNA by NaBH<sub>4</sub> in presence of ZnO nanorods as catalyst in aqueous medium, (b) Plot of ln[A<sub>t</sub>] versus reduction time.
- **5. Figure 5.** (a) UV-spectrum of reduction for TNP by NaBH<sub>4</sub> in presence of ZnO nanorods as catalyst in aqueous medium, (b) Plot of corresponding ln[A<sub>t</sub>] versus reduction time.



Fig. 1 (a) FT-IR spectrum of synthesized ZnO NRs showing the formation of ZnO and analyzing the role of lauric acid as capping agent in the synthesis of ZnO NRs, (b) XRD pattern of synthesized ZnO NRs predicting a hexagonal crystalline stucture, (c) Absorption spectrum of synthesized ZnO NRs showing a broad absorption band around 379 nm (upper right inset represents the corresponding plot of  $(\alpha hv)^2$  versus photon energy, hv), (d) PL spectrum of as-prepared ZnO nanorods ( $\lambda_{ex}$ = 300nm).



Fig. 2(a) TEM image of as-prepared ZnO nanorods having average diameter and length of 5.5-10.0nm and 10-13 nm respectively, (b) HRTEM image of synthesized ZnO nanorods and (c) SAED pattern of synthesized ZnO nanorods having a hexagonal crystal structure.



Fig. 3 (a) Absorption spectra of conversion of PNP to PAP using ZnO nanorods as catalyst, (b) Plot of  $ln[A_t]$  versus reduction time.



Fig. 4 (a) UV-spectra of reduction of PNA by  $NaBH_4$  in presence of ZnO nanorods as catalyst, (b) Plot of  $lnA_t$  versus reduction time.



Fig. 5 (a) UV-spectra of reduction of TNP by  $NaBH_4$  in presence of ZnO nanorods as catalyst, (b) Plot of  $lnA_t$  versus reduction time.



### Table 1: ZnO nanorods catalyzed reduction of toxic aromatic nitro compounds in aqueous medium