Efficient Photo-catalytic Degradation of Acid Red 183 dye in the presence of ZnO nano-whiskers

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This paper reports on ZnO nano-whiskers (ZNWs), synthesized by sol-gel method at a pre-determined speed by using zinc acetate dehydrate and a cationic surfactant, N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB). The effect of pre-determined stirring condition on the particle size, aspect-ratio and morphology of ZNWs has been studied. The SEM and TEM result shows that zinc oxide developed into the huge colony consisting of adequate ZnO nano-whiskers, which contained a large number of long needle-like whiskers and the density of these colonies showed a good amount in each bunch. The average length and diameter of the long needle-like ZnO nano-whiskers are 36 nm and 1.15 nm, respectively, and their average aspect ratio was L/D = 31.3. The photo-catalytic activity of the ZNWs was executed by studying the degradation of Acid Red 183 as a function of irradiation time resulting into 68% of decolouration after 150 min of irradiation in the presence of ZNWs under UV light illumination.

Keywords: Sol-gel, doping additives, ZnO nano-whiskers, Photo-catalytic activity, Acid Red 183.

INTRODUCTION

Zinc oxide (ZnO) is an n-type semiconductor belongs to II-IV group possess 3.3 eV band gap energy along with a large exciton binding energy of 60 meV (at 298 K) [1, 2]. The ZnO bears several splendid properties like good transparency, high electron mobility and strong room temperature blue green luminescence and absorption in UV region, which make it a tailored material for sunscreens, textile industries, catalysts, sensors, photo-detectors and for getting solar energy [3-6].

With the advent of industrialization, it may directly or indirectly harmful results which were related to the environment. The different types of dangerous compounds eluting from the drugs, dyes, surfactants, pharmaceutical and many other chemical industries; insecticide, fungicides, herbicides, etc; all may resulting into the huge contamination of water bodies, soil, air pollution [7-8]. Hence, for the sake of mankind, flora and fauna, it is necessary that all the harmful and poisonous contaminants going into different water bodies (viz. surface water, underground water, etc), could be checked and sound initiatives should be taken to purify the different water resources, used for the betterment of life. After successfully splitting of water into hydrogen and oxygen by Fujishama and Honda [9]. The photocatalysis has been successfully employed for various potential hazardous pollutants and industrial effluents into less harmful materials. Different studies have proved this with different pollutants like dyes, drugs, surfactants, pesticides, herbicides, insecticides and fungicides that can be completely mineralized in the presence of zinc oxide nanostructures [10-12].
Different methods for the synthesis of zinc oxide nanoparticles are sol-gel method, facile hydrothermal method, solution method, electric current heating method; solvothermal method; self-propagating high-ZnO synthesis (SHS) method, spontaneous nucleation method spray pyrolysis, gas-phase reaction method, laser ablation method, thermal evaporation, mechano-solution method, etc [13-14]. The different stirring conditions used in numerous nanoscaled ZnO syntheses generally require steady runs to vigorous stirrings; at low temperatures to elevated temperatures, with the duration of few minutes to few days, etc [15-17].

Zhang et al. grown zinc oxide nanoparticles (ZnO-Nps) by constant stirring of aqueous solution of Zn(NO3)2, LHSDA and bamboo pulp fabric for 40 minutes [15]. L. Yu et al. carried out the stirring of NaOH and zinc acetate solution at for several hours [16]. J. Xie et al. vigorously stirred the solution of Zn(OH)2, sodium dodecyl sulphate and ZnCl2, maintained at 30°C [17]. Shao and Yan prepared the tertiary rare earth complex by performing the stirring at room temperature [18]. K. Elen et al. statistically determined the ZnO synthesis by hydrothermal treatment, both in the absence and presence of constant stirring condition. They reported that stirring had an impact on homogeneity during ZnO precipitation and stirring was accountable for decrease in the average particle diameter. But due to absence of well equipped stirrer in the hydrothermal reactor, they have not studied its effect properly [19].

This study has been performed in order to propose the effect of pre-determined stirring condition (viz. 1800±50 rpm), gradual drop wise addition of NaOH solution till stirred bubbled with atmospheric oxygen for at least 15 minutes in the reaction mixture. At pre-determined stirring condition (viz. 1800±50 rpm), gradual drop wise addition of NaOH solution till colloidal solution with milky appearance occurs. The reactor was cooled and dried after keeping in desiccator and later washed with distilled water followed by methanol. The whole synthesis was carried out without any unusual treatment.

The structural morphology of as prepared ZnO nano-whiskers (ZNWs) sample were formed in single phase. The nature of the precipitates were analyzed by powder X-ray diffraction (XRD; Bruker AXS D8 Advance) with Cu-Kα radiations λ = 1.54178 Å with 4°/min scanning rate in the range of 20-70°. The chemical composition was measured by Fourier transform infrared spectra (FTIR; Thermo Scientific Nicolet is-10) were generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm⁻¹.

The optical property as-prepared ZnO nano-whiskers were analyzed by UV-diffused reflectance spectroscopy and UV-visible absorption spectroscopy at ambient temperature. The photocalytic property of as-synthesized ZnO nano-whiskers was evaluated by successfully monitoring the dye degradation reaction under UV light illumination. The photo-catalytic degradation of Acid Red 183 was carried out in the presence of ZnO nano-whiskers (ZNWs) under UV light illumination as a function of irradiation time. An immersion well photochemical reactor made of Pyrex glass, (125 W medium pressure mercury lamp (1.74-1.78 mWcm⁻²), equipped with a magnetic stirring bar, water circulating jacket and an opening for supply of atmospheric oxygen was used.

IR radiation and short wavelength UV radiation were eliminated by the reactor, and about (2g L⁻¹) of ZNWs was added and than subsequently the resultant aqueous suspension was stirred bubbled with atmospheric oxygen for at least 15 minutes in the dark to allow equilibration of the system.

Then, the stable aqueous dye suspension was allowed to expose to UV light illumination. The sample was taken out after regular interval of time from photoreactor which was further centrifuged to filter out the photocatalyst, and than the absorption of decomposed dye solution was measured by using UV-visible absorption spectrophotometer.

RESULTS AND DISCUSSION

The crystalinity and crystal phase of as-synthesized ZnO nano-whiskers (ZNWs) determined by X-ray diffraction which is depicted in fig. 1. (a). All the diffraction peaks were fully matched with standard peaks which reveal that the as-synthesized ZnO nano-whiskers (ZNWs) sample were formed in single phase. The nature of the samples a and b = 3.24 Å and c = 5.20 Å (c/a = 1.60).

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The growth of ZnO nano-whiskers could be easily understood by exploring the reaction involved in the synthesis process. In typical reaction scheme, first prepared solution of CTAB in which gradually addition of zinc acetate dihydrate solution under continuous stirring condition. It was interesting to note that there was no immediate changes takes place; first zinc acetate dihydrate dissolve to produces zinc cation which was further react with hydroxyl ion to form zinc hydroxide zinc hydroxide Zn(OH)$_2$. [24]. The involved reaction written as:

$$Zn(CH_3COO)\cdot2H_2O + H_2O \rightarrow Zn^{2+} + CH_3COO^-$$  
$$ (CH_3)\cdot3N_\cdot6 + H_2O \rightarrow 6HCHO + 4NH_3$$  
$$NH_4^+ + OH^- \rightarrow Zn(OH)_2$$  

Initially, As the pH of resultant solution was increases with gradually addition of NaOH solution zinc hydroxide Zn(OH)$_2$, which was further react with hydroxyl ion to generate Zn(OH)$_2$. Formulation of Zn(OH)$_2$, was extremely pH and temperature dependent reaction. The nucleation of parent molecules was control by basicity of solution (Zn$^{2+}$/OH$^-$ < 1:10) to produces clear solution without rise in the temperature. It has been found that the pH of resultant solution plays important role in determining structure shape of nanomaterials. It has been successfully also reported that intermediate concentration (1:6 < Zn$^{2+}$/OH$^-$ < 1:7), highly ordered ZnO nano-whiskers was obtained [25]. In the recent years there were many peoples successfully reported that surfactant plays pivotal role in the synthesis of zinc oxide nanostructures. The “oil–water” media, using surfactants as templates, act as efficient nanoreactors or so-called diverse micelles in which the crystal growth occurs. The template role of surfactant is not always convincing, however, as that rather large exceptions are observed for the anisotropic shapes.

Since the experiments were carried out in a high pH and solution was rich in OH$^-$ ions. So the newly produced tiny crystals were preferentially coated with large number of OH$^-$ ions, due to the marked volume difference between the negative OH$^-$, Zn(OH)$_2$ and assembled CTAB. The CTAB also facilitate to transport Zn(OH)$_2$ growth units which come together to forms individual rod-like structure which then self assembled into whisker like morphology. As the reaction proceeds and aged, the Zn(OH)$_2$ ions dissociates to form ZnO nuclei as follow:

$$Zn(OH)_2 \rightarrow ZnO + H_2O + 2OH^-$$

It was interesting to observe that both ends of rods were taping.
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The as-synthesized ZnO nano-whiskers (ZNWs) were applied as photo-catalyst to investigate the photocatalytic degradation of Acid Red 183. Fig. 4. (a) reveals the characteristic UV-visible absorption peak of Acid Red 183 at 494 nm ($\lambda_{\text{max}}$), which was gradually decreases with increases the time from 0 to 150 minutes under illumination. The gradual decrease in the relative intensities of absorption indicates the degradation of Acid Red 183 by the as-synthesized ZnO nano-whiskers (ZNWs) as photo-catalyst under UV light. Fig. 4. (b) depicts time dependent photodegradation reaction efficiency plots in the presence and absence of ZnO nano-whiskers (ZNWs) under UV light illumination. In general, the extent of degradation over the surface of ZnO nano-whiskers (ZNWs) is calculated by relation as:

$$\text{Extent of degradation (\%)} = \left( \frac{C_o - C}{C_o} \right) \times 100$$

Where as, $C_o$ denotes the initial concentration of Acid Red 183 (time = 0) and $C$ denotes the concentration of Acid Red 183 (time = t). Fig. 4. (b) reveals there was no appreciable degradation occurs under UV light illumination in the absence of ZnO nano-whiskers while in the presence of ZnO nano-whiskers it was interesting to note that about 68 % decolorization takes place with in just 150 min time span. Fig. 4. (c) depicts pie chart of degradation reaction which clearly reveals that most of degradation of Acid Red 183 occurs within 90 min.

Figure 4. (a) UV–vis absorbance spectra of Acid Red 183 dye as a function of time over ZnO nano-whiskers under UV illumination, (b) extent of degradation of Acid Blue 183 dye in every successive time interval, (c) Acid Red183 dye degradation pie chart as a function of time and (d) schematic diagram of Acid Red183 degradation reaction mechanism over the surface of ZnO nano-whiskers.

The mechanism of Acid Red 183 degradation reaction mediated over ZnO nano-whiskers under UV light is explained on the basis of reported our pervious papers [28–29]. The photocatalytic reaction also termed as photoinduced reaction because the photocatalytic reaction initiated when a photon with appropriate wavelength (energy equal to or greater than band gap of photocatalyst) causes molecular excitation of photocatalyst. This molecular excitation results in the promotion of electron from valence band to conduction band and generate hole inside the valence band, according to equation and the reaction illustrated in the fig. 4. (d) [30],

$$\text{ZnO} + h_\nu \rightarrow $$

The photocatalytic reaction proceeds via a series of chemical reactions; formation of electron-hole is the initiation step of the reaction. This leads to the utilization of hole for oxidation process and electron for reduction process, which eventually generates super oxides anions and hydrogen peroxide ($\text{H}_2\text{O}_2$) from oxygen. Both the
oxidation and reduction reaction takes place at the surface of the semiconductor and if there the photogenerated electron-hole pair did not separate well there is possibility recombination of electron-hole pairs and this will diminish the efficiency of photocatalytic reaction [28-30]. According to this, the relevant reactions at the semiconductor surface causing the degradation of dyes can be expressed as follows [11]:

\[ \text{O}_2 + e^- \rightarrow \text{O}^2- + H^+ \rightarrow \text{HOO}^\cdot + \text{H}_2\text{O}_2 \]

The recombination of electron-hole pairs is acting as one of major factor that is responsible for inefficiencies of the photocatalytic processes. Every effort to prevent electron and electron-hole recombination will improve the efficiency of heterogeneous photocatalytic processes and will considerably help to achieve the application of efficient degradation.

**CONCLUSION**

The synthesis and characterization of ZnO nano-whiskers (ZNWs) by a simple sol-gel method at a pre-determined stirring condition (viz. 1800±50 rpm) has been reported and the result of stirring conditions on the crystallites size, aspect-ratio, morphologies and optical nature were investigated. The SEM and TEM result shows the zinc oxide developed into the huge colony consisting of adequate ZnO nano-whiskers, which contained a large number of long needle-like whiskers and the density of these colonies showed a good amount in each bunch. The average length and diameter of the long needle-like ZnO nano-whiskers are 36 nm and 1.15 nm respectively and their average aspect ratio was L/D = 31.3. The ZNWs shows significant absorbance of light in UV clearly demonstrates that it can be effectively works as efficient photocatalyst. The photocatalytic activity was effectively measured by clearly monitoring the photodegradation of Acid Red 183 by using the photo-catalyst, ZnO nano-whiskers. It was interesting to observe that about 68% discoloration takes place in just 150 min of irradiation in the presence of ZNWs experiments while there was nil or a little discoloration takes place in the absence of ZNWs photocatalyst.

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**REFERENCES**


[28]. Q.I. Rahman, et al, Efficient degradation of Methylen Blue dye over highly reactive Cu doped strontium titanate (SrTiO3)
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BIOGRAPHY

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