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An investigation of optical properties of zinc oxide nanoparticle synthesized by starch mediated assembly and its application in photocatalytic bleaching of methyl green and rhodamine-B

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ABSTRACT

The self-assembled nanostructure has wide applications in the development of nanosensor and photocell. Here, we synthesized zinc oxide nanoparticle (ZnONP) by sodium hydroxide (NaOH) mediated reduction of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) using starch as a capping as well as assembly agent. The effect of various precursor concentration, and reaction temperature on the size and shape was analyzed. ZnONP was characterized by UV spectroscopy, dynamic light scattering (DLS), zeta potential, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), photolumiscence (PL), as well as thermogravimetric analysis (TGA). In addition, the effect of starch on PL was also evaluated. The results revealed that the use of increasing concentration of $Zn(NO_3)_2 \cdot 6H_2O$ resulted in the increase of ZnONP size, but increasing starch concentration and calcination temperature showed reverse effect. Band gap analysis of ZnONP showed that band gap energy was increased with decreasing size of the nanoparticle (NP). PL analysis showed that ZnONP has excellent absorption in UV region and emission at 380 nm Furthermore, the photocatalytic activity of ZnONP for Methyl green and Rhodamine-B were also investigated. The results revealed that incubation of dyes with ZnONP at a wavelength of 254 nm ultraviolet spectra-C (UV-C) caused bleaching of both dyes and a gradual decrease in the absorption peak. Therefore, the analysis demonstrated that starch capped self-assembled ZnONP have potential use in nanosensor, as UV protectant and in the photocatalytic degradation of the harmful dye.

1. Introduction

Since last decade, research has been focused towards creating nanostructure by various top down and bottom up approaches to utilize properties such as high band gap, transparent nature, and photoluminescence. Due to the unique properties of zinc oxide nanoparticle (ZnONP) like wide band gap (3.37 eV), exciton binding energy (60 meV), it has been explored in various fields such as electronics [1], sensing [2] and medicine [3,4]. Various scientific groups have already developed ZnO nanostructure by mechanical [5], chemical [6,7], and green synthesis [8] method for different applications. However, the problem with mechanical and chemical method is the consumption of a large amount of energy, adsorption of chemical on the

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surface of nanoparticles and removal of hazardous chemicals. Due to these reasons, the synthesis of ZnONP by the green method has emerged as an alternative to the mechanical and chemical methods. Apart from using non-hazardous bio-chemicals, the green method has shown to be highly economical in energy perspective. Since last decades, various green methods has been reported for the synthesis of ZnONP of different size and shape using plant extract [8] and starch as a capping agent [9–12]. Moreover, all the previous methods reported ZnONP synthesis with starch as capping agent, performed either at room temperature or between 75 and 80 °C with a high calcination temperature that may degrade the starch and consume considerable amount of energy.

Moreover, the properties of nanoparticle also vary with their size, shape, and functionality. For example, as we increase the size of the nanoparticle above 100 nm, its nanosize related properties become less dominant than bulk state properties, moreover it results in the reduction of surface to volume ratio (i.e. less number of interfacial atom/area for interaction). The various applications like solar cell, semiconductor based electronic devices, and photocatalysis also use larger particle assembly, however in larger particles, the nanosize related properties diminished. This problem can be solved by the assembly of small particles of 5–10 nm size using scaffold of polymeric compounds. This strategy not only provide higher interfacial area compared to the particle having the same size and formed by the molecular assembly but also maintain the nano-size related properties and ease the handling of nanomaterial. Moreover, assembly of quantum dot or small particles on a support causes a gain of ability to tune photoelectrochemical response and photoconversion efficiency by facilitating charge transport [13].

Here, our aim was achieved by performing the reaction at 60–65 °C, followed by calcination at 60–80 °C for overnight. The rationality behind the experiment was to get the assembly of 5–10 nm size of ZnONP by the reduction of $Zn(NO_3)_2 \cdot 6H_2O$ using NaOH. The optical properties of synthesized ZnONP like UV absorption, and photoluminescence was measured. Moreover, crystallite size and thermal analysis was also performed. In addition, the photocatalytic degradation of methyl green and rhodamine-B dye was analyzed by ZnONP. The photocatalytic degradation analysis was performed in the presence of UV-C light (254 nm) for 12 h and degradation was measured by UV–vis spectroscopic analysis.

2. Material and methods

2.1. Materials

$Zn(NO_3)_2 \cdot 6H_2O$ was purchased from Sigma Aldrich, India. NaOH, starch (potato source) was purchased from Himedia lab, India. All the chemicals were of analytical grade and used without further purification. All the glassware were rinsed using aqua regia and cleaned by Milli-Q water. The dried glassware was used in all the experiments.

2.2. Synthesis of zinc oxide nanoparticle (ZnONP)

We synthesized ZnONP by the wet the chemical method. In brief, 1% (w/v) of starch was mixed with Milli-Q water and heated in a microwave oven for 2 min to get a clear solution. After cooling, 10 mM $Zn(NO_3)_2 \cdot 6H_2O$ was incorporated in the starch solution and kept on a magnetic stirrer and NaOH (20 mM) was added drop-wise. The final volume of solution was made up to 20 mL, and the reaction was continued for 1 h with continuous stirring and further heated at 60–65 °C for 2 h with stirring. The white precipitate was produced and washed three times with distilled water and centrifuged at 10,000 rpm for 10 min to remove impurities. The precipitate was dried in vacuum and calcinated at 70 °C for overnight. Dried powder was collected, and desired concentration of ZnONP was prepared by ultrasonication of the sample for 10 min.

The effect of different concentration of starch (0.5%, 1%, 2%, and 3%), concentration of zinc nitrate (5, 10, 20, 50 mM), and calcination temperature (60, 70, and 80 °C) was also analyzed.

2.3. Characterization of ZnONP

2.3.1. UV–vis spectroscopic analysis

The band gap of ZnONP was analyzed by a spectrophotometer (λ-35, Perkin Elmer pvt. Ltd.). The absorption spectra were measured in the range of 200–700 nm, with a slit width of 2 nm and a scanning rate of 100 nm/min. All the samples were diluted to get absorption and normalized the spectra to compare peak shift. The energy of absorption wavelength was calculated.

2.3.2. Analyzing the hydrodynamic size and stability of ZnONP

The analysis of dynamic light scattering (DLS) was performed and intensity percent of NP with respect to size using zeta sizer (Nano-ZS, Malvern pvt. Ltd.) were plotted. Simultaneously, the stability of NP was determined by zeta potential analysis. The samples were prepared in Milli-Q water (filtered using 0.22 μm membrane filter) and investigated by using dynamic light scattering (laser light (λ is 633 nm), at 90° scattering). The data was analyzed using DTS 7.0 software provided by the company.

2.4. X-ray diffraction analysis

All the samples were deposited on a quartz slide and dried in vacuum. The baseline correction of spectra was done using quartz slide. The samples were analyzed by an X-ray diffractometer (XRD ULTIMA-IV, Rigaku, Japan) in the range of 25–90°, at 2θ/min scanning rate. The data (intensity) were fitted and matched with the XRD data file of ZnO powder from JCPDS card no. 36-1451 of ICDD database.

2.5. Electron microscopy

For field emission scanning electron microscopy (FESEM, JSM-7600F, Jeol) analysis, the samples were diluted and deposited on a silicon wafer by a drop casting