Optimized synthesis of ZnO nanostructures by egg-white content ratio manipulation for photocatalytic applications

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Abstract

Zinc oxide nanoparticles (ZnO NPs) were prepared through a green egg-white (EW) mediated method and characterized by x-ray diffraction (XRD), Field emission-scanning electron microscopy (FESEM), Photoluminescence (PL), and ultraviolet-visible (UV–vis) spectroscopy studies. Three egg-white content to zinc nitrate ratio were applied to synthesis the ZnO structures. Crystallite size of 48, 42, and 29 nm was obtained for 1:1, 2:1, and 3:1 wt ratio of EW: Zn(NO₃)₂ which indicated the impact of EW concentration on ZnO NPs size. FESEM shows that EW controls the nucleation, growth, and morphology of ZnO. The sample with 2:1 wt ratio found to be the most efficient photocatalytic performance by degrading almost 99% of methylene blue (MB) within 60 min in water under natural irradiation with a pseudo-first-order rate constant of k = 5.89 × 10⁻² min⁻¹. It is demonstrated that morphology, size and surface oxygen vacancy of ZnO NPs are responsible to the efficient photocatalytic activity towards degradation of the MB dye under natural sunlight irradiation.

1. Introduction

Chemical dyes are major sources of harmful wastewater all over the world which mainly originate from dyeing textile, paper, and pulp and continuously released into the environment and water system [1, 2]. Most dyes contain a degree of aromaticity, substituted with azo and hydroxyl groups that are hazardous to health and not to be degradable by biological methods [3–6]. Therefore, many different techniques such as adsorption, precipitation, physicochemical, biological and sedimentation have been applied for wastewater refinement. However, these methods are not fully effective because they do not completely degrade the pollutants from the water. Hence, advanced oxidation processes (AOPs) degradation of organic dyes in the aqueous phase have been developed as a clean and cost-effective technique for treating such environmental pollutants [7, 8]. Photocatalysis is one of the most widely developed AOP methods for treating wastewater. Photocatalysis by semiconductors is a considerable AOP method and results from the interaction between photo-generated electron and hole pairs on semiconductor surfaces irradiated by appropriate (UV or visible) light. As a semiconductor, ZnO has received much attention in many fields such as solar cells, electrical, antibacterial devices, gas sensors and photocatalytic applications [9–13]. The photocatalytic activity of ZnO is depended on various factors including its crystallinity, morphology, surface area, and particle size that are widely depended on fabrication method.

A wide range of methods has been employed for the preparation of ZnO NPs such as hydrothermal and solvothermal processes, precipitation and co-precipitation [14–16]. However, the synthesis of ZnO photocatalysts using sol-gel method has attracted considerable attention because of its acceptable costs, simple experimental conditions, crystalline quality and easy to handle. This method is also helpful for the synthesis of ZnO with different morphologies, various sizes, and higher surface area. Controlling the morphology of ZnO can increase the area to valium ratio of particles and consequently enhance the photodegradation rate of pollutants [17–19].

Herein, we report the synthesis of ZnO NPs using an EW-assisted sol-gel method [20–22]. The method is simple and effective and introduces oxygen defects [23–25] into ZnO materials through annealing in ambient...
condition. The influence of the ZnO NPs morphology on photocatalytic activities was investigated by the degradation of methylene blue (MB) aqueous solutions under the natural sunlight irradiation. The prepared ZnO NPs exhibit high photocatalytic activity and good stability during aqueous environmental remediation with competitive photocatalytic efficiency comparing to literature works. Moreover, the crystal structure, grain size, and morphology of samples were investigated and the relationship between their surface states and photocatalytic properties was discussed.

2. Experimental

2.1. Materials
Zinc nitrate analytical grade (≥99%, Merck), Chicken egg provided from a local supermarket.

2.2. ZnO nanoparticles synthesis
To prepare ZnO NPs with 1:1, 1:2, and 1:3 wt ratios, various amounts of 9, 12, and 18 g of EW were slowly added into each magnetically stirred solutions of zinc nitrate (6 g) in distilled water (100 ml), at room temperature in three separate 250 ml beakers and named C1, C2, and C3, respectively. The solution became milky white immediately after adding the EW to zinc nitrate solution. The solutions were kept at 80 °C on vigorous magnetic stirring for about 5 h. After evaporation 80% of the water content, the heater was turned off and the solutions were stirred for a further 1 h at room temperature and finally, ice cream like gel was obtained. Then, distinct samples were calcined at 450, 600 and 700 °C, for 3 h and at 3 °C min⁻¹ and finally stored in for further use. The samples C1, C2, and C3 which annealed at 600 °C are denoted by C1600, C2600, and C3600, respectively. In the same way, the sample C2 named C2450 and C2700 after annealing at 450 and 700 °C, respectively.

2.3. Photocatalytic activity
The Photocatalytic activities of ZnO samples were evaluated by the degradation of MB solution as a pollutant under natural sunlight irradiation. In a typical experiment, 25 mg of each sample was added into 50 ml of 15 mg l⁻¹ MB aqueous solution. To reach the adsorption–desorption equilibrium and to avoid any error from the initial adsorption effect, the solution was stirred for 30 min in darkness before the irradiation of sunlight. During the irradiation, aliquots of 2 ml of solutions were taken at a regular interval of time. The concentration of MB in the solution was evaluated by recording the absorbance peak as a function of reaction time using a UV–vis spectrophotometer.

2.4. Characterization
X-ray diffraction (XRD) patterns were explored using a Panalytical, X’ Pert Pro instrument with Cu-Kα radiation (λ = 0.154 056 nm). Field emission-scanning electron microscope (FE-SEM) analysis was conducted using a ZEISS instrument SIGMA VP with the EDS spectrometer operating at 15-20 kV accelerating voltage. The ultraviolet-visible (UV–vis) absorption spectra were measured using a Perking-Elmer UV–vis spectrophotometer. Photoluminescence (PL) spectra were measured by a Perking-Elmer spectrometer with a Xenon lamp at the excitation wavelength of 325 nm.

3. Results and discussion
The structural characterization of the ZnO NPs including crystallinity, phase, and purity of the as-prepared samples was examined by XRD and recorded as a function of 2θ range of 10°–70° with a step size of 0.01° and a scanning rate of 0.02 steps per second. Obtained XRD patterns of the ZnO NPs are shown in figure 1. Eleven major peaks are observed for ZnO NPs at 2θ values of 31.82°, 34.49°, 36.31°, 47.60°, 56.64°, 62.91°, 66.41°, 67.99°, 69.13°, 72.62°, and 77.00° which corresponds to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) crystal planes of the hexagonal ZnO structure (JCPDS: 36-1451). The sharp and intense peaks show the highly crystalline ZnO NPs with polycrystalline structure. The average crystallite size of ZnO NPs was calculated using the Scherrer formula and found to be 48, 42, and 29 nm for C1600, C2600, and C3600, respectively. As shown in figure 1(a), it is seen that compared with two other samples, C3600 has the finer calculated crystallite size. This can be due to the optimized amount of EW in synthesis processes which provides efficient photocatalytic performance. Besides, the XRD patterns of C2 which were annealed in three temperatures of 450, 600, and 700 °C are depicted in figure 1(b). The increasing in annealing temperature causes the sharper peaks and lager crystallite sizes.

To study the morphology of ZnO NPs and influence of EW on the surface of the obtained structures, FESEM analysis was carried out (figure 2). In the FESEM images, the morphology exhibited a variety of shapes from dodecahedral like to spherical like particles. Utilizing the Dimizer software, the size of ZnO particles was
estimated to 130, 47, and 80 nm for C1600, C2600, and C3600, respectively. It is observed from figures 2(a)–(c) that the sample C2600 has the lesser particle size and narrow distribution in compared to the C1600 and C3600 samples. However uniformly distributed much smaller particle of ZnO can be considered due to presence of the EW as an overall matrix. Few of elongated dodecahedral like particles are observed in the product, which could be resulted from aggregation of ZnO nanoparticles in higher (700 °C) temperature (figure 2(f)).

In annealing processes, the temperature is an effective factor in the size and morphology of materials. To evaluate the effect of thermal treatment the C2 sample was calcined at three temperatures. Images of annealed C2 at 450, 600, and 700 °C temperatures are illustrated in figures 2(d)–(f).

For unit volume, the surface area to volume ratio increases for polyhedral shapes, so polyhedral morphologies could be useful for sunlight capturing process [26]. Also, as it is observed from FESEM images that ZnO surfaces show an evident roughness which is a consequence of the use of EW in synthesis processes. The roughness of the surfaces along with polyhedral morphology is responsible for enhancing the photocatalytic activity of prepared ZnO particles.

The experiment conducted with a lower concentration of EW (C1 with 1:1 ratio) resulted in large particles and leads to low photocatalytic activity. However, the sample prepared with a larger concentration of EW (C2 with 2:1 and C3 with 3:1 ratio) showed considerably better photocatalytic degradation activity.

The energy dispersive spectra (EDS) of C1600, C2600, and C3600 are shown in figure 3. Also, elemental analyze of EDS analysis is summarized in table 1 and it is clear that Zn:O ratio is non-stoichiometric by an
Figure 2. FESEM images of samples annealed at 600 °C: C1 (a), C2 (b), and C3 (c); C2 annealed at 450 °C (d), 600 °C (e), and 700 °C (f).

Figure 3. Energy dispersive spectra (EDS) of (a) C1600, (b) C2600, and (c) C3600.
oxygen content about 15% versus approximately 85% of Zinc for all samples which inducting a good oxygen vacancy. It has been already described that ZnO with oxygen vacancies is more effective as a photocatalyst \[24\]. Therefore, in the present case too, this reason may stand valid for effective photodegradation of sample C2 annealed at 600 °C for the MB during the photocatalytic process.

UV–vis spectroscopy was performed to study the optical properties of ZnO NPs samples. As depicted in figure 4, the absorption spectra for C1600, C2600, and C3600 samples gave rise to a peak at about 375 nm which is in the range of many reported values \[1\]. The optical band gap (E_g) of the samples was derived by extrapolating the linear region of the plot of (a(hν)^2) against photon energy (hν) into the energy axis where α is the absorption coefficient. It is found that the band gap of ZnO NPs decreases significantly from literature values \[2\] which can be assigned to the oxygen vacancy induct by EW. The calculated band gap was 2.7, 2.5, and 2.9 eV for C1600, C2600, and C3600 samples, respectively. The reduction in band gap values of samples can be assigned to the

**Table 1.** Shows the weight percentage of C1600, C2600, C3600, C2450, and C2700.

| Sample   | C1600 | C2600 | C3600 | C2450 | C2700 |
|----------|-------|-------|-------|-------|-------|
| Oxygen (Weight%) | 17.1  | 13.3  | 14.5  | 13.1  | 15    |
| Zinc (Weight%)    | 82.9  | 86.7  | 85.5  | 86.9  | 85    |

![Figure 4](image-url)
oxygen vacancy defects [3, 4] and consequently enables the possibility of high photoactivity of the nanoparticles in the visible region.

As a convenient method to study the various defects in a semiconductor structure such as ZnO, the fluorescence spectrum was taken in the band edge emission region. This emission is a result of the recombination of photogenerated electrons and holes. The spectrum was taken for the comparative study of fluorescence intensity between C1600, C2600, and C3600 samples. Figure 5 shows the fluorescence emission spectra of three samples which were observed in the range 375–700 nm. All C1600, C2600, and C3600 samples shown strong ultraviolet emission spectra of narrow violet (388 nm) and a broad green emission band in the visible region at 425–625 nm which were due to defects such as oxygen vacancy defect. The near band edge (NBE) emission is a relatively strong UV emission band at about 390 nm, is responsible for the recombination of the free excitons of ZnO nanostructure of C1600, C2600, and C3600 samples [5]. The blue emission at about 405 nm could be attributed to the surface vacancy. The blue emission at 446 nm may be related to the trapped electrons located within the depletion regions of ZnO—ZnO grain boundaries [6]. The emission at about 485 nm originates from a transition between the oxygen vacancy and oxygen interstitial and lattice defects [7]. The green emission at 527 nm that is common for all samples is nearly in concordance with the energy gap between the level of oxygen vacancy and the valence band. Although, the strong fluorescence
corresponds to high recombination of photogenerated electron–hole carriers and resulting in low photocatalytic activity; however, in the fluorescence spectra of samples that depicted in figure 4(a), the peak intensity of C2600 is stronger than that of C3600. But, on the contrary, the photocatalytic activity of the C2600 is much higher than those of the C1600 and C3600. The reason that might be argued for this contradiction is due to the increase in the oxygen vacancy of C2600 that can be confirmed by the EDS results previously shown in table 1. With this in mind, along with a noticeable reduction in particle size for C2600 and enhancing in the specific area, the electron–hole production in C2600 is much affluent compared to C1600 and C3600. Therefore, the increase of fluorescence peak intensity in C2600 looks natural. Moreover, the fluorescence spectra of C2 that were annealed at three 450, 600, and 700 °C temperatures are illustrated in figure 4(b). Again, compared with other samples, the increase in the C2600 peak intensity, coming from the well-ordered oxygen vacancy defects in ZnO lattices due to the optimized annealing temperature of 600 °C.

To monitoring the photocatalytic activity of prepared samples, the degradation of the pollutant was done in direct sunlight using MB as a cationic Azo dye which has been widely studied as a model in photocatalyst researches. MB has two major absorption peaks in water located at 292 nm and 664 nm which have been originated from benzene ring and heteropolyyaromatic linkage, respectively. The absorption peak at 664 nm was selected to study the MB degradation according to literature. The photocatalytic degradation of MB was investigated with synthesized ZnO matrix structures under sunlight irradiation. The decreasing in the absorption intensity of MB (664 nm) was monitored by UV–vis spectroscopy. From the photocatalyst measurements, the photocatalytic activity of the catalyst samples is ordered as C1600 < C3600 < C2600. Compared to C1600 and C3600, sample C2600 indicated the best photocatalytic activity. The initial concentration of MB was 20 mg L⁻¹ in total, and the ZnO catalyst amount was 0.5 g L⁻¹. The complete decolorization of MB in the presence of C2600 was faster than other samples and achieved in 120 min under direct irradiation.

Figure 6 represents the Sunlight-induced photocatalytic behavior of C1600, C2600, and C3600 samples towards the degradation of MB dye. It is evident from figures 6(a)–(c) that ZnO NPs have the capability to almost fully degrade the MB dye within 120 min However, C2600 can fully degrade the same only within 60 min as shown in figure 6(b). For better comparison of the degradation efficiency of the samples, C/C₀ versus time graph was plotted for C1600, C2600, C3600, C2450, and C2700. As it can be observed from figure 7(a), C2600 have the fastest degradation rate. Further, in order to evaluate the photocatalytic behavior of samples and calculate the pseudo-first-order rate constant, Ln(C₀/C) versus time is plotted. The analysis result is shown in figure 7(b) and demonstrates that the photocatalytic degradation of MB dye confirms the pseudo-first-order decay kinetics, Ln(C₀/C) = kt, where k, C₀, and C denote surface reaction rate constant, initial concentration of solution and concentration of dye after irradiation at various time interval (t) respectively. As it is evident, C2600 with the constant of 5.89 × 10⁻² min⁻¹ is the best sample for photocatalytic degradation of MB under sunlight irradiation.

Based on the above analysis, as shown in figure 7(b), it can be concluded that the enhancement of the photocatalytic activity of the C2600 nanostructures for MB dye may be mainly attributed to the enhanced surface area of ZnO polyhedral shapes and excess of oxygen vacancies created on ZnO surfaces via EW mediating processes which leading to enhanced adsorption ability and superior trap electron transition.

The mechanism for the photocatalytic degradation of MB with a ZnO photocatalyst is shown in figure 8. The effectiveness of ZnO NPs in MB decomposition can be explained based on the OH· and O· radicals and holes present on the surface of ZnO NPs, which break down MB dye in aqueous solutions.

When a photon with energy (hν) is absorbed in a semiconductor that matching or exceeding of semiconductor bandgap energy (Eg), an electron is excited from the valence band (VB) to the conduction band (CB) and leaving a hole behind. Various destinies may occur for the photo-generated electrons and holes. As a probable occurrence, they may be recombined and dissipate the input bandgap energy as heat, get trapped in metastable surface states, or react with electron donors and acceptors adsorbed on the semiconductor surface or within the surrounding double electrical layer of charged particles. However, when oxygen vacancies exist, the surface defect states are available to trap electrons or holes. This can reduce the probability of recombination and subsequent redox reactions may occur. Thus, oxygen vacancies play an important role in the dye degradation under light irradiation. A conventional mechanism is to create an impurity level between the CB and VB of the semiconductor particle. This energy level acts as a deep donor defect level, near the top of VB [8]. The denoted defect energy levels in figure 6 have been obtained by calculating the emission energy corresponding to the peak around 465 nm (fluorescence spectrum shown in figure 5). The calculated bandgap energy of 3.16 eV corresponds to the band-edge emission peak at around 394 nm, as shown in figure 6. Indeed, an ‘empty’ oxygen site can trap either one electrons [9], thereby effectively reducing the recombination rate of the e−h pairs and finally more electron and hole migrate to the surface of the ZnO matrices and promote the photocatalytic degradation reactions.
Moreover, the photocatalytic activity of a material is strongly related to its particle size. In particular, this phenomenon is more tangible when the particle size decreases and leading to a quantum confinement effect. Therefore, the decrease in size may improve the photocatalytic efficiency by extending the effective bandgap.
Figure 7. (a) Plot of $C_t/C_0$ versus time for comparative study of C1600, C2600, C3600, C2450, and C2700. (b) Plot of $\ln(C_0/C_t)$ versus time for evaluating the kinetic constant of C1600, C2600, C3600, C2450, and C2700 in the photocatalytic degradation of MB.

Figure 8. Schematic of ZnO NPs photocatalytic activity for decolorization of MB.
[10]. A careful look at FESEM images in figure 2(b) leads us to conclude that fine particles on C2600 surfaces are responsible for the enhancement in photocatalytic effect. Also, reducing the particle size leads to the larger specific surface area and cause a more effective photocatalytic effect. These two stated evidence cause a synergetic effect on increasing in the number of active sites and photodegradation of MB under sunlight irradiation.

4. Conclusion

In summary, we have successfully synthesized the ZnO nanoparticles by a simple and facile sol-gel method using zinc nitrate hexahydrate as precursor and EW as coordinator. The XRD studies indicated the formation of phase pure polycrystalline ZnO. The morphological characterizations revealed that the synthesized ZnO nanostructures possessed polyhedral morphology with an average diameter of about 130, 47, and 80 nm for C1600, C2600, and C3600, respectively. The synthesized ZnO nanostructures showed good photocatalytic activity towards the photo-degradation of MB dye under sunlight irradiation. A rapid MB degradation with the degradation rate of 99% within 60 min was observed over the surface of ZnO nanostructures following the first-order rate constant with 5.89 $\times$ 10$^{-2}$ min$^{-1}$. The EW to zinc nitrate ratio of 2:1 (C2600) resulted in smaller particle size which allows utilization of more light, greater separation of electron-hole pairs and more adsorption of MB on the surface of ZnO and better photocatalytic activity for the degradation of MB dye under visible light. The enhanced photocatalytic activity of ZnO nanoparticles may be due to the smaller particle size, higher surface area, and excess of oxygen vacancy.

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Conflicts of interest

The authors declare no conflicts of interest.

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