Preparation of strontium doped mesoporous ZnO nanoparticles to investigate their dye degradation efficiency

Balvinder Kumar1,2,*, Suresh Kumar1,2, Virender Singh1,2, Anil Vohra1,2,*, Nikhil Chauhan1,2, and Rajesh Goyal1,2

1 Department of Electronic Science, Kurukshetra University, Kurukshetra-136119, India
2 Haryana State Board of Technical Education Panchkula-134104, India

E-mail: balvinderbangar60@gmail.com

Keywords: mesoporous, strontium, ZnO nanoparticles, hydrothermal, photocatalysis

Abstract

Mesoporous strontium doped ZnO nanoparticles are synthesized as photocatalyst by using zinc nitrate hexahydrate, surfactant P123, strontium nitrate hexahydrate via the hydrothermal process. X-ray diffraction (XRD), UV-visible spectroscopy (UV), Fourier transform infrared (FTIR), Photoluminescence (PL), Energy-dispersive x-ray (EDX), Scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM), and Brunauer–Emmett–Teller (BET) characterizations are used for the analysis of all the samples. XRD spectra disclose the disparity in the crystal size 14.98 to 22.74 nm. The study of UV spectroscopy revealed the energy bandgap difference between 3.3–2.92 eV. PL spectroscopy shows the effect of doping on the electron–hole recombination rate of the sample. FTIR analysis has utilized to determine the functional groups such as –OH, C=O=C, and –C=O present in the sample. EDX spectra show the elemental compositions of the sample. SEM images show the agglomerated morphology and TEM images show the different shape morphology of the sample. BET analysis shows the occurrence of 39.9 m² g⁻¹ surface area with mesoporous morphology. The effect of the increasing percentage of strontium on the photocatalytic capability of ZnO is checked against methylene blue and congo red dyes with 75% and 80% degradation.

1. Introduction

In today’s world, there are many environmental problems. One of them is water pollution. A lot of polluted water comes out from the industries which contain dyes [1]. Due to modern civilization, there is an increment in the formation of dyes. There are various semiconductor metal oxides nanostructures such as SnO₂, ZnO, and TiO₂ which are used to treat wastewater via the eco-friendly process called solar photocatalysis [2–4]. To treat the waste-water, ZnO (n-type semiconductor) is preferred over other semiconductor metal oxides just because of its excellent electron mobility and 3.37 eV of band gap energy with chemically stable nature and ability to degrade a variety of dyes with antifungal and anti-corrosive property. Doping is a productive and rapid technique to make the photocatalytic properties better. Here we have used strontium as a doping element. The selection of a doping element having a bigger radius as compared to the Zn⁺ causes major lattice defects due to charge compensation. The difference in ionic radius between Sr²⁺ (2.45 Å) and Zn²⁺ (0.74 Å) influences the optical characteristics of ZnO. The role of strontium doping is to diminish the energy bandgap and electron–hole recombination of the pure ZnO nanoparticles. As the percentage of strontium doping increases, the energy bandgap of the ZnO nanoparticles is reduced progressively. K Pradeep raj et al synthesized strontium doped ZnO nanoparticles to quest their structural, optical, photoluminescence, and photocatalytic activity [5]. S Lakshmana Perumal et al investigated the structural, optical, and photocatalytic properties of strontium doped ZnO nanoparticles [6]. S Salvi et al synthesized strontium doped ZnO photocatalyst [7]. Linhua Xu et al investigate the structural and optical properties of strontium doped ZnO thin films [8]. Ramin Yousefi et al investigate the improved visible-light photocatalytic activity of strontium doped ZnO nanoparticles [9]. There are various techniques for the synthesis of pure and strontium doped ZnO nanoparticles just like the sol-gel
method, thermal deposition, co-precipitation method, hydrothermal method, etc [10]. In the present research, samples are prepared by the hydrothermal method. There is sufficient water available on earth [11]. Every chemical is easily soluble in water. Another advantage of using the hydrothermal method above diverse forms is its capability to build crystalline phases which are unstable at the melting point [12]. The hydrothermal method is performed in a pressure vessel also defined as an autoclave, whereas processing conditions are controlled by adjusting the temperature/pressure.

The purpose of the experiment is to notice the influence of the strontium doping on the photocatalytic performance of ZnO nanoparticles with mesoporous morphology against Methylene Blue (MB) and Congo Red (CR) Dyes.

2. Experimental

2.1. Material used
Zinc Nitrate Hexahydrate (Zn(NO)_3·6H_2O), Strontium Nitrate Hexahydrate (Sr(NO)_3·6H_2O), Sodium Hydroxide (NaOH), Pluronic P123 ([H(CH_2CH_2O)20(CH_2(CH_3)O)70(CH_2CH_2O)20H]). All these chemicals are of analytical grade (Sigma Aldrich).

\[
\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{ZnO} + 7\text{H}_2\text{O} + 2\text{NaNO}_3
\]

2.2. Synthesis of pure and doped ZnO
As shown in figure 1, Solution 1: - 17.437 g zinc nitrate hexahydrate (1 M) with 0.1 g of P123 in 25 ml of DI water under stirring for 1 h at 60 °C. Solution 2: - 1 g of sodium hydroxide in the 25 ml of DI water. Solution 2 was mixed dropwise to solution 1, under stirring at 60 °C (solution 3). Hydrothermal treatment is provided to solution 3 (gel) by autoclave adjusting temperature for hours and after that, all the solutions were filtered and washed to obtain dry and white powder. For drying the samples were placed into the electric oven at 120 °C and for calcination placed in a muffle furnace at 450 °C (to remove the surfactant).

To the synthesis of doped samples required the amount of strontium nitrate hexahydrate is added to solution 3 for the different molar percentages (1%, 2%, and 3%), (table 1).

2.3. Characterization
Instrument Quantochrome is used to determine the type-IV Nitrogen adsorption-desorption plot of the powder samples at 250 °C of outgas temperature. PL spectra are determined by the Aligent Cary Eclipse spectrophotometer. Instrument Perkin Elmer is used to confirm the FTIR spectra. Powder samples at room temperature are used without any specific conditions of the sample preparation in FTIR, PL, XRD, and UV–vis. PANalytical x-ray diffractometer and Perkin Elmer LAMBDA 650 instruments are used to determine XRD as well as UV–vis spectra. Ethanol with sonication is used to prepare a suspension of powder sample to obtain the TEM images via the Tecnai™ G2 20 instrument. SEM images are obtained by using Hitachi instrument.
2.4. Photocatalytic degradation

The photocatalytic performance of the ZnO nanoparticles is performed by the use of Methylene Blue (MB) and Congo Red (CR) dyes. The calculated amount of dye ($10^{-5}$ M) is added in 100 ml of DI water. Now, put the 100 ml solution with 0.05 gm of photocatalyst on the sonication for the 1 h in the dark region before displaying to the visible light (mercury vapor lamp, 420–520 nm, placed 1 cm above in vertical position). At a regular interval of 20 min, drop out 10 ml from the solution to check the percentage degradation through the UV–visible spectrophotometer. A similar process is performed for the degradation of congo red dye and degradation is calculated.

$$\eta = \left( A_0 - A_T / A_0 \right) \times 100$$

$A_0$ = initial adsorption

$A_T$ = adsorption at time $t$.

3. Results and discussion

3.1. Structural studies

The results of the XRD analysis of the samples can be revealed in figure 2. Table 1 displays the different peaks at the diffraction angle of 31.69°, 34.39°, 36.25°, 47.44°, 56.57°, 67.78°, 69.14° with their respective miller indices (100), (002), (101), (102), (110), (103), (112), (201) describes the hexagonal wurtzite arrangement of ZnO (JCPDS file no. 800075) with the extra peak at 32.85° (001), 38.74° (112), 46.95° (202), and 58.40° (113) (JCPDS file no. 060520) corresponds to strontium oxide. It is observed that there is a slight shift in the (101) peak facing diminished diffraction angles. This crystal size is determined from the Scherrer formula and varies from 14.98–22.74 nm as shown in table 2, but not in a continuous manner [13].
3.2. Morphology and structural analysis

It is noticed that with the addition of strontium doping the agglomerated morphology of the ZnO nanoparticles increases as per displayed in figure 3. TEM images are presented in figure 4. TEM pictures show the exact shape and size of ZnO nanoparticles, mesoporous assembly of nanoparticles is visible in all the images. EDX reveals the presence of all elements with ZnO as shown in figure 5.

The study of BET analysis is used to investigate the pore diameter, pore-volume, and surface area. Three images associated with isothermal (figure 6), BJH (figure 7) and multi-point BET analysis (figure 8). The pore diameter of 6.5 nm with 0.08 cc g\(^{-1}\) of pore volume was analyzed through BJH analysis. The multipoint BET shows the surface area of 39.9 m\(^2\) g\(^{-1}\). The presence of type-IV hysteresis in the isothermal displays that there is the existence of the mesoporous nature of sample A having slit-like pores [14].

3.3. UV-visible spectroscopy analysis

The key step to observe the change in the energy band gap of pure and doped samples is UV-visible spectroscopy (figure 9). ZnO has a direct bandgap of 3.3 eV. Analysis of UV-vis spectroscopy shows that as there is an increase in doping the energy band gap of doped ZnO nanoparticles reduces consecutively. The ethics of the reduced energy band gap are picked up from Tauc’s plot as shown in figure 10. The energy bandgap varies from 3.3 eV–2.92 eV [9, 15].
3.4. Fourier transform infrared spectroscopy analysis (FTIR)
As shown in figure 11, the results found from the study of FTIR spectra show that the functional groups lay in the region between 4000 cm$^{-1}$–400 cm$^{-1}$, both the stretching and bending modes are shown. The functional groups such as O–H stretching (3500–4000 cm$^{-1}$)$^{[16]}$, C=O=C(2360 cm$^{-1}$)$^{[17]}$, O–H bending (1520 cm$^{-1}$)
C–O (1340 cm$^{-1}$), C–H bend (843 cm$^{-1}$), C–C (670–615 cm$^{-1}$) attained in the samples. There is no major change in the functional group as the number of doping rises.

3.5. Photoluminescence spectroscopy (PL) analysis

Analysis of photoluminescence spectra describes that the electron-hole pair recombination decreases concerning the doping. The minimum intensity is observed from the maximum doping concentration (3%) [19]. Following their luminescence color, their corresponding defects were obtained and shown in figure 12. The PL-emission is obtained at 441 nm, 452 nm, and 470 nm shows the blue emission with the existence of Zinc vacancy, at 481 nm the blue-green emission with Zinc interstitial, at 494 nm green emission with oxygen antisite and oxygen interstitial [20, 21].
3.6. Photocatalytic degradation activity
The deterioration of methylene blue (MB) and congo red (CR) at a pH value of 8, has been performed by the pure and strontium doped samples to illustrate their photocatalytic competence. The electrons in the valance band were shifted to the conduction band when exposed to the visible light \[22\]. The holes in the valence band break down the water particles to custom the hydroxyl radicals and electrons in the conduction band act in response with an oxygen particle to custom superoxide anion. As we increase the doping concentration the efficiency of photocatalysis increases and shifted toward visible light due to lower bandgap energy and electron-hole recombination speed as shown in figures 13 and 14. In the visible light, the maximum degradation of dye is shown by sample D against congo red (80%), table 3. The pattern of degradation is the same for both the dyes i.e. degradation increases with doping percentage.

Figure 8. Multi-point BET graph of sample A.

Figure 9. Absorption spectra of all the samples.
4. Conclusion

The pure and strontium doped ZnO nanoparticles are magnificently characterized following the hydrothermal method. XRD pattern shows that entire synthesized samples contain the hexagonal wurtzite structure and the crystalline dimension of nanoparticles varies from 14.98–22.74 nm. UV-visible spectroscopy analyses that the energy band gap shrinks (3.3–2.92 eV) as the doping concentration increase. In the FTIR spectra, the presence of diverse functional groups is found in the sample. PL spectra show that the electron-hole recombination drops with an increase in the doping percentage. The agglomerated morphology of the samples in the nanometre range is displayed in the SEM images. TEM images show the exact shape and size of the crystal. The existence of all
elements (Zn, O, and Sr) that exist in the sample is shown by the EDX results. BET analysis shows the existence of a mesoporous structure along a high surface area. Thus, all the characterizations show that the strontium doped ZnO nanoparticles as an efficient photocatalyst are executed successfully by the hydrothermal method.

**Conflict of interest**

Author has no conflict of interest.
Figure 14. Photocatalytic deterioration action of samples across methylene blue dye.

| Sample | Congo Red | Methylene Blue |
|--------|-----------|----------------|
| P1     | 10%       | 6%             |
| P2     | 60%       | 38%            |
| P3     | 67%       | 51%            |
| P4     | 80%       | 75%            |

Table 3. Percentage degradation of various dyes after 90 min under visible light irradiation.

ORCID iDs

Balvinder Kumar @ https://orcid.org/0000-0002-5619-7397
Anil Vohra @ https://orcid.org/0000-0002-8651-7697
Nikhil Chauhan @ https://orcid.org/0000-0002-4908-7376

References

[1] Shivajirao P A 2012 Treatment of distillery wastewater using membrane technologies International Journal of Advanced Engineering Research and Studies 1 275
[2] Khan M I 2017 Investigations of structural, morphological and optical properties of Cu: ZnO/TiO$_2$/ZnO and Cu:TiO$_2$/ZnO/TiO$_2$ thin films prepared by spray pyrolysis technique Results in Physics 7 3176–80
[3] Tripathy N, Ahmad R, KuK H, Hahn Y B and Khand G 2016 Mesoporous ZnO nanoclusters as an ultra-active photocatalyst Ceramic International. 8 9519–26
[4] Chauhan N, Singh V, Kumar S, Kumari M and Sirohi K 2019 Preparation of silver and nitrogen codoped mesoporous zinc oxide nanoparticles by evaporation induced self assembly process to study their photocatalytic activity J. Sol-Gel Sci. Technol. 90 390–403
[5] Raj K P, Sadaiyandi K, Kennedy A and Thamizselvi R 2016 Structural, optical, photoluminescence and photocatalytic assessment of Sr-doped ZnO nanoparticles Mater. Chem. Phys. 183 24–36
[6] Perumal S L, Hemalatha P, Alagara M and Pandiyaraj K N 2015 Investigation of structural, optical and photocatalytic properties of Sr doped Zno nanoparticles International Journal of Chemical and Physical Sciences 4 1–13
[7] Salvi S, Lokhande P and Mujavvar H 2016 Photodegradation of Rhodamine 6G dye by Cd, Sr doped ZnO photocatalyst Synthesized by Mechanochemical Method. In Int. Conf. on Communication and Signal Processing (2016(Atlantis Press) (https://doi.org/10.2991/iccasp-16.2017.8)
[8] Xu L, Xiao S, Zhang C, Zheng G, Su J, Zhao L and Wang J 2014 Optical and structural properties of Sr-doped ZnO thin films Mater. Chem. Phys. 3 720–26
[9] Yousefi R, Jamali-Shenini F, Cheraghizade M, Khorasani-Gandomani S, Saeedi A, Huang N M and Azarang M 2013 Enhanced visible-light photocatalytic activity of strontium-doped zinc oxide nanoparticles Mater. Sci. Semicond. Process. 32 152–59
10. Chauhan N, Singh V, Kumar S, Sirohi K and Siwatch S 2019 Synthesis of nitrogen- and cobalt-doped rod-like mesoporous ZnO nanostructures to study their photocatalytic activity J. Sol-Gel Sci. Technol. 91 567–77
11. Ng Z-N, Chan K-Y, Muslimin S and Knipp D 2018 P-type characteristic of nitrogen-doped ZnO films J. Electron. Mater. 47 5607–13
12. Thirukumararan P, Atchudan R, Parveen A S, Kalaiarasan K, Lee Y R and Kim S C 2019 Fabrication of ZnO nanoparticles adorned nitrogen-doped carbon balls and their application in photodegradation of organic dyes Sci. Rep. 9 1–13
13. Roy A, Maitra S and Chakrabarti S 2018 Sonoochemical syntheses of iron doped zinc oxide nanoparticles at different sonication powers and temperatures with their application for photocatalytic degradation of PVC-ZnO composite film International Journal of Nanoparticles 10 178–95
14. Devi S A, Harshiny M, Udaykumar S, Gopinath P and Matheswaran M 2017 Strategy of metal iron doping and green-mediated ZnO nanoparticles: dissolubility, antibacterial and cytotoxic traits Toxicology Research 6 854–65
15. Wu X, Wei Z, Zhang L, Wang X, Yang H and Jiang J 2014 Optical and magnetic properties of Fe doped ZnO nanoparticles obtained by hydrothermal synthesis Semicon ductor Nanomaterials for Energy Conversion and Storage 2014 1–7
16. Ashraf R, Riaz S, Kayani Z N and Naseem S 2015 Structural and magnetic properties of iron doped ZnO nanoparticles Materials Today: Proceedings 2 5384–89
17. Chauhan N, Singh V, Kumar S and Dhiman R L 2019 Influence of Nickel, Silver, and Sulphur Doping on the Photocatalytic Efficiency of Mesoporous ZnO Nanoparticles 45 249–59
18. Bindu P and Thomas S 2014 Estimation of lattice strain in ZnO nanoparticles x-ray peak profile analysis Journal of Theoretical and Applied Physics 8 123–34
19. Pan J H, Zhang X, Du A J, Bai H, Ng J and Sun D 2012 A hierarchically assembled mesoporous ZnO hemisphere array and hollow microspheres for photocatalytic membrane water filtration Phys. Chem. Chem. Phys. 14 7481–89
20. Putz A M, Len A, Janasi C, Savii C and Almasy L 2016 Ultrasonic preparation of mesoporous silica using pyridinium ionic liquid Korean J. Chem. Eng. 33 749–54
21. Goh E G, Xu X and McCormick P G 2014 Effect of particle size on the UV absorbance of zinc oxide nanoparticles Scr. Mater. 78–79 49–52
22. Kazeminezhad S S and Yousufi R 2016 Effect of transition metal elements on the structural and optical properties of ZnO nanoparticles Bulletin of Material Science. 39 719–24