

Photocatalytic degradation of methylene blue dye with novel poly (1-naphthylamine)/zinc oxide nanocomposites

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Introduction

Organic dyes are one of the major pollutants in waste water produced from textile and other industrial processes [1]. Photocatalytic degradation is an economical and easy method to decompose organic pollutants into less dangerous matter. The semiconducting metal oxides like Zinc oxide (ZnO) nanomaterials exhibit promising photocatalytic activities due to their non-toxic nature, inexpensive, excellent chemical and mechanical stability with the wide band gap of 3.4 eV which allows to absorb the ultraviolet (UV) light [2, 3] and thus, could be an alternative material for the removal of organic pollutants (dyes). Poly (1-naphthylamine) (PNA) is an aromatic conducting polymer with lower band gap than polyaniline [4]. PNA nanocomposites could be expected as potential catalyst for the photocatalytic activities. This study investigates the photocatalytic degradation of MB dye under visible light using poly (1-Naphthylamine)/ZnO nanocomposites as a photocatalyst. The PNA/ZnO nanocomposites are synthesized with different wt% of ZnO nanomaterials and are examined for their structural, morphological, optical and photocatalytic activities.

Experimental

2.1 Synthesis of ZnO nanoparticles

The 0.2 mol dm^{-3} Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$), dissolved in 50 ml of deionized (DI) water was added to 2 mol dm^{-3} aqueous sodium hydroxide (NaOH) solution and subjected to ultrasonic wave irradiation for 2 h. The obtained white precipitates were filtered and washed with ethanol and DI water and dried in an oven at 60°C for 3 h.

2.2 Preparation of PNA/ZnO nanocomposites

The PNA/ZnO nanocomposites were prepared by the in-situ chemical polymerization of 1-naphthylamine monomer. The different wt% of ZnO nanomaterials (0.09wt%, 0.19wt% and 0.39wt%) were first suspended into the fixed ratio of 0.2 M 1-naphthylamine monomer and added in a mixture of ethyl alcohol (20 ml) and 2 M HClO_4 (20 ml). Thereafter, 10 ml ethanolic solution of cupric chloride (0.2 M) as an oxidant was added into the above reaction mixture with constant stirring at $0-5^\circ\text{C}$. The polymerization was carried out for 24 h. The obtained nanocomposite was washed thoroughly with distilled water and methyl alcohol and dried at 40°C for 24 h.

2.2 Measurements of photocatalytic activities

The photocatalytic degradation of MB dye was performed under the illumination of Xenon arc lamp (300W, Hamamatus: L 2479), attached with UV cut-off filter of wavelength 400 nm (FSQ-GG 400) which limited the illumination in a range of 400–800 nm i.e visible light. The

photocatalytic activities were performed as reported elsewhere [5], using optimum PNA/0.39wt%ZnO nanocomposite as effective catalyst. The degradation rate of MB dye over PNA/ZnO is estimated by the following equation

$$\text{Degradation rate (\%)} = (C_0 - C / C_0) \times 100 = (A_0 - A / A_0) \times 100$$

Where C_0 represents the initial concentration, C denotes variable concentration, A_0 shows initial absorbance, and A corresponds to variable absorbance.

Results and Discussion

The pristine PNA displays random morphology with large irregular spherical particles (Fig. 1 a). Fig. 1 (b-d) shows the drastic changes in the morphology of PNA by the addition of ZnO nanomaterials in the PNA/ZnO nanocomposites. The tendency of PNA agglomeration and its penetration with ZnO nanomaterials have increased with varied wt% of ZnO nanomaterials, which might due to the effective interaction between PNA and ZnO nanomaterials. The PNA/0.39wt% ZnO nanocomposite displays advanced morphology due to well penetrated and uniformly distributed PNA molecules into ZnO nanomaterials compared to the other prepared PNA/ZnO nanocomposites.

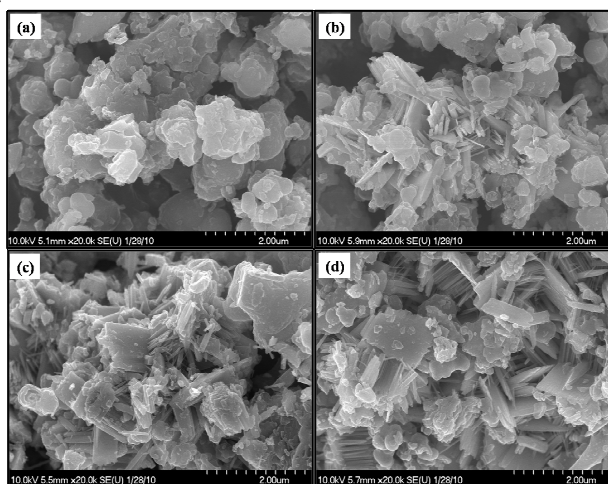


Figure 1. Surface FESEM images of (a) Pristine PNA, (b) PNA /0.09wt% ZnO, (c) PNA /0.19wt % ZnO and (d) PNA /0.39 wt% ZnO nanocomposites.

The crystalline properties of pristine PNA and PNA/ZnO nanocomposites are measured by XRD patterns, as shown in Fig. 2 (a). For pristine PNA, the broad peak centered at $\sim 15^\circ$ - 25° suggests the ordered structure of PNA. It is noticed that the increased wt% of ZnO nanomaterials in the nanocomposites has decreased the intensity of the PNA peak. The observed ZnO peaks are well indexed to the JCPDS 36-1451 values at 31.6° , 34.2° , 36.2° , 47.4° , 56.6° , 62.7° , 67.8° and 68.1° , which represents the typical hexagonal wurtzite structure of ZnO nanomaterials in the nanocomposites. Thus, the crystalline behavior of ZnO has not affected by the incorporation of PNA molecules. The FTIR spectra of PNA and PNA/ZnO nanocomposites are shown in Fig. 2(b). The peaks at 3443cm^{-1} , 3332cm^{-1} and 3045cm^{-1} represent the NH-stretching vibration for a secondary amine. The peaks at 1390cm^{-1} and 1584cm^{-1} are assigned to benzenoid (N-B-N) ring and the quinonoid (N=Q=N) ring of PNA respectively. The prepared PNA/ZnO nanocomposites exhibit similar IR bands like pristine PNA. Importantly, the peak intensity at

1584 cm^{-1} , 3029 cm^{-1} , 3332 cm^{-1} and 3443 cm^{-1} has credibly increased in the nanocomposites, indicating the interaction between PNA molecules and ZnO nanomaterials might due to the formation of hydrogen bonding between ZnO nanomaterial and PNA moieties. The existence of peak at 762 cm^{-1} confirms the polymerization of 1-naphthylamine monomer to PNA in the nanocomposites.

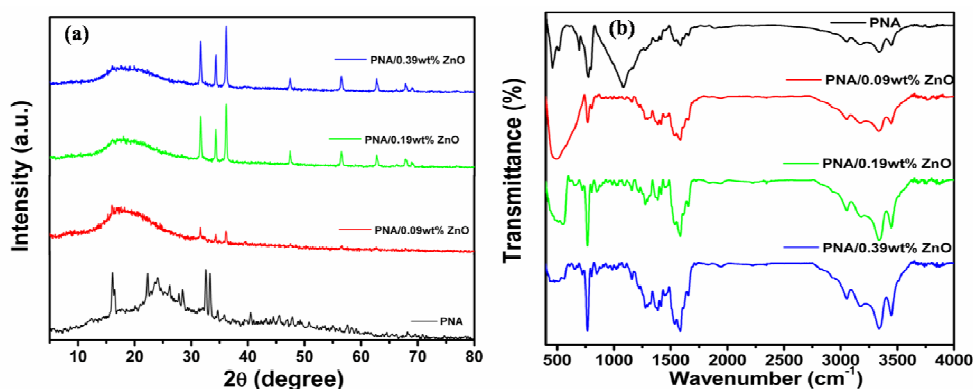


Figure 2. XRD patterns (a) and (b) FTIR spectra of pristine PNA and PNA/ZnO nanocomposites.

Photocatalytic activity is investigated by the degradation of MB dye in the presence of prepared PNA/ZnO nanocomposites under visible light irradiation. Fig. 3 (a) shows the UV-Vis absorption spectra of PNA/0.39wt%ZnO nanocomposites. The amount of MB dye degradation is measured by the relative intensity of the UV spectra. After every 20 min measurement, it has been observed that the maximum absorbance peak at 664 nm continuously decreases in the presence of PNA/0.39wt%ZnO nanocomposites catalyst, suggesting the degradation of MB with the formation of some intermediates. On exposure to visible light for the duration of 140 min, the MB dye degrades by ~ 22% over the surface of PNA/0.39wt%ZnO nanocomposites catalyst. Fig. 3 (b) and inset show the variation in the relative concentration (A/A_0) of MB dye solution with the time intervals for PNA and PNA/ZnO nanocomposites. The degradation rate of MB gradually increases with the increased wt% of ZnO nanomaterials in PNA molecules. Under visible light irradiation, the optimum PNA/0.39wt%ZnO catalyst presents the highest degradation rate as compared to pristine PNA (9%) and other PNA/ZnO nanocomposites (12% and 13% for 0.09wt% ZnO and 0.19wt% ZnO respectively), which may arise due to the occurrence of high charge separation between PNA and ZnO.

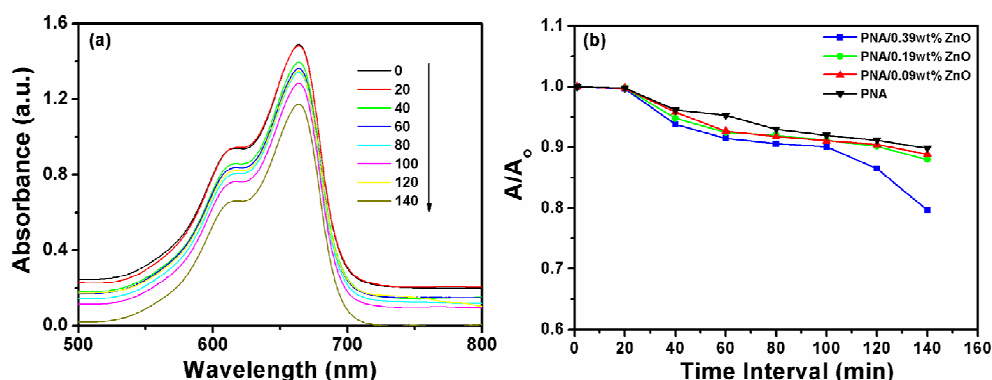


Figure 3. (a) UV-Vis absorbance spectra of decomposed MB dye solution by visible light over PNA/0.39wt% ZnO nanocomposite, (b) Extent of decomposition of MB dye with respect to time intervals over pristine PNA and PNA/ZnO nanocomposites.

Conclusion

The advanced PNA/ZnO nanocomposites have been synthesized by the in-situ polymerization of 1-naphthylamine monomer with ZnO nanomaterials and used as photocatalyst for an efficient degradation of MB dye. By varying the wt% of ZnO nanomaterials, the crystalline and morphological properties of PNA/ZnO nanocomposites significantly alter. The structural and the absorption studies confirm the effective interaction through the hydrogen bonding between imine (-NH) of PNA and hydroxyl (-OH) group of ZnO nanomaterials. Under the visible light irradiation, MB dye degrades by ~ 22% over the surface of optimum PNA/0.39wt%ZnO nanocomposite catalyst due to the efficient high charge separation of electron and hole pairs in the excited states of coupled PNA and ZnO nanomaterials.

References

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