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High performance visible light photocatalysis of electrospun PAN/ZnO hybrid nanofibers

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Highlights

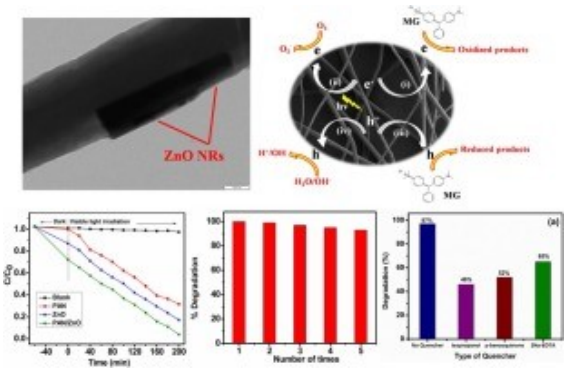
- Fabrication of PAN/ZnO hybrid nanofibers using electrospinning technique at room temperature.
- Uniform, well defined and bead free smooth nanofibers were fabricated using 1-D ZnO nanorods, which were monodispersed and were aligned parallel to axis of nanofibers.
- Photocatalytic activity was studied towards both cationic and anionic dye under visible light irradiation and detailed mechanism was elaborated.
- PAN/ZnO hybrid nanofibers show..s high degradation efficiency of 93% towards malachite green dye (200 min), 91% towards methyl orange dye (280 min).

Abstract

ZnO nanorods (NRs) immobilized PAN nanofibers were prepared using electrospinning technique. ZnO were dispersed uniformly, which helps to overcome the difficult recycling of powder catalyst.

The as-obtained fibers were characterized with wide-angle powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), UV-vis diffuse reflectance spectrophotometry (UV-vis-DRS), Thermogravimetry analysis (TGA), N_2 adsorption–desorption isotherms (BET), and X-ray photoelectron spectrometer (XPS). The morphological studies revealed that ZnO NRs were aligned parallel to the axis of fibers. PAN/ZnO hybrid NFs shows better regularity and uniformity in diameter (˜800 nm) with large specific surface area and smaller energy band gap comparted to ZnO NRs. Under visible light irradiation, PAN/ZnO hybrid nanofibers have had excellent photocatalytic performances for the degradation of cationic MG dye (200 min, 99%) and anionic MO dye (280 min, 99%) respectively. Due to the electrostatic attraction between cationic dye and anionic PAN/ZnO, the degradation rate towards MG dye was higher than MO dye. Recyclability study shows that after fifth cycle, 93% efficiency was observed.

Graphical abstract



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Introduction

Effluents generated from textile industries contains large amount of hazardous organic dyes and heavy metals which possess serious environmental concerns due to their toxicity, potential carcinogenicity and non-biodegradability [1], [2], [3]. Several techniques are used for waste water management such as chemical oxidation [4], adsorption [5], [6], photocatalysis [7] and membrane separation [8] which are costly with several limitations. Among them ‘photocatalysis’ is considered to be a greener technology which has lower energy consumption and cost effective for environmental problems [7], [9]. Photocatalyst are nanostructured semiconductors which are either doped, defect-induced [10], [11], [12] or hybrid nanomaterials to impart a synergistic effect [13]. These hybrid nanomaterials lead to higher photocatalytic activity as compared to pristine due to synergistic effect as well as plasmonic effect [14], [15]. Various semiconducting metal oxides and

composites such as TiO_2 [16], ZnO [17], CuO [18], TiO_2/ZrO_2 [19], TiO_2/SnO_2 [20], H-BN/TiO_2 [21], ZrO_2-TiO_2 [22], NiCoFe [23] and others have been explored recently for effective photocatalysis, which are efficient materials for eco-friendly, novel and low cost technology for the removal of hazardous dyes.

ZnO is a n-type semiconductor (3.37 eV) with high chemical and thermal stability, non-toxicity, and exceptional optical and photo-electrochemical properties [24]. ZnO has high quantum yield [25] and inherent surface defects [26] which become render active under visible light irradiation. Various nanostructures of ZnO are studied for their photocatalytic properties such as nanospheres [27], nanorods [28], nanofilms [29], nanofibers [30] and nanocubes [31]. Among them, nanofibers (NFs) are most promising nanostructures, which provide high aspect ratio and a defined flow pattern for enhanced photocatalytic property [32]. There are several methods to prepare NFs such as self-assembly, phase separation and template synthesis, electrospinning is found to be most promising due to its several advantages [33], [34], [35]. It leads to high aspect ratio, formation of porous mesh with tunable diameters, low cost and high production efficiency [36], [37]. Considering following advantages and ability of easy spunning using electrospinning, polyacrylonitrile (PAN) is a widely used polymer with several advantages [38], [39]. PAN based NFs have higher surface to volume ratio, which leads to more active sites of the nanostructured photocatalyst. Moreover, PAN NFs has 3-D macroscopic structure and high hydrophobicity for reduced agglomeration which makes them easily, floated on the surface of liquid and increases the photocatalytic efficiency [38], [40].

Various reports have been published which shows low photocatalytic degradation of organic dyes using ZnO nanoparticles [41]. However, when ZnO gets embedded over PAN NFs surface, it reduces agglomeration and increase in photocatalytic activity was observed with enhanced adsorption of dye [42]. Similar results were obtained for several dyes such as methyl orange (MO) dye under UV light irradiation. Tissera et al. shows 95% reduction in coloration of MO dye using PAN/ZnO NFs synthesized using electrospinning, while 20% reduction was observed for PAN NFs [43]. Considering this; the present work reports fabrication of ultra long one-dimensional ZnO nanorods (NRs) embedded PAN NFs using electrospinning technique. The photocatalytic activity of fabricated PAN/ZnO hybrid NFs was studied by degradation behavior of aqueous anionic dye (Methyl orange) and cationic dye (Malachite green). PAN/ZnO hybrid NFs shows remarkable photoactivity for the complete degradation of both dyes (MO and MG) effectively with reusability up to several cycles.

Section snippets

Materials, preparation and characterization

All chemicals and reagents used for fabrication of NFs were purchased from commercial sources

(Sigma Aldrich). The crystalline or amorphous nature of ZnO NRs, PAN NFs and PAN/ZnO hybrid NFs was analysed using powder X-ray diffractometer (XRD) (Shimadzu, Maxima 7000 S) using CuKα (λ = 1.5418 Å at 40 kV and 40 mA. 2θ range was from 5 to 80º (scanning speed = 5º min^{-1}). X-ray photoelectron spectroscopy (XPS) data was obtained using monochromatic aluminium with an Al Kα (1486.6 eV) with source…

Structural and morphological characterization

X-ray diffraction patterns for ZnNRs, PAN NFs and PAN/ZnO hybrid NFs are shown in Fig. 1. XRD of ZnO NRs shows strong diffraction peaks, which corresponds to hexagonal wurtzite phase (JPCDS 36-1451) [45]. PAN NFs shows crystalline peak at 2θ = 17° (110), represents orthorhombic packing which is due to stretching of chains during spinning [46]. Beside this, diffraction peak observed at 2θ = 26° corresponds to (002) crystal plane of the PAN NFs [47]. As compared to pure PAN NFs, PAN/ZnO hybrid…

Conclusion

In this work, PAN NFs with well dispersed aligned ZnO NRs were successfully electrospun at room temperature. Due to incorporation of ZnO NRs into the PAN, hybrid NFs shows significant improvement in mechanical properties. The hybrid nanofibers possess high specific surface area (98.05 m^2/g) along with structural flexibility, which resulted in high photocatalytic efficiency. Degradation of MG and MO dyes was studied in aqueous solution under visible light and it was observed that degradation of…

Conflict of interest

Authors have no conflict of interest.…

Acknowledgement

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