Polymeric nanostructures for photocatalytic dye degradation: polyaniline for photocatalysis

Shreya Saha¹ · Nahid Chaudhary¹ · Arun Kumar¹ · Manika Khanuja¹

Received: 2 January 2020 / Accepted: 15 May 2020 / Published online: 22 May 2020
© Springer Nature Switzerland AG 2020

Abstract

The motivation for the work presented in this paper comes from the need to explore novel and efficient photocatalysts for the degradation of contaminants from waste water. In this regard and in addition to the existing class of semiconductor photocatalysts, polymeric structures such as polyaniline, have emerged with the potential to degrade common water contaminants through photocatalysis. This paper elucidates the preparation of polyaniline (PANI) nanofibers and its implementation as a photocatalyst for the degradation of organic dyes such as Methylene Blue (MB) and Methyl Orange (MO). PANI was obtained using oxidative polymerisation and was examined for morphological and structural properties using XRD, SEM, TEM and FTIR which confirmed the formation of fibrous PANI sample. The chemical composition and the bonding states were studied using XPS. Subsequently, photo induced degradation of MB was performed in the presence of PANI as photocatalyst which indicated 42% degradation while MO was degraded by 97% in less than 3 h. Kinetic analysis by pseudo first order, second order and intra particle diffusion model, showed well-fit results for first order kinetic model with a rate constant of $0.0505 \text{ (g mg}^{-1} \text{ min}^{-1})$. The photocatalytic efficiency of PANI was assigned to the π - π^* transition wherein the excited state electrons were transferred from the π to the π^* orbital. Therefore, polyaniline was observed to be a promising photocatalyst for the degradation of environmental pollutants.

Keywords Conducting polymers · Dyes/pigments · Catalysis · XPS

1 Introduction

Since the last few decades, there has been a continuous search for suitable and efficient catalysts for degradation of dye contaminants in waste water, splitting of water to produce hydrogen, etc. In this regard, semiconductor photocatalysis has been superior in attracting attention of researchers, which is mainly attributable to its low cost, clean and environment friendly technology [1]. In wake of the need for semiconductor photocatalysts, several nanostructured materials have been developed and studied, such as TiO_2 [2, 3], ZnO [4, 5] and CdS [6, 7], etc. Among these, TiO_2 has been broadly investigated due to its stability and versatility [8]. However, the use of

this germane material is limited by its inability to absorb photons beyond the UV range due to its large band gap [9]. This drawback maybe resolved by doping TiO_2 with transition metals like nickel and zirconium which allows greater absorption of visible light [10]. Core shell nanoparticles of TiO_2 with neodymium, have also shown effectiveness in degrading organic dyes such as Methyl Orange and Rhodamine B [11] while neodymium oxide has shown photocatalytic activity towards degradation of industrial azo dye Eriochrome black T [12]. In addition to TiO_2 , nanoparticles of ZnO , synthesized using plant extracts, have been successfully employed for the photocatalytic degradation of organic dyes [13, 14]. Based on similar lines, green synthesis of silver nanoparticles

✉ Manika Khanuja, manikakhanuja@gmail.com | ¹Center for Nanoscience and Nanotechnology, Jamia Millia Islamia, New Delhi 110125, India.

and magnetic nanocomposites (Fe, Si, Cu–Ag) using fruit extracts, for the purpose of organic dyes' degradation, have also been reported [15, 16]. Apart from nanoparticles, ZnO nanorods doped with different amounts of copper, synthesized by thermal decomposition process, for degradation of organic dyes has shown promising results [17, 18]. Hydrothermally synthesized BiVO₄ nanoparticles, tested for environmental remediation activities, have also been successful in degrading water pollutants [19]. Nanocomposites of boron oxides and bismuth oxides and oxyhalides have also been obtained using sol gel method, as catalysts for photochemical destruction of water pollutants [20–24]. Although semiconductor nanoparticles lead as successful photocatalysts in the degradation of industrial water effluents, they still offer a major disadvantage which results from the rapid recombination of electron hole pairs, thereby reducing their photocatalytic efficiency [25]. Therefore, there's a need to look for alternate solutions to address the shortcomings posed by conventional photocatalysts and this may be addressed by introducing novel photocatalysts such as polymers.

Another class of novel materials that holds the potential to serve as a promising photocatalyst is, conducting polymers. These polymers have found usage in a number of fields such as electronic devices like light emitting diodes, transistors and solar cells [26, 27] and may also be employed for degradation of water contaminants. Polymeric photocatalysts offer several advantages such as chemical inertness, thermal stability and high surface areas [28, 29]. By selecting different combinations and ratios of building blocks and the degree of polymerization, different optoelectronic and photophysical properties can be administered in the polymer, such as high absorption area, tunable band gaps, and stable excited states, etc. [30]. Also, charge migration in 2D polymers can be improved by pi stacking, which provides a percolation channel within the layers [31]. Among the reported polymeric photocatalysts, poly(diphenylbutadiyne) (PDPB) nanofibers have shown high photocatalytic efficiency under visible light for the degradation of pollutants like phenol and methylene blue [25] while poly(3-hexylthiophene) (P3HT) has indicated higher degradation profiles compared to commercial titania [9]. In view of above, conducting polymers may be considered a fitting solution to the problems posed by existing technologies for waste water treatment.

Herein, we report the photocatalytic activity of conducting polymer polyaniline (PANI) which is known for its easy synthesis and environmental stability [32]. Applications of PANI have been widely explored, including rechargeable batteries [33], organic field transistors [34, 35] and polymer light diodes [36]. However, the photocatalytic efficiency of PANI has not been examined yet

which could open new possibilities for this material to be utilized for photocatalysis and therefore an attempt has been made to discover the usefulness of this promising polymer for the same.

2 Experimental section

2.1 Materials

Aniline (C₆H₅NH₂ with max impurity limit of 0.02%, Central Drug House Pvt. Ltd), Hydrochloric Acid (HCl·H₂O with max impurity limit of 0.0316%, Thermo Fisher Scientific India Pvt. Ltd) and Ammonium per sulphate ((NH₄)₂S₂O₈ with max. impurity limit of 0.005%, Sisco Research Laboratories Pvt. Ltd.

2.2 Synthesis procedure

The first step in the synthesis of polyaniline involved the refrigeration of a mixture of aniline (1 ml), HCl (3 ml) and DI water (16 ml), for 3 h. This step was followed by the addition of APS (13 ml, 0.1 M in 50 ml) to the refrigerated suspension, and stirring for 3 h. The next step involved filtration of the solution and subsequent washing of the precipitate with DI water and ethanol. The precipitate was dried in vacuum at 80 °C for 2 h and PANI was finally obtained. The schematic process is shown in Fig. 1.

2.3 Characterization

The morphology and structural properties of PANI were observed using a Quanta 3D FEG, (FEI's) Scanning Electron Microscope (SEM) and TECNAI F30 S-Twin Transmission electron microscopy (TEM) operating at an acceleration voltage of 300 kV. Rigaku Smart Lab X-ray diffractometer with Cu K_α radiation at 1.540 Å in the 2θ range of 20°–90° was used to study crystal structure and phase determination. High Resolution Fourier Transform Infrared Spectroscopy (HR-FTIR) was carried out using Bruker Optik, Vertex 70 V spectrometer. The sample was scanned in the range of 400–4000 cm^{−1} with a step size of 4 cm^{−1}. Chemical composition of the synthesized sample was examined using X-Ray photoelectron spectroscopy. The high resolution XPS measurements were carried out using monochromatic Al K_α radiation source (1486.7 eV) at 300 W. An Omicron Hemispherical analyzer with 7 channels detector system was used for data acquisition. The calibration of the spectrometer and binding energy (BE) was carried out using standard gold (Au) sample procedure.

Fig. 1 Synthesis procedure of PANI

2.4 Photocatalytic experiments

The photocatalytic activity of PANI was investigated using Newport Research Arch Lamp Housing, model no. 66902 (50–500 W) which was connected to an external power supply. The concentration of PANI for photocatalysis of MB, was kept at 5 mg/100 ml while the quantity of MB taken was 0.33 mg. For photocatalysis of MO, the concentration of MO was kept at 1 mg/100 ml while variable quantities, 10, 30 and 50 mg of PANI were taken for the experiments. The dark reaction was performed for 30 min followed by irradiation with UV light (100 W cm^{-2}). After fixed time intervals of 15 and 30 min for MB and MO respectively, 1 ml aliquots were sampled out of the main solution to study the change

in the concentration of MB and MO by observing their absorption spectra at 664 and 475 nm, respectively, using UV–Vis spectroscopy.

3 Results and discussion

3.1 TEM analysis

The micromorphology and structure of synthesized PANI samples were analyzed by TEM as shown in Fig. 2a, b. The figure shows thin layers of PANI that stack together to form agglomerates. The PANI layers appear to be dark and blurry which may be due to poor crystallinity.

Fig. 2 a, b TEM images of PANI; c, d SEM images of PANI sample

3.2 SEM analysis

Figure 2c, d shows typical SEM images of PANI at different magnifications. The images clearly indicate the nanofibrous structure of PANI, aligned randomly, confirming the formation of PANI [37]. PANI nanofibers are usually formed during homogenous nucleation where rapid consumption of reactants prevents secondary growth [38].

3.3 FTIR analysis

FTIR studies, as shown in Fig. 3 revealed characteristic peaks of PANI at 608, 801, 1131, 1273 and 1414–1550 cm^{-1} . The peak at 608 cm^{-1} indicates C–C bonding mode of aromatic ring, while the peak at 801 cm^{-1} is assigned to the C–H out of plane deformation in the benzene ring. The small peak at 1131 cm^{-1} is characteristic of PANI and represents the aromatic in-plane bending vibration of C–H. The peak at 1273 cm^{-1} is attributed to C–N stretching vibration of aromatic amine. The peaks from 1414 to 1550 cm^{-1} are a result of C=C stretching mode of vibration for the benzenoid and quinoid rings and C–H stretching in the polymer produces characteristic peak at 2520 cm^{-1} [39–41].

3.4 UV–Vis analysis

The UV–Vis absorbance spectrum of polyaniline is shown in Fig. 4. Two characteristic peaks were observed in the range of 296–326 nm and at 666 nm. The peak positioned at 296 nm is assigned to π – π^* transition occurring in the polymer backbone of the benzenoid ring and corresponds to a bandgap of 4.18 eV. The second adsorption peak positioned at 666 nm appears as a result of formation of

Fig. 3 FTIR analysis of PANI

Fig. 4 UV–Vis absorbance spectrum of PANI

exciton in the quinoid ring of PANI corresponding to the bandgap of 1.86 eV [42–44].

3.5 XPS analysis

The electronic state of PANI was analyzed using XPS and the survey scans of XPS spectra are as shown in Fig. 5. The deconvolution spectrum of C 1s revealed four peaks at 284.6, 286.01, 287.56 and 289 eV. The standard peak at 284.6 eV is attributed to neutral C–C/C–H bonds which form the backbone of PANI, while the second peak at 286.01 eV represents carbon bonded to oxygen i.e. C=O/C–O bond [45]. The third peak at 287.56 eV represents sp^2 bonded carbon [46] while the peak positioned at 289 eV indicates O–C=O bond [47]. The deconvoluted spectrum for N 1s shows three peaks positioned at 398.9, 399.6 and 400.9 eV. The first peak is assigned to quinone diimine nitrogen while the second peak is attributed to benzenoid diamine nitrogen [45]. The third contribution at 400.9 eV indicates positively charged nitrogen [48]. The resolved spectrum of O 1s showed three peaks. The first peak at 531.6 eV occurs as a result of formation of carboxylate groups. The second peak centered at 533.4 eV occurs due to the formation of hydroxides while the peak at 535.7 eV is a result of chemisorbed oxygen/water [48, 49].

4 Kinetic analysis

Aqueous solutions of MB and MO (mg) were used to examine the effect of PANI as a photocatalyst on the degradation of dye particles, when irradiated with UV light for a period of over an hour. The decrease in the concentration of MB and MO was determined by recording the reduction in the

Fig. 5 XPS deconvoluted spectra for **a** general scan, **b** C 1s, **c** N 1s, **d** O 1s of PANI

absorbance spectra of MB at 664 nm and MO at 475 nm, at time intervals of 15 min and 30 min respectively. There was almost 42% degradation in the concentration of MB (Fig. 6), in a span of less than 2 h which is higher than that of some polymeric nanocomposites [50] and composite semiconductors for the degradation of anionic dyes [51]. PANI also exhibited a remarkable photocatalytic efficiency by showing 97% degradation in the concentration of MO (Fig. 7a). The difference in the degradation efficiency for MB and MO can be corroborated by the zeta potential of PANI which was found to be +15.7 eV (Fig. 8). This explains the improved photodegradation efficiency of PANI for anionic dyes which is facilitated by the positive zeta potential value. Hence, PANI shows poor selectivity towards cationic dyes such as MB. Figure 7b shows the degradation profile of MO as a function of variable PANI concentration. The concentration of MO was maintained at 1 mg/100 ml while 3 different concentrations of PANI were studied i.e. 10, 30 and 50 mg. Prior to UV irradiation, the solution was kept in the dark for 30 min. As seen from the figure, the degradation of MO was enhanced with the increase in the concentration of PANI. The values of C/C_0 for 10, 30 and 50 mg PANI were: 1, 0.79, 0.60, 0.26, 0.16, 0.06, 0.05; 1, 0.65, 0.48, 0.37, 0.24, 0.13, 0.03; 1, 0.17, 0.05, 0.02, respectively.

Fig. 6 Degradation of MB in the presence of PANI, inset graph shows the photocatalytic efficiency of PANI photocatalyst for MB degradation

MO showed faster degradation in the presence of 50 mg PANI, comparatively moderate degradation in the presence of 30 mg PANI and much slower degradation when

Fig. 7 a Degradation of MO in the presence of PANI, inset graph shows the photocatalytic efficiency of PANI photocatalyst; Effect of different concentrations, 10, 30 and 50 mg of PANI on photocatalysis showing **b** degradation profile and **c** efficiency of PANI

Fig. 8 Zeta potential of PANI

10 mg of PANI was used. In terms of photocatalytic efficiency, 10 mg PANI showed 94.84% degradation of MO in 5 h while 30 mg PANI could degrade 96.66% of MO in 3 h, whereas 50 mg PANI took 2 h to produce an efficiency of 97.95% as shown in Fig. 7c.

Based on the performance of PANI in degrading MB, its photocatalytic efficiency (η) was calculated using the formula:

$$\eta = \frac{C - C_0}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration, C is the concentration at time t (min). Figure 6 shows the effect on the absorbance spectra of MB in the presence of PANI, while the inset graph shows the efficiency of PANI as a photocatalyst.

The degradation profile (C/C_0 vs. time) is shown in Fig. 9a. It can be deduced from the graph that the initial

adsorption stage is faster as a result of high concentration, followed by a slower adsorption stage as the concentration decreases. Further investigations for kinetic analysis were carried out using two popular adsorption kinetic representations, pseudo first order and second order adsorption models. For these experiments, a small quantity (5 mg) of MB was used to slower down the adsorption process.

The pseudo first order adsorption model is given by the equation:

$$Q_t = Q_e (1 - e^{-k_1 t}) \quad (2)$$

where

$$Q_e = (C_0 - C_e) \times V/W$$

$$Q_t = (C_0 - C_t) \times V/W$$

Here Q_t (mg g^{-1}) is the amount of dye adsorbed at time t (min), Q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium time, k_1 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo first order rate constant, C_e (mg L^{-1}) is the equilibrium concentration, C_t is the concentration at time t (min), V (L) is the volume of the solution and W (g) is the amount of PANI used for MB dye adsorption [52, 53]. The pseudo first order equation describes adsorption taking place at certain conditions such as low solute concentration or when equilibrium is reached [54]. This equation illustrates a weak adsorption process i.e. physisorption which is dependent on van der Waals interaction between the adsorbate (MB) and adsorbent (PANI). There is negligible chemical interaction involved between the adsorbate and adsorbent [52]. The fitting results of pseudo first order model are shown in Fig. 9b. The slope of the graph gave the value of the first order rate constant (k_1) which was 0.0505. The value of

Fig. 9 **a** Degradation profile of MB in the presence of PANI, **b** pseudo first order plot, **c** pseudo second order plot, **d** intra-particle diffusion model with two different rate constants k_1 and k_2

correlation coefficient (R^2) was 0.9894 and this high value indicated that the reaction followed first order kinetics.

The Pseudo second order adsorption model is given by the equation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (3)$$

where k_2 is the second order rate constant. The second order equation signifies chemisorption process wherein stronger bonds exist between the adsorbent and adsorbate, unlike physisorption process.

Figure 9c shows the fitting results of pseudo second order adsorption model. The second order rate constant was found to be 0.0838 with very low values of R^2 (0.0048) confirming the inapplicability of second order rate kinetics.

Apart from pseudo first order and second order adsorption models, diffusion based model was also employed to study adsorption kinetics of MB. Basically, heterogeneous adsorption process involves four types of resistances: Bulk, Film diffusion, Intra particle diffusion and Adsorption processes.

Among these, the intra-particle diffusion model involves pore (crack)/surface diffusion and is given by the following equation:

$$Q_t = k_{id} t^{0.5} + C \quad (4)$$

where k_{id} is the intra particle diffusion rate constant and C is the intercept which represents the boundary layer thickness. If the above Eq. (4) passes through the origin, the rate determining step is explained by intra particle diffusion. On the other hand, if the equation does not pass through the origin, film diffusion, in addition to intra particle diffusion, is involved which causes difference in the initial and final mass transfer rates. Figure 9d shows the fitting plot of intra particle diffusion model. Two correlation coefficients were obtained as 0.9604 and 0.9915. Since the plot passes through the origin, intra particle diffusion is the rate determining step for the adsorption process. Also, two different rate constants were obtained which can be explained as follows:

Fig. 10 Mechanism of photocatalytic dye degradation by PANI

- (1) Steep slope represents fast adsorption process implying electrostatic interaction between the dye molecules and the nanoparticles.
- (2) Gradual slope signifies the slow process of diffusion of dye molecules into PANI.

5 Mechanism

The process of photo excitation, charge separation and electron-hole generation, is shown in Fig. 10. The energy of the polymer system is increased due to positive charges localized on neighboring nitrogen atoms which result in redistribution of electron density. In case of a polymer chain, the delocalized cation radicals provide electron conductivity. For PANI, the electron conductivity increases with the degree of protonation, and this is characteristic of polyaniline [32]. The lowest occupied molecular orbital (LOMO) and highest occupied molecular orbital (HOMO) of PANI is positioned at -1.9 and 0.8 eV respectively [55]. When irradiated with visible light, conducting PANI absorbs photons and causes π - π^* transition wherein the excited state electrons of HOMO and LUMO orbital undergo separation and are then transferred from the π to the π^* orbital [55, 56]. The oxidative species that are formed on the catalyst surface, degrade the dye to form intermediates and final products like CO_2 , SO_4^{2-} , NO_3^- , NH_4^+ [55]. Thus, the rapid charge generation and slow charge recombination leads to enhanced photocatalytic activity.

6 Conclusion

Herein, we outline the synthesis of Polyaniline through polymerization of aniline, for exploring its photocatalytic efficiency. The sample was prepared successfully using oxidative polymerization and was characterized using SEM,

TEM, FTIR, UV-Vis Spectroscopy and XPS which confirmed the morphological, optical and chemical bonding characteristics. PANI sample functioned effectively as a photocatalyst for both dyes, MB and MO, with high activity and stability. Kinetic analysis indicated that the reaction followed pseudo first order kinetics ($k_1 = 0.0505$). The π - π^* transition occurring in PANI is responsible for the generation of electron-hole pairs which enhance the degradation of the particles thus confirming efficient photocatalytic ability of PANI.

Acknowledgements Funding was provided by Science and Engineering Research Board (Grant No. ECR/2017/001222).

Author contributions MK: deduced and designed the experiment; NC, SS, AK: synthesized the material; SS, NC, AK: performed photocatalytic experiments, analyzed the data; SS: prepared the draft; MK, NC, SS: proofread the final draft; All authors approved the final manuscript.

Compliance with ethical standards

Conflict of interest The authors declare no competing financial interests.

References

1. Cao S, Low J, Yu J, Jaroniec M (2015) Polymeric photocatalysts based on graphitic carbon nitride. *Adv Mater* 27:2150–2176
2. Yu J, Li Q, Liu S, Jaroniec M (2013) Ionic-liquid-assisted synthesis of uniform fluorinated B/C-codoped TiO_2 nanocrystals and their enhanced visible-light photocatalytic activity. *Chem A Eur J* 19:2433–2441
3. Yu J, Low J, Xiao W, Zhou P, Jaroniec M (2014) Enhanced photocatalytic CO_2 -reduction activity of anatase TiO_2 by coexposed 001 and 101 facets. *J Am Chem Soc* 136:8839–8842
4. Jang ES, Won JH, Hwang SJ, Choy JH (2006) Fine tuning of the face orientation of ZnO crystals to optimize their photocatalytic activity. *Adv Mater* 18:3309–3312

5. Wang X, Liao M, Zhong Y, Zheng JY, Tian W, Zhai T, Zhi C, Ma Y, Yao J, Bando Y (2012) ZnO hollow spheres with double-yolk egg structure for high-performance photocatalysts and photodetectors. *Adv Mater* 24:3421–3425
6. Hu Y, Gao X, Yu L, Wang Y, Ning J, Xu S, Lou XWD (2013) Carbon-coated CdS petalous nanostructures with enhanced photostability and photocatalytic activity. *Angew Chem* 125:5746–5749
7. Xiang Q, Cheng B, Yu J (2013) Hierarchical porous CdS nanosheet-assembled flowers with enhanced visible-light photocatalytic H₂-production performance. *Appl Catal B* 138:299–303
8. Hoffmann MR, Martin ST, Choi W, Bahnemann DW (1995) Environmental applications of semiconductor photocatalysis. *Chem Rev* 95:69–96
9. Muktha B, Madras G, Guru Row T, Scherf U, Patil S (2007) Conjugated polymers for photocatalysis. *J Phys Chem B* 111:7994–7998
10. Khojasteh H, Salavati-Niasari M, Mortazavi-Derazkola S (2016) Synthesis, characterization and photocatalytic properties of nickel-doped TiO₂ and nickel titanate nanoparticles. *J Mater Sci Mater Electron* 27:3599–3607
11. Mortazavi-Derazkola S, Salavati-Niasari M, Mazhari M-P, Khojasteh H, Hamadani M, Bagheri S (2017) Magnetically separable Fe₃O₄@SiO₂@TiO₂ nanostructures supported by neodymium(III): fabrication and enhanced photocatalytic activity for degradation of organic pollution. *J Mater Sci Mater Electron* 28:14271–14281
12. Zinatloo-Ajabshir S, Mortazavi-Derazkola S, Salavati-Niasari M (2017) Schiff-base hydrothermal synthesis and characterization of Nd₂O₃ nanostructures for effective photocatalytic degradation of eriochrome black T dye as water contaminant. *J Mater Sci Mater Electron* 28:17849–17859
13. Bhuyan T, Mishra K, Khanuja M, Prasad R, Varma A (2015) Biosynthesis of zinc oxide nanoparticles from *Azadirachta indica* for antibacterial and photocatalytic applications. *Mater Sci Semicond Process* 32:55–61
14. Sharma R, Khanuja M, Islam S, Singhal U, Varma A (2017) Aspect-ratio-dependent photoinduced antimicrobial and photocatalytic organic pollutant degradation efficiency of ZnO nanorods. *Res Chem Intermed* 43:5345–5364
15. Ebrahimzadeh MA, Naghizadeh A, Amiri O, Shirzadi-Ahodshti M, Mortazavi-Derazkola S (2020) Green and facile synthesis of Ag nanoparticles using *Crataegus pentagyna* fruit extract (CP-AgNPs) for organic pollution dyes degradation and antibacterial application. *Bioorg Chem* 94:103425
16. Ebrahimzadeh MA, Mortazavi-Derazkola S, Zazouli MA (2019) Eco-friendly green synthesis and characterization of novel Fe₃O₄/SiO₂/Cu₂O-Ag nanocomposites using *Crataegus pentagyna* fruit extract for photocatalytic degradation of organic contaminants. *J Mater Sci Mater Electron* 30:10994–11004
17. Singh S, Pendurthi R, Khanuja M, Islam S, Rajput S, Shivaprasad S (2017) Copper-doped modified ZnO nanorods to tailor its light assisted charge transfer reactions exploited for photo-electrochemical and photo-catalytic application in environmental remediation. *Appl Phys A* 123:184
18. Bhuyan T, Khanuja M, Sharma R, Patel S, Reddy M, Anand S, Varma A (2015) A comparative study of pure and copper (Cu)-doped ZnO nanorods for antibacterial and photocatalytic applications with their mechanism of action. *J Nanopart Res* 17:288
19. Sharma R, Singh S, Verma A, Khanuja M (2016) Visible light induced bactericidal and photocatalytic activity of hydrothermally synthesized BiVO₄ nano-octahedra. *J Photochem Photobiol B* 162:266–272
20. Ranjeh M, Beshkar F, Amiri O, Salavati-Niasari M, Moayedi H (2020) Pechini sol–gel synthesis of Cu₂O/Li₃BO₃ and CuO/Li₃BO₃ nanocomposites for visible light-driven photocatalytic degradation of dye pollutant. *J Alloys Compd* 815:152451
21. Ranjeh M, Beshkar F, Salavati-Niasari M (2019) Sol–gel synthesis of novel Li-based boron oxides nanocomposite for photodegradation of azo-dye pollutant under UV light irradiation. *Compos B Eng* 172:33–40
22. Najafian H, Manteghi F, Beshkar F, Salavati-Niasari M (2018) Efficient degradation of azo dye pollutants on ZnBi₃8O₅₈ nanostructures under visible-light irradiation. *Sep Purif Technol* 195:30–36
23. Najafian H, Manteghi F, Beshkar F, Salavati-Niasari M (2019) Fabrication of nanocomposite photocatalyst CuBi₂O₄/Bi₃ClO₄ for removal of acid brown 14 as water pollutant under visible light irradiation. *J Hazard Mater* 361:210–220
24. Najafian H, Manteghi F, Beshkar F, Salavati-Niasari M (2019) Enhanced photocatalytic activity of a novel NiO/Bi₂O₃/Bi₃ClO₄ nanocomposite for the degradation of azo dye pollutants under visible light irradiation. *Sep Purif Technol* 209:6–17
25. Ghosh S, Kouame NA, Remita S, Ramos L, Goubard F, Aubert P-H, Dazzi A, Deniset-Besseau A, Remita H (2015) Visible-light active conducting polymer nanostructures with superior photocatalytic activity. *Sci Rep* 5:srep18002
26. Ma D, Aguiar M, Freire JA, Hümmelgen IA (2000) Organic reversible switching devices for memory applications. *Adv Mater* 12:1063–1066
27. Sirringhaus H, Tessler N, Friend RH (1998) Integrated optoelectronic devices based on conjugated polymers. *Science* 280:1741–1744
28. Vyas VS, Lotsch BV (2015) Materials chemistry: organic polymers form fuel from water. *Nature* 521:41–42
29. Kumar S, Wani MY, Arranja CT, e Silva JdA, Avula B, Sobral AJ (2015) Porphyrins as nanoreactors in the carbon dioxide capture and conversion: a review. *J Mater Chem A* 3:19615–19637
30. Vyas VS, Lau VW, Lotsch BV (2016) Soft photocatalysis: organic polymers for solar fuel production. *Chem Mater* 28:5191–5204
31. Calik M, Auras F, Salonen LM, Bader K, Grill I, Handloser M, Medina DD, Dogru M, Löbermann F, Trauner D (2014) Extraction of photogenerated electrons and holes from a covalent organic framework integrated heterojunction. *J Am Chem Soc* 136:17802–17807
32. Boeva ZA, Sergeyev V (2014) Polyaniline: synthesis, properties, and application. *Polym Sci Ser C* 56:144–153
33. Ghanbari K, Mousavi M, Shamsipur M (2006) Preparation of polyaniline nanofibers and their use as a cathode of aqueous rechargeable batteries. *Electrochim Acta* 52:1514–1522
34. Jussila S, Puustinen M, Hassinen T, Olkkonen J, Sandberg HG, Solehmainen K (2012) Self-aligned patterning method of poly(aniline) for organic field-effect transistor gate electrode. *Org Electron* 13:1308–1314
35. Wang W, Lu X, Li Z, Lei J, Liu X, Wang Z, Zhang H, Wang C (2011) One-dimensional polyelectrolyte/polymeric semiconductor core/shell structure: sulfonated poly(arylene ether ketone)/ polyaniline nanofibers for organic field-effect transistors. *Adv Mater* 23:5109–5112
36. Choi MR, Han TH, Lim KG, Woo SH, Huh DH, Lee TW (2011) Soluble self-doped conducting polymer compositions with tunable work function as hole injection/extraction layers in organic optoelectronics. *Angew Chem* 123:6398–6401
37. Zhang Y, Chen P, Wen F, Huang C, Wang H (2016) Construction of polyaniline/molybdenum sulfide nanocomposite: characterization and its electrocatalytic performance on nitrite. *Ionics* 22:1095–1102
38. Tian Z, Yu H, Wang L, Saleem M, Ren F, Ren P, Chen Y, Sun R, Sun Y, Huang L (2014) Recent progress in the preparation of polyaniline nanostructures and their applications in anticorrosive coatings. *RSC Adv* 4:28195–28208

39. Ayad M, Zaghlol S (2012) Nanostructured crosslinked polyaniline with high surface area: synthesis, characterization and adsorption for organic dye. *Chem Eng J* 204:79–86
40. Xu F, Zheng G, Wu D, Liang Y, Li Z, Fu R (2010) Improving electrochemical performance of polyaniline by introducing carbon aerogel as filler. *Phys Chem Chem Phys* 12:3270–3275
41. Rangel-Vazquez N-A, Sánchez-López C, Felix FR (2014) Spectroscopy analyses of polyurethane/polyaniline IPN using computational simulation (Amber, MM + and PM3 method). *Polímeros* 24:453–463
42. Pruneanu S, Veress E, Marian I, Oniciu L (1999) Characterization of polyaniline by cyclic voltammetry and UV–Vis absorption spectroscopy. *J Mater Sci* 34:2733–2739
43. Gruger A, Novak A, Regis A, Colomban P (1994) Infrared and Raman study of polyaniline part II: influence of ortho substituents on hydrogen bonding and UV/Vis—near-IR electron charge transfer. *J Mol Struct* 328:153–167
44. Jain S, Chakane S, Samui A, Krishnamurthy V, Bhoraskar S (2003) Humidity sensing with weak acid-doped polyaniline and its composites. *Sens Actuators B Chem* 96:124–129
45. Golczak S, Kanciurzevska A, Fahlman M, Langer K, Langer JJ (2008) Comparative XPS surface study of polyaniline thin films. *Solid State Ion* 179:2234–2239
46. Pandiselvi K, Fang H, Huang X, Wang J, Xu X, Li T (2016) Constructing a novel carbon nitride/polyaniline/ZnO ternary heterostructure with enhanced photocatalytic performance using exfoliated carbon nitride nanosheets as supports. *J Hazard Mater* 314:67–77
47. Sha C, Lu B, Mao H, Cheng J, Pan X, Lu J, Ye Z (2016) 3D ternary nanocomposites of molybdenum disulfide/polyaniline/reduced graphene oxide aerogel for high performance supercapacitors. *Carbon* 99:26–34
48. Binkauskienė E, Jasulaitienė V, Lugauskas A (2009) Effect of *Aspergillus niger* Tiegh. L-10 on the physical and chemical properties of a polyaniline coating in the growth substrate. *Synth Met* 159:1365–1368
49. Subramanian N, Viswanathan B (2015) Nitrogen-and oxygen-containing activated carbons from sucrose for electrochemical supercapacitor applications. *RSC Adv* 5:63000–63011
50. Saha S, Chaudhary N, Mittal H, Gupta G, Khanuja M (2019) Inorganic–organic nanohybrid of MoS₂-PANI for advanced photocatalytic application. *Int Nano Lett* 9:127–139
51. Singh SA, Madras G (2013) Photocatalytic degradation with combustion synthesized WO₃ and WO₃TiO₂ mixed oxides under UV and visible light. *Sep Purif Technol* 105:79–89
52. Han S, Liu K, Hu L, Teng F, Yu P, Zhu Y (2017) Superior adsorption and regenerable dye adsorbent based on flower-like molybdenum disulfide nanostructure. *Sci Rep* 7:43599
53. Massey AT, Gusain R, Kumari S, Khatri OP (2016) Hierarchical microspheres of MoS₂ nanosheets: efficient and regenerative adsorbent for removal of water-soluble dyes. *Ind Eng Chem Res* 55:7124–7131
54. Hwang K-J, Shim W-G, Kim Y, Kim G, Choi C, Kang SO, Cho DW (2015) Dye adsorption mechanisms in TiO₂ films, and their effects on the photodynamic and photovoltaic properties in dye-sensitized solar cells. *Phys Chem Chem Phys* 17:21974–21981
55. Wang Q, Hui J, Li J, Cai Y, Yin S, Wang F, Su B (2013) Photodegradation of methyl orange with PANI-modified BiOCl photocatalyst under visible light irradiation. *Appl Surf Sci* 283:577–583
56. Deng Y, Tang L, Zeng G, Dong H, Yan M, Wang J, Hu W, Wang J, Zhou Y, Tang J (2016) Enhanced visible light photocatalytic performance of polyaniline modified mesoporous single crystal TiO₂ microsphere. *Appl Surf Sci* 387:882–893

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.