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PHOTOCATALYTIC DEGRADATION STUDIES OF POLYANILINE BASED ZnO-Al_2O_3 NANOCOMPOSITE

Baiju V[1], Dedhila Devadathan[2], Biju R[3], Raveendran R[4]

Nanoscience Research Laboratory, Department of Physics, Sree Narayana College, Kollam 691001, Kerala,(India)

Abstract

In the present work polyaniline based ZnO-Al_2O_3 nanocomposite and its counterparts were synthesized. The synthesized materials were characterized using XRD. UV/Vis absorption spectroscopy of the synthesized samples was studied. From band gap calculation it was seen that all of them showed subgaps. The photocatalytic activities of the synthesized samples for the degradation of organic dye Congo Red were studied. The study also investigates the factors affecting photocatalytic processes of the nanocomposite such as dye concentration, illumination time and amount of catalyst loading.

Keywords:* *Nanocomposite, Conducting Polymer, Photocatalysis

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I. INTRODUCTION

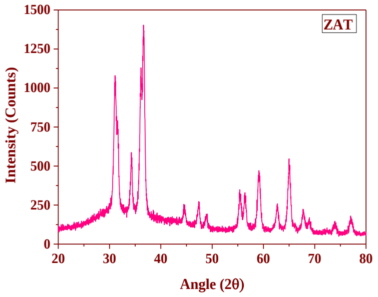
Water contamination has become a serious issue due to the fact that 2% of dyes produced in the industries are discharged directly in aqueous effluent [1]. So it was necessary to find a new way to remove coloured dyes [2, 3] before discharging them into the environment. Due to the economic constraints, development of a cost effective and clean process is essential. The various conventional technologies currently employed in the removal of effluents in industrial water are classical and do not lead to complete destruction of pollutants. In the case of industrial dyes, these methods do not work efficiently due to high solubility of dyes as well as their resistance to chemical and biological degradation; also they just transfer the contaminants from one phase to another [4]. Therefore, there is a need to develop a novel treatment method that is more effective. Photocatalysis is a promising technology in the field of green technology for the removal of dyes. Presently nanotechnology is widely applied for purification and treatment of waste water. The novel properties of nanomaterials such as large surface area, potential for self assembly, high specificity, high reactivity and catalytic potential make them an excellent candidate for both applications [5]. An expanding trend for the nanomaterials is the fabrication of composite structures and devices with materials capable of enhancing the properties of the composite material. This can be achieved either by utilizing the size advantage through templating on the nanomaterials and enhancing the properties to drive new synergetic properties of two combined materials [6]. In the present study polyaniline based ZnO-Al_2O_3 nanocomposite was prepared, analyzed and used as photocatalyst for the degradation of Congo red.

II. EXPERIMENTAL

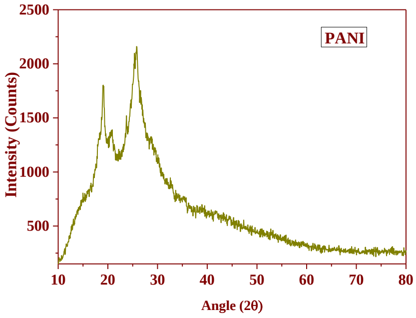
AR grade chemicals obtained from Merck were used for the preparation of ZnO-Al_2O_3, polyaniline and the polyaniline based nanocomposite. ZnO-Al_2O_3 (ZAT) was prepared by the combustion method, polyaniline (PANI) and polyaniline based ZnO-Al_2O_3 nanocomposite (PANIZA) was prepared using chemical oxidation method. ZnO-Al_2O_3 annealed at 1200^0c for three hours and polyaniline based nanocomposite in the as prepared form were used for analysis. For the preparation of the nanocomposite ZAT was used. XRD study was carried out using XPERT-PRO model powder diffractometer (PAN analytical, Netherlands) employing Cu- K_α radiation (λ = 1.54060A^o) operating at 40kV, 30mA.

III RESULTS AND DISCUSSIONS

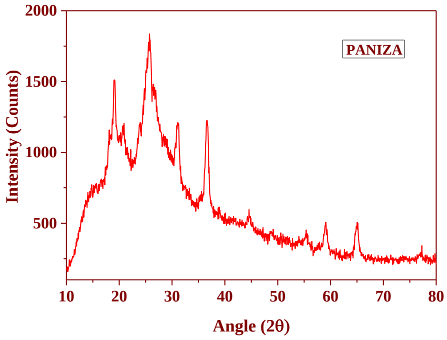
3.1 XRD Analysis



ZAF



PANI



PANIZA

Fig. 1 XRD patterns of (a) ZAF (b) PANI (c) PANIZA

XRD diffractograms of ZAT, PANI and PANIZA are shown in Figures 1. The well defined X-ray diffraction peaks in the case of ZAT indicate that all are crystalline. Also, the diffraction peaks are notably broadened indicating the small crystallite size. In order to confirm the phase purity of the sample prepared, the interplanar spacing (d_{hkl} values), 2θ values and relative intensity values corresponding to the observed diffraction peaks were compared with the standard values reported by JCPDS-International Centre for Diffraction Data. The data obtained for ZAT matched with JCPDS-ICDD pattern number #80-0074 of ZnO and JCPDS-ICDD pattern number #42-1468 of Al_2O_3 separately. The variation observed in the d values of the crystal planes in case of ZAT when compared to ZnO and Al_2O_3, confirms the formation of composites. This is also supported by the appearance of new peaks corresponding to d values 7.58, 3.78, 2.87, 2.45, 1.65 and 1.86. Crystal planes of ZnO (100), (002), (101), (102), (110), (103), (112), (201) and the crystal planes of Al_2O_3 (113), (211), (214), (208) with slight variation in d values was observed in ZAT. The d value 1.23 may be (202) of ZnO or (1010) of Al_2O_3. From the XRD spectra, the particle size was calculated using Scherrer equation,

$$D = k\lambda / (\beta_{hkl})\text{measured} * \cos\theta_{hkl} \ldots\ldots\ldots\ldots(1)$$

Here, D is the average crystallite size normal to the reflecting planes, k – is the shape factor which lies between 0.95 and 1.15 depending on the shape of the grains (k =1 for spherical crystallites), λ-is the wavelength of x-ray used and $(\beta_{hkl})_{measured}$ is the FWHM of the diffraction line in radians and θ_{hkl} is the Bragg angle corresponding to the diffraction line arising from the planes designated by Miller indices (hkl). The particle size for the sample is 15.32 ± 3 nm. From the XRD's of the polyaniline based nanocomposite it is clear that the metal oxide particles are well distributed in the polymer matrix. The well defined peaks of the metal oxides were found to be incorporated into the XRD peaks of polyaniline.

3.2 UV/Vis Spectrum Analysis

The UV/Vis absorption spectra of all the samples were taken in the wavelength range 210 to 870 nm with 1 nm resolution. In case of ZAT one weak band with λ_{max} situated at 257 nm between 223nm and 265 nm and another peak with λ_{max} situated at 323 nm between 270 nm and 420 nm were observed. The absorption edge is found to be 4.85 eV and 3.84 eV for the peaks corresponding to 256 nm and 323 nm respectively. The optical band gap of the material determined from the absorption spectrum using Tauc's relation.

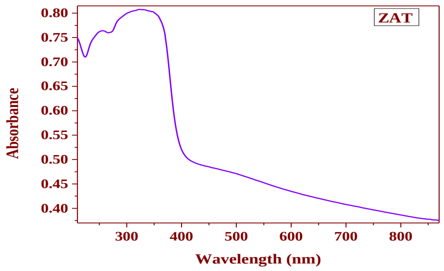


Fig.2 UV/Vis Absorbance spectra of ZAT

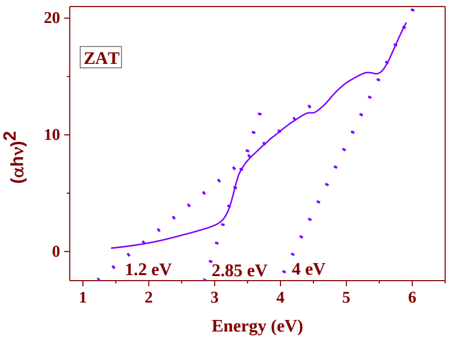


Fig.3 UV/Vis Absorbance spectra of ZAT

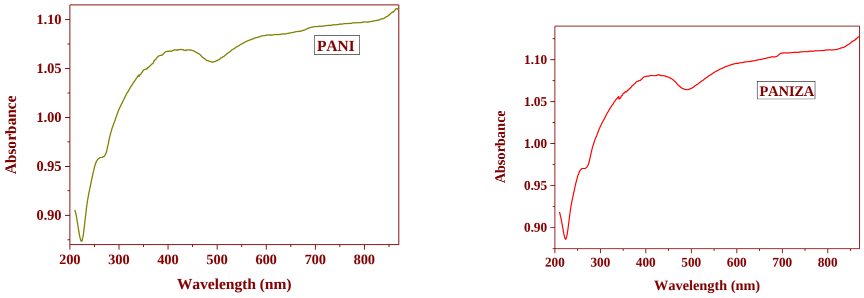


Fig. 4 UV/Vis Absorbance of PA and PANIZA

The absorption spectra of PANI and PANIZA are shown in the Figure 4. In case of PANI presence of a weak absorption band was observed in the range 220 nm – 265 nm with λ_{max} situated at 258 nm, which can be attributed to the conjugation of benzene ring in the indole unit and also another strong absorption band in the range 270 nm – 490 nm with λ_{max} situated at 426 nm was also obtained, which could be due to the π - π^* transitions of the benzene ring in the PI molecular chains [7]. The results indicate presence of enhanced conjugated segments and easy flow of charge in PANI molecular matrix. This band also relates to the extent of conjugation between adjacent rings in the polymer chain.. The absorption edge is found to be 4.81 eV and 2.91 eV for the peaks corresponding to 258 nm and 426 nm respectively. In case of PANIZA, the peak values were observed at 260 nm between 223 nm and 265 nm. The second peak was observed at 428 nm between 265 nm and 490 nm. The absorption edge is found to be 4.77 eV and 2.9 eV for the peaks corresponding to 260 nm and 428 nm respectively. All the samples showed sub band gaps. Due to large value of the optical band gap, the material is most suited in many applications in modern electronic industries.

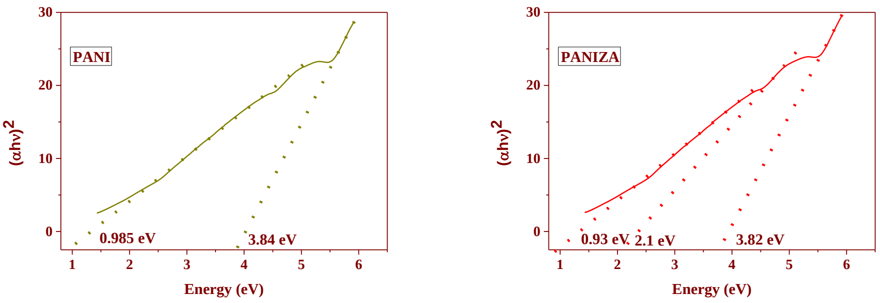


Fig.5 Tauc Plot of PANI and PANIZA

Surface area and surface defects play an important role in photocatalytic efficiency and many other practical properties. In the present work the nanocomposite showed good visible light absorption in addition to UV absorption. Hence proper tuning could make these nanocomposites excellent candidates for many practical applications such as photocatalysis, anti-bacterial, deodorizing, air purifying, anti fogging and as other surface purification agents.

3.3 Photocatalytic Activity Evaluations

A set of Photocatalytic degradation of Congo red was carried out to measure the photocatalytic activity of PANIZA and its counter parts as photocatalyst in presence of UV illumination. The experiments were performed by suspending photocatalyst into reactor with Congo red dye solution. The reaction was carried out isothermally at 30^0C. The concentration of residual Congo red in the solution after irradiation was determined by monitoring the absorbance intensity of solution samples at their maximum absorbance wavelength by using UV-Vis spectrophotometer which was recorded on a JASCO V 650 with a spectrometric quartz cuvette at room temperature. Figure 2 shows the UV-Vis spectrum analysis for different time intervals done for PANIZA.

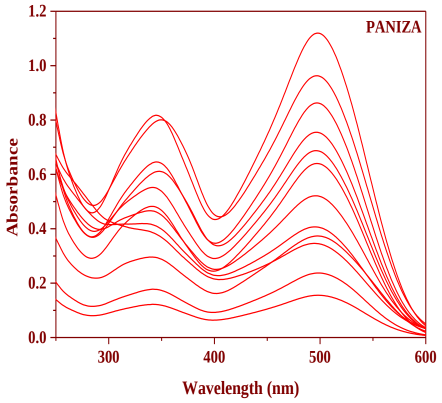


Fig.6 Absorbance spectrum showing photocatalytic degradation of Congo Red using PANIZA

The variations in different experimental conditions affecting on photocatalytic oxidation of Congo Red using catalysts such as, illumination time, dye concentration and amount of catalyst loaded were taken into account to reach to integrated model for the photocatalytic degradation of Congo red. The effect of illumination time on photodegradation efficiency of Congo Red was carried out by measuring the photodegradation efficiency at different periods of time using 0.1 gm of catalyst and 300mL of 50 ppm dye solution under UV light at 30^0C. The results revealed that the photocatalytic activity increases with increase of the illumination time and reaches to 100% after 150 minutes illumination time. Such data reveals the relative high activity of the prepared catalysts which enables the complete degradation of the Congo red in such short illumination time and the catalyst has active sites for carrying out the reaction. The effect of catalyst loading dose on the photodegradation efficiency of Congo red was observed by taking different amounts of catalyst ranging from 0.05 to 0.15 gm into 300mL of 50 ppm dye solution under UV light at 30^0C for two hours. The results showed that increment of catalyst loading from 0.05 to 0.1 gm increased the photodegradation efficiency of Congo red from 95 to 100% and after that the further increase in catalyst loading dose above 0.125 gm does not affect on the photodegradation efficiency. This is attributed to the increase in the catalyst loading dose which increased the number of active sites available on the catalyst surface for the reaction, which in turn increased the number of holes and hydroxyl radicals. The increase in initial dye concentration showed decreased photodegradation efficiency.

VI. CONCLUSIONS

XRD analysis confirmed the formation of nanocomposite. From the present work it is concluded that proper tuning of the formation of PANIZA nanocomposite can make it a good photocatalyst.

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