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Production of Nano TiO_2 Coatedon Polypyrole Film for Degradation of Organic Dye

Razieh Razavi*, **Sayed Mohammad Ali Hosseini**

Department of Chemistry, Shahid Bahonar University, Kerman, Iran

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Abstract

Polypyrol film was deposited on SS304by employing CPCvoltametery method, then coated with nano TiO_2 (PPy/TiO_2)and used as a photocatalysis for degradation of somedyesacid fushin, methylenblue, methyl orange and methyl red. The SEM and XRD analysis indicated nano size of TiO_2 deposits as 20nm on the polypyrol film. The UV result of absorption revealed that this film increased the rate of degradation of dyes comparing with TiO_2 powder.

Keywords: *Organic Dye, Polypyrol Film, Nano*TiO_2*, Photocatalyst.*

Introduction

Titanium dioxide (TiO_2) photocatalysis has been well-studied with the best concern for environmental and practical protection, because of its inexpensive, non-toxic and excellent photoelectric properties [1–4]. However, the band gap of TiO_2 (Eg = 3.2 eV) is so wide that it greatly limits the application of sunlight as an energy source for the photoreaction since about 3–4% of solar light falls in the UV range [5–10]. In response to the defect, many researchers have been made to improve the photocatalytic efficiency of TiO2 under visible-light irradiationby shifting its optical response from the UV to the visible range, such as noble metal deposition [11–16], metal [17–19] and nonmetal doping [20–22], forming composites with narrow semiconductors[23-24] and surface dye sensitization [25]. But, among these modification methods, photocatalysis applications of dye-sensitized TiO2 are limited due to the dissolution and photocatalytic degradation of the organic dyes itself during the process [25].

Conductive polymers such as polyaniline and polypyrrole (PPy) have attracted considerable attention due to their high absorption

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***Corresponding author:** *Razieh Razavi, Department of Chemistry, Shahid Bahonar University, Kerman, Iran. Email: raz8122000@yahoo.co.in. Tel:09131993014, Fax:03413222012.*

coefficients in the visible part of the spectrum, high mobility of charge carriers and good environmental stability.Moreover, many conductive polymers are efficient electron donors and good hole transporters under visible light excitation [26]. Therefore, conductive polymers are used as stable photosensitizersto modify TiO_2 nanoparticles and replace the dyes [27].

Among various conductive polymers, PPy is one of the mostpromising conductive polymers due to its superior conductivity, electrochemical reversibility, high polarizability, and the ease of preparation through chemical or electrochemical routes [28]. Moreover, PPy is chemically and thermally stable and undergoesonly slow degradation in ambient atmosphere because of overoxidation,so the conductivity of it decreases slightly for a long time[29]. In addition, PPy shows good stability in acidic and neutralsolution [30]. Therefore, it is used as a stable photosensitizer to prove the photocatalys is of TiO_2 and utilize visible light. Severalstudies [3] have been reported that PPy/TiO_2 nanocomposites were prepared by polymerization method at the air–water interface which showed better photocatalytic activity than TiO2nanoparticles [31].

Among various photocatalytic studies, the field dealing with thin film nano titanium dioxide (TiO_2) catalyst has recently received special attention. The thin film nano-TiO_2/UV process is an advanced oxidation process [32].

In this study, PPy/TiO_2 film for degradation of organic dyes methylen blue (MB), methyl orange (MO), methyl red (MR) and acid fuchin (AF), was prepared by electrochemical process (CPC).Scanning electron microscopy and XRD have been employed to find out the size of deposited TiO_2 particles.

Experimental

Materials

Pyrrole (≥97%, Fluka), Oxalic acid (pure, Merck), TiO2micron mesh (99%,Merck), Methylen blue, Methyl orange, Methyl red and acid fuchin (Merck) were purchased.

Methods

Electrochemical syntheses of PPy/TiO_2 film

Electrochemical syntheses were performed at room temperaturein a one-compartment cell using autolab potentiostat–galvanostat (PGSTAT302N) under computer control. The working electrodewas a stainless steel rod (304,4 cm length × 4mmdm) and counter electrode was platinum wire that placed 2.0 cm apart of working electrode. All potentials were referred to an Ag/AgCl electrode that was immersed directly in thesolution.

The procedure of preparation of the PPy/TiO_2 composite films is schematically illustrated in Figure 1. First, a pure PPy layer was deposited on the working electrode by direct oxidation of 0.1molL^{-1} pyrrole in an aqueous solution of 0.1 mol L^{-1} oxalic acid potentiostatically

(CPC) at 0.8 mVfor 1000 s Figure 1a. Secondly, the PPy coated working electrode immersed in 20 mL of TiO_2 (50 ppm) and kept on the ultrasonication for 24 hoursuntil a TiO_2 layer was successively deposited on the PPy layer Figure 1b. Other techniques [36-39] used for preparing conductive polymer/ TiO_2 nano composites. In this research sono electrochemical synthesis was taken.

Nano structure of PPy/TiO_2 film was studied by a scanning electron microscopy (SEM) Camscan 2600 mV system with electron beam energy of 20 keV. XRD pattern was obtained by an ARLX$^+$ instrument.

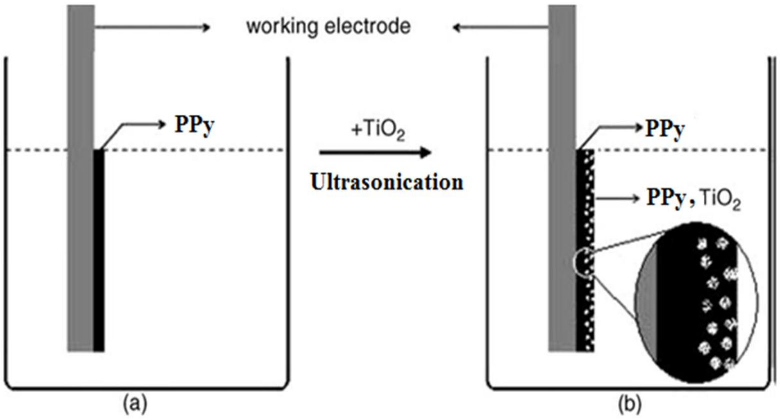

Figure 1. Electrochemical (a) and sono electrochemical(b) Preparation process of PPy/TiO_2 composite film.

Photocatalyst reactor

The photochemical reactor used, was made by a jacketed quartz tube. A high-pressure mercury lamp of 30W (Philips Lamps,) was placed inside the quartz reactor after careful removal of outer jacket of the lamp. The ballast and capacitor were connected in series to lamp which avoid any voltage fluctuations. The assembly of lamp and the quartz reactor were placed concentrically inside a Pyrex glass outer reactor, filled with solution. The solution taken in the outer reactor was stirred continuously using a magnetic stirrer. Furthermore,water was circulated in the annular space of jacketed reactor to ensure getting constant temperature. Finally, the whole system was confined in a dark enclosure to prevent any interruption due to stray light. The applied lamp predominantly emitted the whole UV wavelength especially 365 nm corresponding to the energy of 3.4 eV or photon flux of 5.8×10^{-6} mol of photons/s.

Degradation of organic dyes

The degradation experiments were done with different initial concentrations of the organic compounds with a catalyst film.All reactions were carried out for about 1 h till the concentration reduces.

The concentration of the organic dye in the samples was measured by UV-visible spectrophotometer Carry,Varian 50 Cons.

Results and discussion

Characterization

The cyclic voltammograms (CVs) of an as-grown PPy/TiO_2 film on the working electrode surface were carried out in an aqueous solution at $30mVs^{-1}$, the curves are illustrated in Figure 2. As can be seen from the figure, each CV cyclehas a couple of broad redox waves.

The CV of a PPy/TiO_2 film reveals a broad reductionwave centered at approximately -0.80V and an oxidation wave at approximately 0.30V (Figure 2, solid line). In contrast, the CV of pure PPy film has a broad oxidation wave at 0.08Vand a broad reductionwaveat-0.62V, and has a ΔE_p=0.7V (Figure 2, dashed line).

This is possibly because the conductivity of the composite film islower than that of the pure PPy film. Therefore CVs voltammograms shows the strong interaction between PPy and TiO2. Some studies indicated a strong interaction between them by other methods [36, 37]. As the figure illustrate, potential shifting indicate the change of working electrode surface before and after the TiO_2 coating.

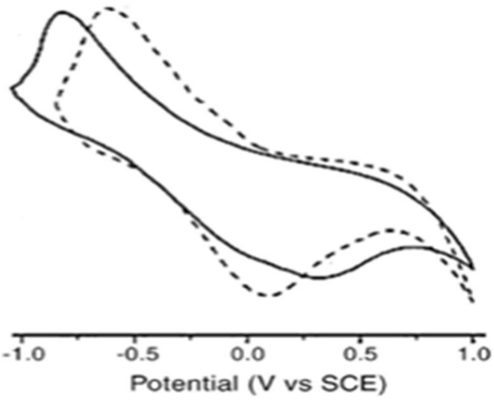

Figure 2. Cyclic voltammograms of a PPy/TiO_2 film (solid line) and a pure PPy film (dashed line).

The SEM images of a pure and a PPy/TiO_2 composite film are shown in Fig. 3 thatshows for a pure PPy film, the surface of PPy is compact and smooth where asthe surface of the PPy/TiO_2 film is rough and irregular Figure 3b.These micrographs suggest that the incorporation of TiO_2 nanoparticles affects the morphology of the PPy film significantly. Therefore after the deposition of titanium dioxide, the TiO_2 was grownwith spherical morphology and their particles size are 20 nm which is smaller than thereported one [35].

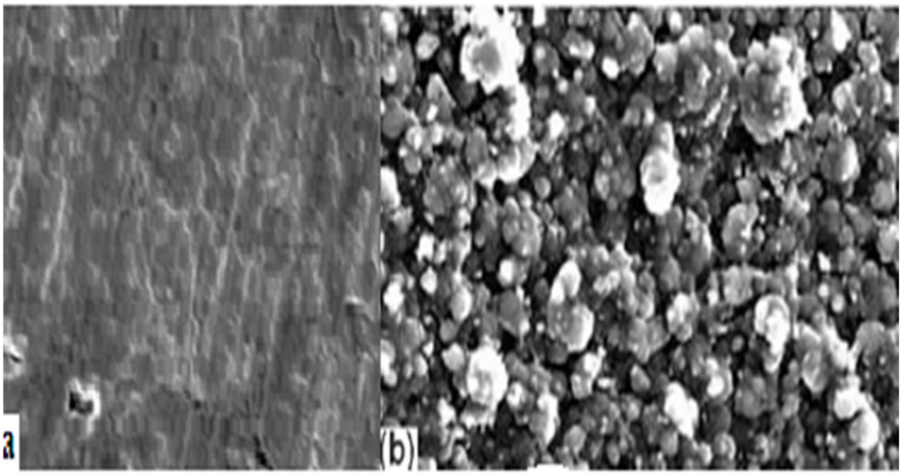

Figure 3. SEM images of (a) a purePPy film and (b) a PPy/TiO_2 film.

EDX Figure 4 of PPy/TiO_2 indicates that presence of TiO_2 on the structure of the nano composite film. After that, the phase and size of coated TiO_2 are revealed by XRD pattern.

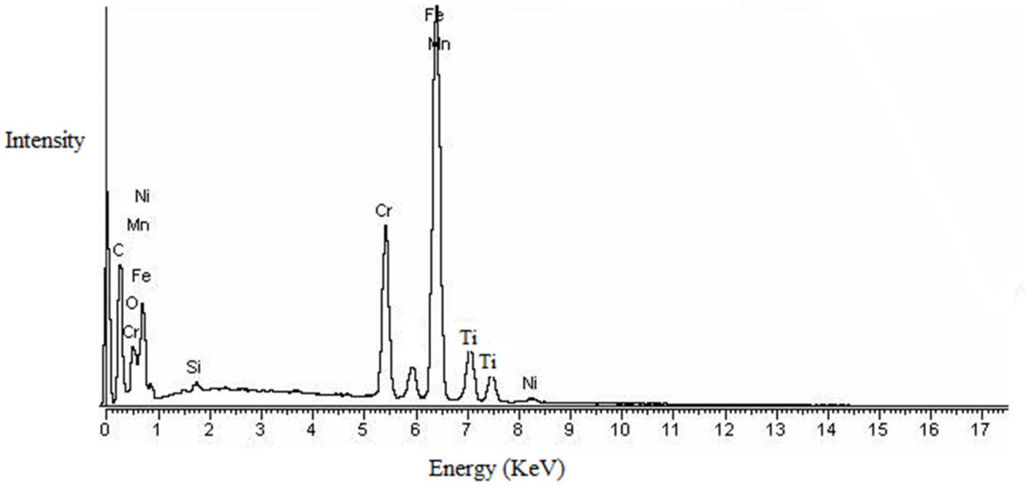

Figure 4. EDX of PPy/TiO_2.

The identification of TiO_2 phases was achieved by X-ray diffraction analysis Figure 5 using Cu-Kα radiation. The intensities of the strongest peaks of anatase (101) (2θ=25.4°) and rutile (110) (2θ=27.4°) were used to make a relative comparison of phase content between the different types of TiO_2 powders. A quantitative estimation of the weight fraction of the rutile phase in the sample was made by the following equation:

$$W_R=1/(1+0.81_A/I_R) \qquad (1)$$

Where WR, IA and IR are the weight fraction of the rutile present, X-ray integrated intensities of anatase and rutile reflection, respectively. The primary crystallite size of the obtained powders was estimated using the Scherrer equation [33]

$$D_c=K\lambda/(B\cos\theta) \qquad (2)$$

Where D_c the average crystallite size, K =0.89 the Scherrer constant and λ =15.406 nm the X-ray wavelength, B and θare the full-width at half-maximum (FWHM) the diffraction angle respectively. By applying equation 2, the coated nano TiO_2 size is 20nm. The data of XRD confirms the SEM result.

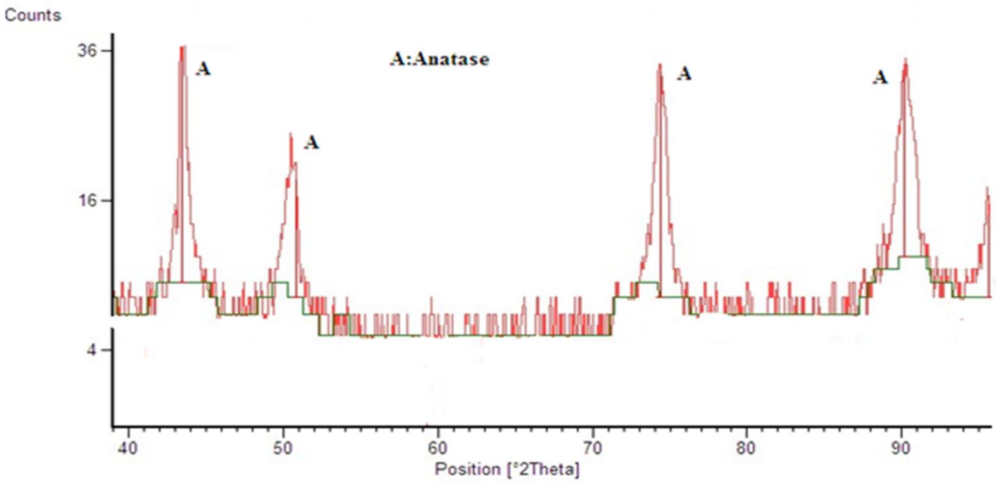

Figure 5. XRD pattern of coated TiO_2 onPPy film.

Photocatalysis degradation

Figure 6 shows the decreasing of ultra violet absorbance of each organic dye versus time. According to degradation plotsbyproducedfilm, decomposition of organic dyes has been proceeding in good manner Figure 6. Report [34] indicated that this occur with TiO2 powder but nano composite PPy/TiO_2 film proved better degradations of organic dye with increasing the rate of degradation Table 1.This means that the concentration of each organic dye decreases during the period of time in presence of PPy/TiO_2 nano composite film and UV light same as TiO_2 photocatalyst alone [34]. Thusthe film increases the rate of decomposition Figure 7 and has good life time.

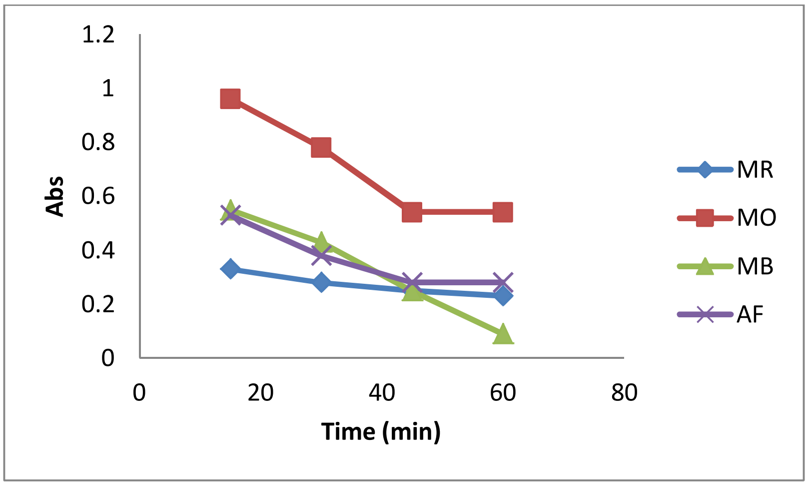

Figure 6. Degradation plot of organic dye.

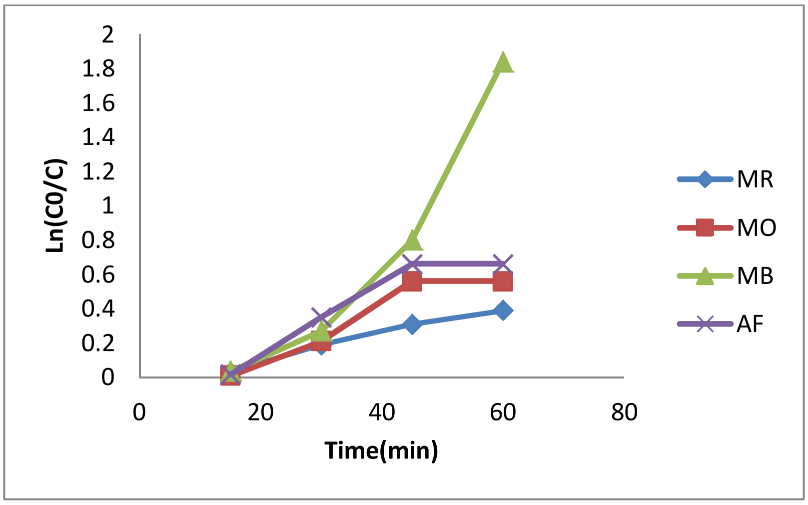

Figure 7. Ln (C_0/C) organic dyes versus time.

To study reproducibility life time of nano composite film, the employed film after degradation washed and reapplied as photocatalyst electrode after 1 week again. The process was repeated for 1 and 2 months andthe results are presented in Table 2.

Table 1. Comparing with degradation rate of MB organic dye by nano TiO_2 powder [34] and Nano composite PPy/TiO_2film.

Photocatalyst	Concentration after 60 min
nano TiO_2 powder [34]	43 ppm
Nano composite PPy/TiO_2	15.78 ppm

It has been reported [35, 36] that the decomposition rate increases with the increasing PPy/TiO_2 molar ratio up to optimal value. Now in this study different organic dyes were degradated and the same resultswere achieved as the other reports that have been done on one organic dye (methylen blue) [35]. Previously [35-38], conductive polymer/ TiO_2 nano composites have been reported as photocatalysts.

Table 2. UV absorption of 100 ppm concentration of Organic Dyes after 60 min for reproducibility of nano composite PPy/TiO_2 film.

Organic Dye	Absorption	After 1 week	After 1 month	After 2 months
MR	0.23	0.22	0.23	0.20
MO	0.54	0.55	0.54	0.53
MB	0.40	0.41	0.42	0.41
AF	0.28	0.28	0.27	0.26

Conclusion

Nano composite PPy/TiO_2 film has been prepared by sono electrochemical method which is fast, simple and inexpensive. Cyclic voltammetry diagram revealed the strong interaction between PPy and TiO_2. Result of EXD of the composite PPy/TiO_2 film illustrated the presence of TiO_2 in it. The size of nano coated TiO_2 was about 20nm. The nano composite film was applied as photocatalyst showed the good behavior for degradation of organic dyes by decreasing the concentration of them and increasing the rate of degradation reaction compare to TiO_2 powder.Having long life time with least preparation time is another advantage of nano composite PPy/TiO_2 film.

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