



## Production of Nano $\text{TiO}_2$ Coated on Polypyrrole Film for Degradation of Organic Dye

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### Abstract

Polypyrrole film was deposited on SS304 by employing CPC voltametry method, then coated with nano  $\text{TiO}_2$  (PPy/ $\text{TiO}_2$ ) and used as a photocatalysis for degradation of some dyes acid fushin, methylenblue, methyl orange and methyl red. The SEM and XRD analysis indicated nano size of  $\text{TiO}_2$  deposits as 20 nm on the polypyrrole film. The UV result of absorption revealed that this film increased the rate of degradation of dyes comparing with  $\text{TiO}_2$  powder.

**Keywords:** Organic Dye, Polypyrrole Film, Nano  $\text{TiO}_2$ , Photocatalyst.

### Introduction

Titanium dioxide ( $\text{TiO}_2$ ) 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  $\text{TiO}_2$  ( $E_g = 3.2$  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  $\text{TiO}_2$  under visible-light

irradiation by 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  $\text{TiO}_2$  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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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 photosensitizers to modify  $\text{TiO}_2$  nanoparticles and replace the dyes [27].

Among various conductive polymers, PPy is one of the most promising 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 undergoes only 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 neutral solution [30]. Therefore, it is used as a stable photosensitizer to prove the photocatalysis of  $\text{TiO}_2$  and utilize visible light. Several studies [3] have been reported that PPy/ $\text{TiO}_2$  nanocomposites were prepared by polymerization method at the air–water interface which showed better photocatalytic activity than  $\text{TiO}_2$  nanoparticles [31].

Among various photocatalytic studies, the field dealing with thin film nano titanium dioxide ( $\text{TiO}_2$ ) catalyst has recently received special attention. The thin film nano- $\text{TiO}_2$ /UV process is an advanced oxidation process [32].

In this study, PPy/ $\text{TiO}_2$  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  $\text{TiO}_2$  particles.

## Experimental

### Materials

Pyrrole ( $\geq 97\%$ , Fluka), Oxalic acid (pure, Merck),  $\text{TiO}_2$  micron mesh (99%, Merck), Methylene blue, Methyl orange, Methyl red and acid fuchin (Merck) were purchased.

### Methods

#### Electrochemical syntheses of PPy/ $\text{TiO}_2$ film

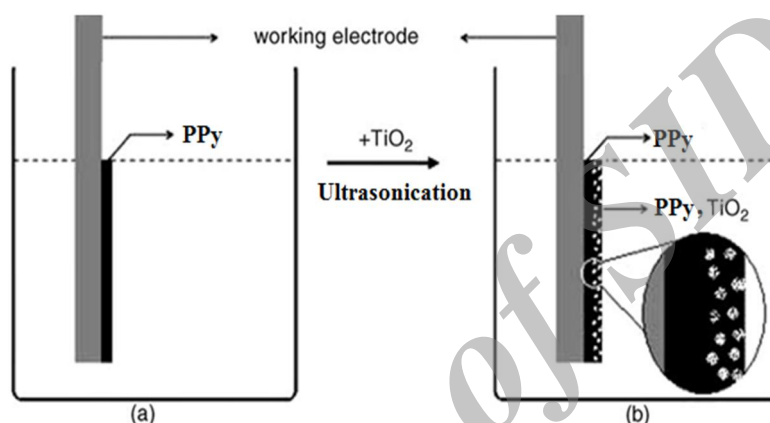
Electrochemical syntheses were performed at room temperature in a one-compartment cell using autolab potentiostat–galvanostat (PGSTAT302N) under computer control. The working electrode was a stainless steel rod (304, 4 cm length  $\times$  4 mm diameter) and counter electrode was platinum wire that placed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

The procedure of preparation of the PPy/ $\text{TiO}_2$  composite films is schematically illustrated in Figure 1. First, a pure PPy layer was deposited on the working electrode by direct oxidation of  $0.1 \text{ mol L}^{-1}$  pyrrole in an aqueous solution of  $0.1 \text{ mol L}^{-1}$  oxalic acid potentiostatically

(CPC) at 0.8 mV for 1000 s Figure 1a. Secondly, the PPy coated working electrode immersed in 20 mL of  $\text{TiO}_2$  (50 ppm) and kept on the ultrasonication for 24 hours until a  $\text{TiO}_2$  layer was successively deposited on the PPy layer Figure 1b. Other techniques [36-39] used for preparing conductive polymer/

$\text{TiO}_2$  nano composites. In this research sono electrochemical synthesis was taken.

Nano structure of PPy/ $\text{TiO}_2$  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<sup>+</sup> instrument.



**Figure 1.** Electrochemical (a) and sono electrochemical (b) Preparation process of PPy/ $\text{TiO}_2$  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  $5.8 \times 10^{-6}$  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

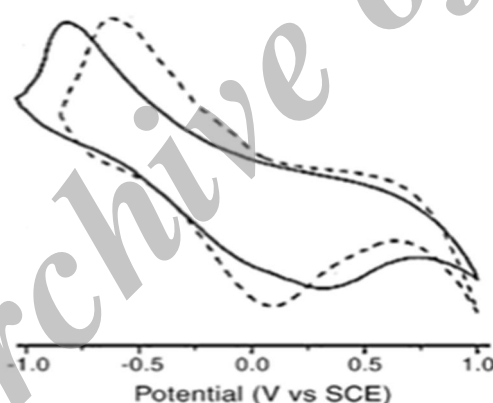
### Characterization

The cyclic voltammograms (CVs) of an as-grown PPy/TiO<sub>2</sub> film on the working electrode surface were carried out in an aqueous solution at 30 mV s<sup>-1</sup>, the curves are illustrated in Figure 2. As can be seen from the figure, each CV cycle has a couple of broad redox waves.

The CV of a PPy/TiO<sub>2</sub> film reveals a broad reduction wave centered at approximately -0.80 V and an oxidation wave at approximately

0.30 V (Figure 2, solid line). In contrast, the CV of pure PPy film has a broad oxidation wave at 0.08 V and a broad reduction wave at -0.62 V, and has a  $\Delta E_p = 0.7$  V (Figure 2, dashed line).

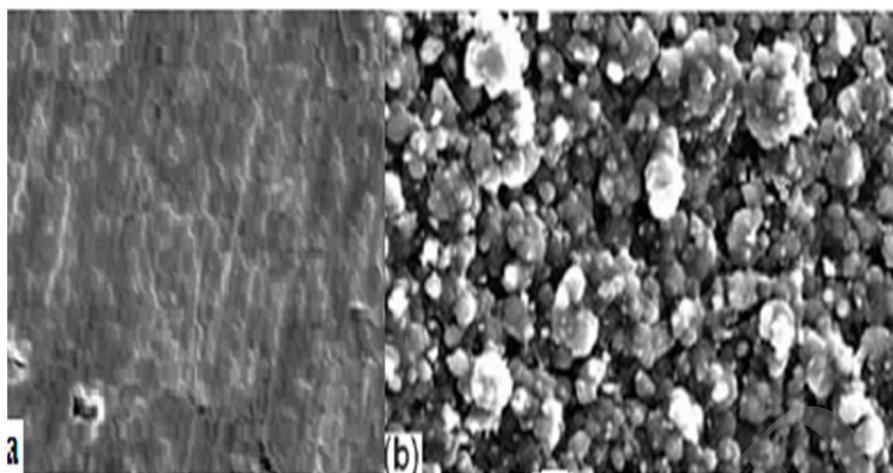
This is possibly because the conductivity of the composite film is lower than that of the pure PPy film. Therefore CVs voltammograms shows the strong interaction between PPy and TiO<sub>2</sub>. Some studies indicated a strong interaction between them by other methods [36, 37]. As the figure illustrates, potential shifting indicates the change of working electrode surface before and after the TiO<sub>2</sub> coating.



**Figure 2.** Cyclic voltammograms of a PPy/TiO<sub>2</sub> film (solid line) and a pure PPy film (dashed line).

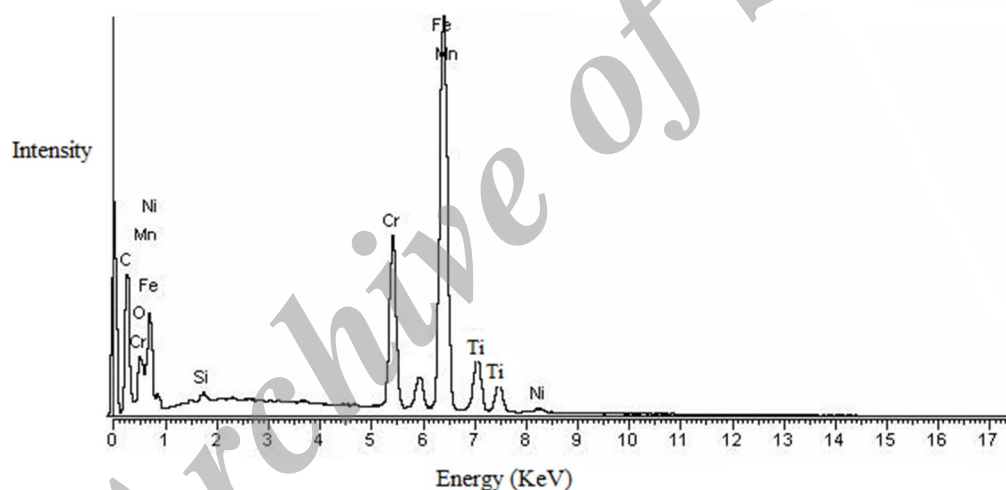
The SEM images of a pure and a PPy/TiO<sub>2</sub> composite film are shown in Fig. 3 that shows for a pure PPy film, the surface of PPy is compact and smooth where as the surface of the PPy/TiO<sub>2</sub> film is rough and irregular Figure 3b. These micrographs suggest that the

incorporation of TiO<sub>2</sub> nanoparticles affects the morphology of the PPy film significantly. Therefore after the deposition of titanium dioxide, the TiO<sub>2</sub> was grown with spherical morphology and their particles size are 20 nm which is smaller than the reported one [35].



**Figure 3.** SEM images of (a) a pure PPy film and (b) a PPy/TiO<sub>2</sub> film.

EDX Figure 4 of PPy/TiO<sub>2</sub> indicates that composite film. After that, the phase and size presence of TiO<sub>2</sub> on the structure of the nano of coated TiO<sub>2</sub> are revealed by XRD pattern.



**Figure 4.** EDX of PPy/TiO<sub>2</sub>.

The identification of TiO<sub>2</sub> phases was achieved by X-ray diffraction analysis Figure 5 using Cu-K $\alpha$  radiation. The intensities of the strongest peaks of anatase (101) ( $2\theta=25.4^\circ$ ) and rutile (110) ( $2\theta=27.4^\circ$ ) were used to make a relative comparison of phase content between the different types of TiO<sub>2</sub> powders. A quantitative estimation of the weight fraction of the rutile phase in the sample was made by

the following equation:

$$W_R = 1 / (1 + 0.81 I_A / I_R) \quad (1)$$

Where  $W_R$ ,  $I_A$  and  $I_R$  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]

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

Where  $D_c$  the average crystallite size,  $K=0.89$  the Scherrer constant and  $\lambda = 15.406$  nm the X-ray wavelength,  $B$  and  $\theta$  are the full-width

at half-maximum (FWHM) the diffraction angle respectively. By applying equation 2, the coated nano  $\text{TiO}_2$  size is 20nm. The data of XRD confirms the SEM result.

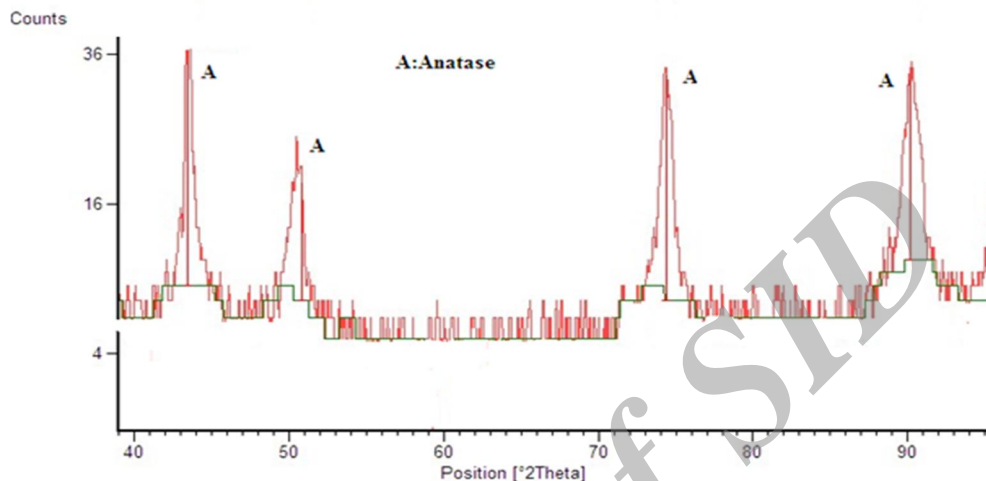


Figure 5. XRD pattern of coated  $\text{TiO}_2$  on PPy film.

#### Photocatalysis degradation

Figure 6 shows the decreasing of ultra violet absorbance of each organic dye versus time. According to degradation plots by produced film, decomposition of organic dyes has been proceeding in good manner Figure 6. Report [34] indicated that this occur with  $\text{TiO}_2$  powder but nano composite PPy/ $\text{TiO}_2$  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/ $\text{TiO}_2$  nano composite film and UV light same as  $\text{TiO}_2$  photocatalyst alone [34]. Thus the film increases the rate of decomposition Figure 7 and has good life time.

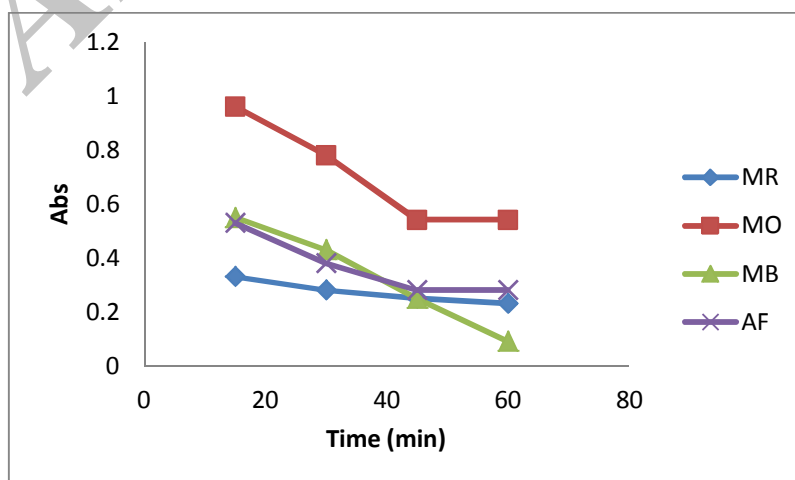
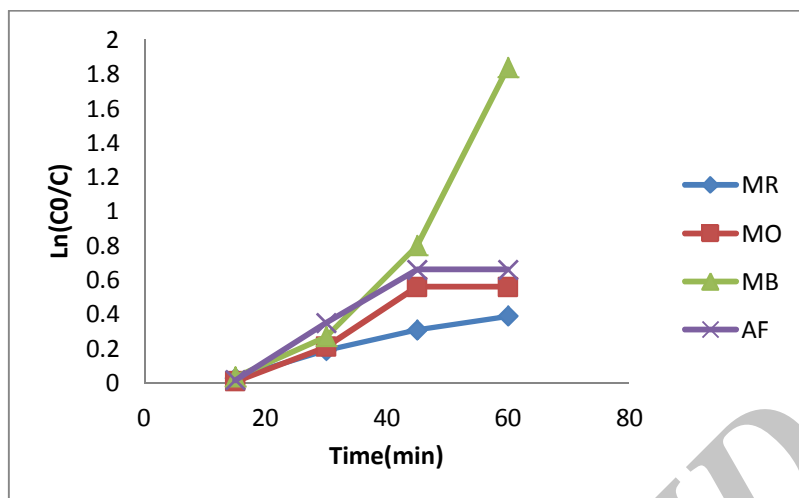


Figure 6. Degradation plot of organic dye.



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

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

**Table 1.** Comparing with degradation rate of MB organic dye by nano  $\text{TiO}_2$  powder [34] and Nano composite PPy/ $\text{TiO}_2$  film.

Photocatalyst	Concentration after 60 min
nano $\text{TiO}_2$ powder [34]	43 ppm
Nano composite PPy/ $\text{TiO}_2$	15.78 ppm

It has been reported [35, 36] that the decomposition rate increases with the increasing PPy/ $\text{TiO}_2$  molar ratio up to optimal value. Now in this study different organic dyes were degraded and the same results were achieved as the other reports that have been done on one organic dye (methylene blue) [35]. Previously [35-38], conductive polymer/ $\text{TiO}_2$  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/ $\text{TiO}_2$  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<sub>2</sub> 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<sub>2</sub>. Result of EXD of the composite PPy/TiO<sub>2</sub> film illustrated the presence of TiO<sub>2</sub> in it. The size of nano coated TiO<sub>2</sub> 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<sub>2</sub> powder. Having long life time with least preparation time is another advantage of nano composite PPy/TiO<sub>2</sub> film.

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