SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE/TiO_2 COMPOSITES AS A PHOTOCATALYST

Ljerka Kratofil Krehula, Vanja Gilja, Marijana Kraljić Roković, Zlata Hrnjak-Murgić

Faculty of Chemical Engineering and Technology, University of Zagreb,
Marulićev trg 19, HR-10000, Zagreb, Croatia

INTRODUCTION

The great advantage of conductive polymers is that their chemical, physical and optical properties can be adjusted according to the demand of application. In this study the structure of conductive polymer polypyrrole (PPy) was studied during the chemical synthesis. It is of great importance to explore the appropriate structure of polypyrrole that can induce activation of TiO_2 photocatalysts since the synthesis of organic/inorganic hybrid materials can result in a synergistic and complementary feature, increasing TiO_2 photocatalytic efficiency. As conductive polymers are also photosensitive, they can be activated by light absorption, which starts the transition of electrons from a conductive polymer by injection in the conductive band of TiO_2. However, despite intensive research, the relationship between structure and conductivity is still not completely understood. It is assumed that the conductivity increases with a higher degree of crystallinity but this is not confirmed for all conducting polymers, only for some of them.

In this paper different conditions of synthesis of pure polypyrrole and titanium dioxide/polypyrrole (TiO_2/PPy) composites were studied. Samples of polypyrrole and TiO_2/PPy composites were characterized by Fourier transform infrared spectroscopy (FTIR) and cyclic voltammetry (CV). The results show that due to the changes in the fraction of oxidant during the synthesis of PPy its structure was changed and thus the conductivity. The photocatalytic activity of the samples was tested by the decomposition of the dye Reactive Red 45 (RR45).

EXPERIMENTAL

❑ Preparation of the samples

- preparation of polypyrrole:
  polymerization of pyrrole monomer
  T = 5 °C - ice bath, intensity of stirring: 250 rpm

- molar ratio ***pyrrole : $FeCl_3$ = from 1:0.5 to 1:5***
- duration of polymerization: 90 or 180 min

- preparation of polypyrrole/TiO_2 composites:
  polymerization of pyrrole monomer in the presence of TiO_2

❑ Characterization

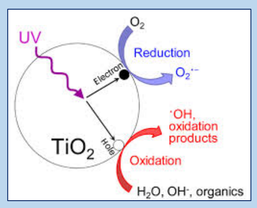
FTIR spectroscopy

FTIR spectrophotometer *Spectrum One, Perkin Elmer*
- ATR, 4000 – 650 cm^{-1}

Cyclic voltammetry

- potentiostat/galvanostat *PAR Model 263A*
- potential range: from -0.8 V to 0.6 V, scan rate: 0.05 Vs^{-1}, in 0.5 M NaCl
- reference electrode: calomel electrode
- counter electrode: Pt foil
- polymer layer mixed with carbon paste was applied to Au support (A = 0.07 cm^2)

Photocatalysis



- quartz tube hosting *lamp UVP-Ultra Violet Products, UK*
- model contaminant: azo dye *C.I. Reactive Red 45 (RR45)*
- 75 mg catalyst/75 ml RR45 (c RR45= 30 mg/dm^3)
- dye decomposition was monitored by UV/VIS spectrophotometer *Perkin Elmer Lambda EZ 201,* tracking the changes of wavelength characteristic for RR 45 (max = 542 nm)

CONCLUSIONS

Results show that the properties of polypyrrole highly depend on the synthesis conditions. Lower monomer/oxidant ratio influences the formation of shorter polymer chains, which is proved by FTIR spectroscopy.

The shift of peaks (~1520 and ~1170 cm^{-1}) to higher frequencies indicates that polypyrrole contains mainly shorter polymer chains and a lower degree of oxidation.

Polypyrrole synthesized with lower monomer/oxidant ratio shows better photocatalytic activity. TiO_2/PPy composites show good photocatalytic activity in a relatively short time.

Cyclic voltammetry showed that polypyrrole has good activity. All synthesized polypyrrole samples show behaviour characteristic for this conductive polymer.

The better results (reversibility) are obtained by CV for the samples with lower monomer/oxidant ratio (PPy 1:1, PPy 1:1.5).

RESULTS

❑ Conversion of pyrrole

Sample	Conversion / %
synthesis: 90 min	
PPy 1: 0.5	15.60
PPy 1:1	24.99
PPy 1:1.5	28.02
PPy 1:2	41.54
PPy 1:3	68.66
PPy 1:5	76.11
synthesis: 3h	
PPy 1:1	41.70
PPy 1:1.5	40.94
PPy 1:2	51.77
PPy 1:5	92.71

❑ Photocatalysis

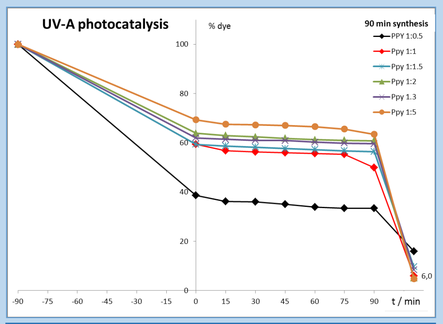


Figure 1 – Photocatalytic activity of PPy conducting polymers synthesized for 90 min

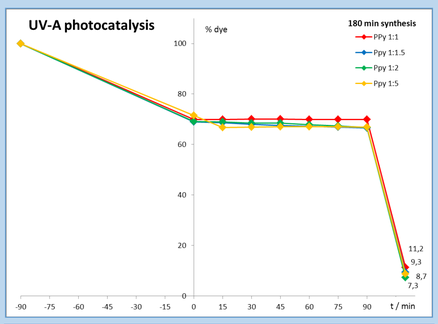


Figure 2 – Photocatalytic activity of PPy conducting polymers synthesized for 180 min

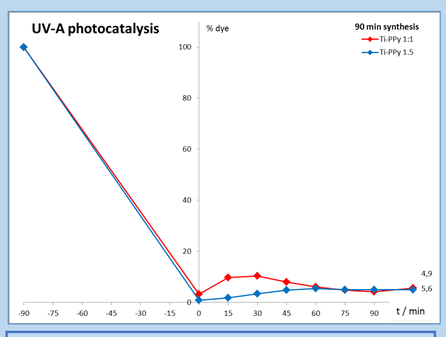


Figure 3 – Photocatalytic activity of TiO_2/PPy composites, synthesized for 90 min

❑ Cyclic voltammetry

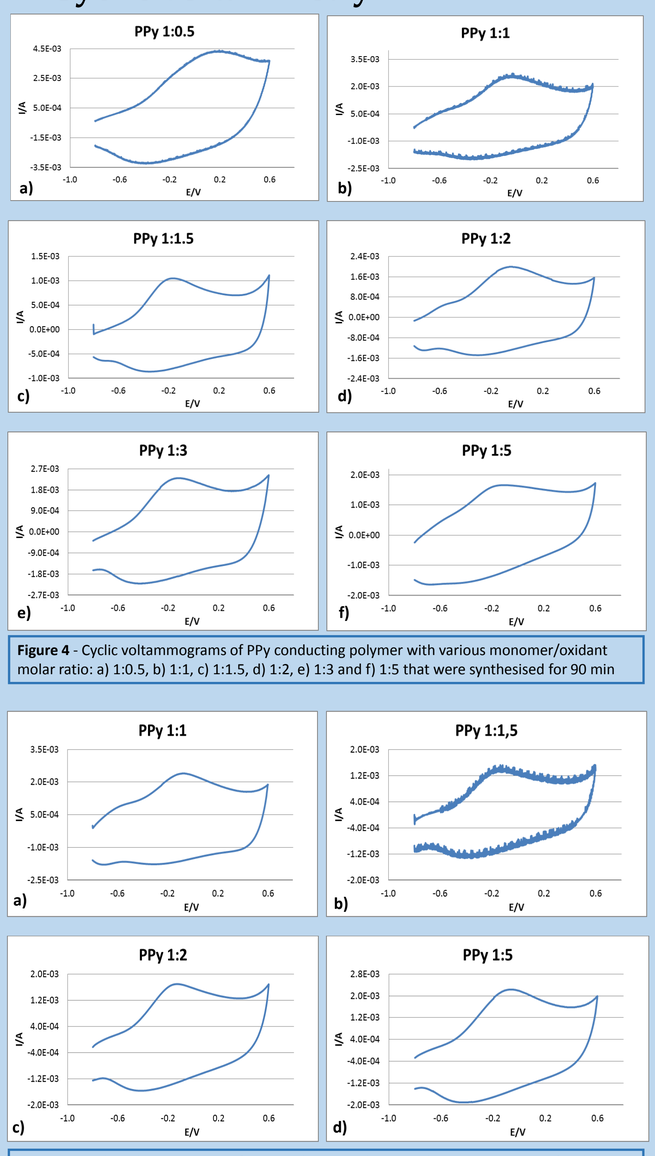


Figure 4 - Cyclic voltammograms of PPy conducting polymer with various monomer/oxidant molar ratio: a) 1:0.5, b) 1:1, c) 1:1.5, d) 1:2, e) 1:3 and f) 1:5 that were synthesised for 90 min

Figure 5 - Cyclic voltammograms of PPy conducting polymer with various monomer/oxidant molar ratio: a) 1:1, b) 1:1.5, c) 1:2 and d) 1:5 that were synthesised for 180 min

❑ FTIR spectroscopy

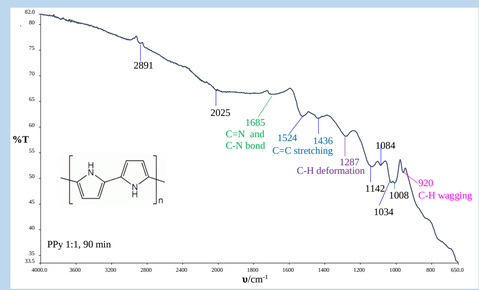


Figure 6 – FTIR spectra of polypyrrole, synthesized for 90 min

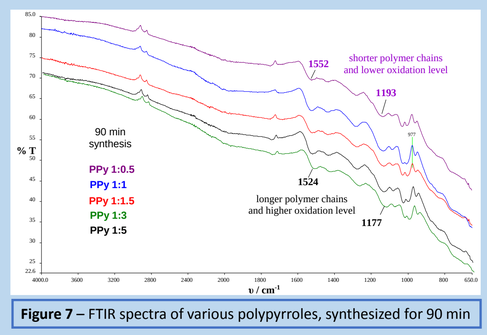


Figure 7 – FTIR spectra of various polypyrroles, synthesized for 90 min