Hybrid PVDF-P(L-DOPA)-ZnO membranes for efficient pollutants removal

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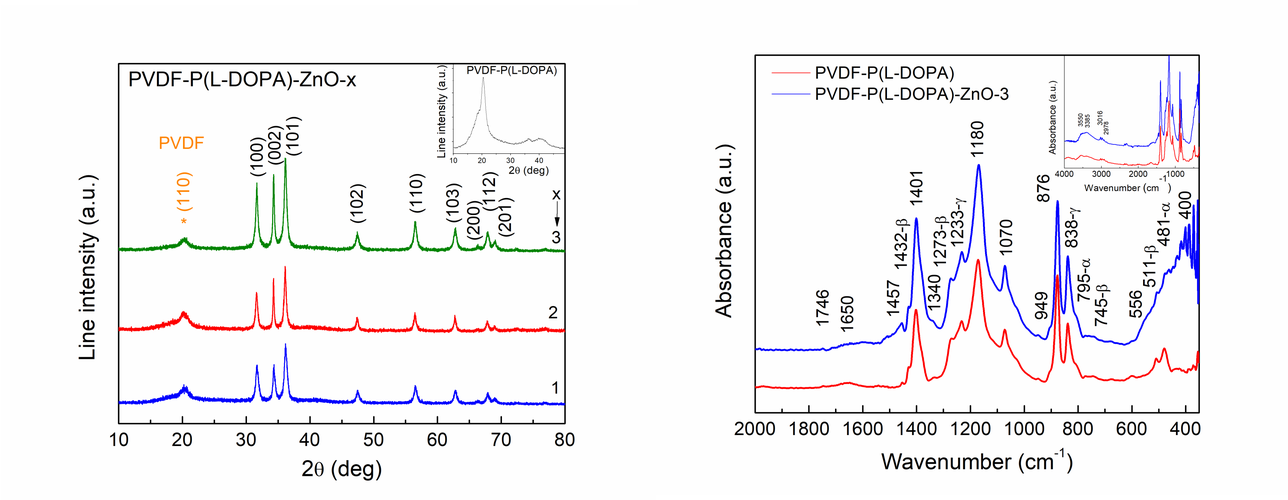
INTRODUCTION

Membrane filtration is one of the most promising technologies for the treatment of wastewater due to the easy operation, energy saving and high separation efficiency. But the hydrophobic nature of the membrane drives to organic pollutants adsorption on its surface resulting on a severe fouling. One solution to solve this issue is to use nanoparticles to modify the membrane surface. The nanoparticles offer hydrophilic character to membranes and by its photocatalytic activity contributes to pollutant removal from membranes surface. PVDF-P(L-DOPA)-ZnO hybrid membranes were prepared and tested against two classes of water pollutants: cationic dyes and antibiotics. The structural and morphological properties of the hybrid membranes were evaluated by X-Ray diffraction (XRD), Attenuated Total Reflection- Fourier Transform Infrared Spectroscopy (ATR-FTIR), Scanning Electron Microscopy (SEM). The firm P(L-DOPA)-ZnO coating on PVDF membrane surface converted its hydrophobic nature to a hydrophilic one. Under UV light irradiation of PVDF-P(L-DOPA)-ZnO hybrid membranes, the removal rate for Rhodamine B (RhB) and oxytetracycline (OTC) reached 80% and 71%, respectively. The hybrid membrane is characterized by a high stability and reusability in the process of dye removal. The generation of reactive oxygen species involved in photocatalysis was proved by ESR

SAMPLE PREPARATION

The Polyvinylidene fluoride (PVDF) membrane was prepared by phase inversion method and then a P(L-DOPA) layer was deposited using commercially available L-DOPA and TrisCl buffer solution (pH=8.5) . In order to growth ZnO on PVDF-P(L-DOPA) membranes, the decoration process was performed by two combined chemical processes, sol-gel and chemical precipitation starting from $Zn(CH_3COO)_2x2H_2O$.

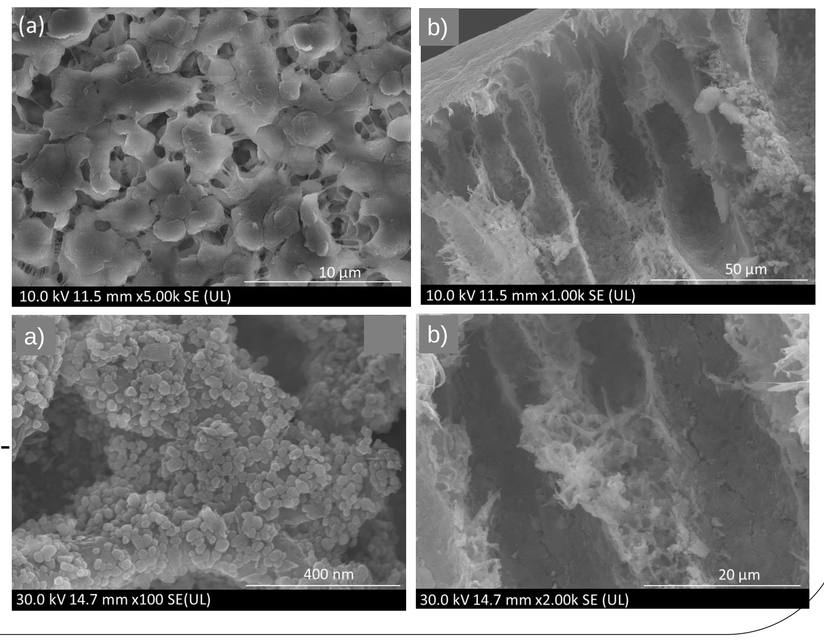
STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION



- ZnO with wurzite structure
- The mean crystallite size in 25 nm

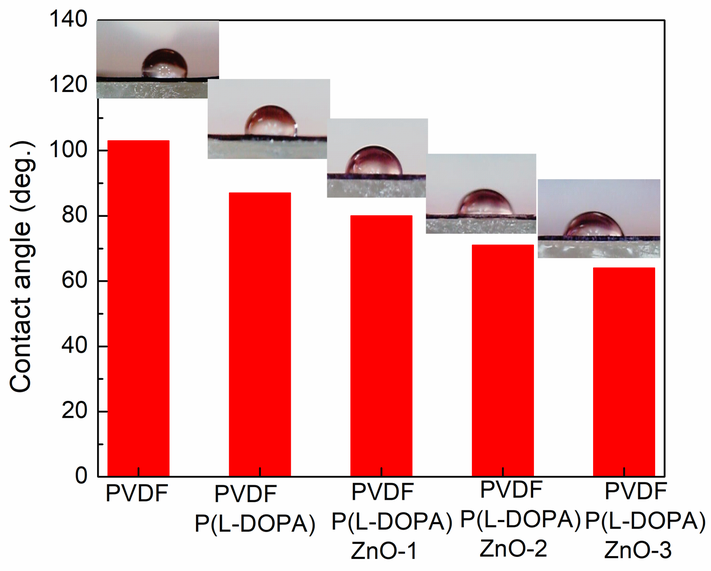
- The α, β and γ phases polymorphic phases of PVDF were identified.

- PVDF membrane
(a) surface image
(b) cross section image



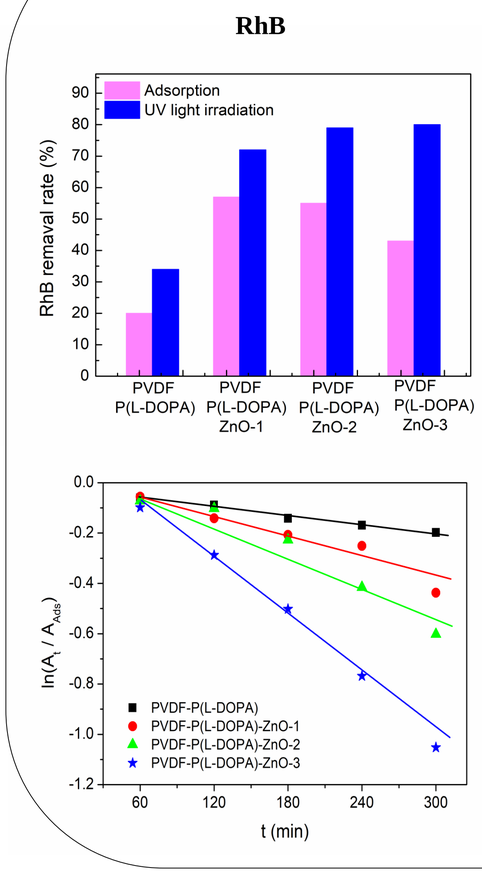
- PVDF-P(L-DOPA)-ZnO membrane

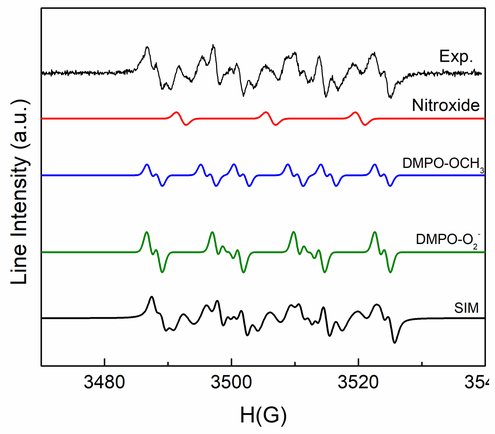
CONTACT ANGLE



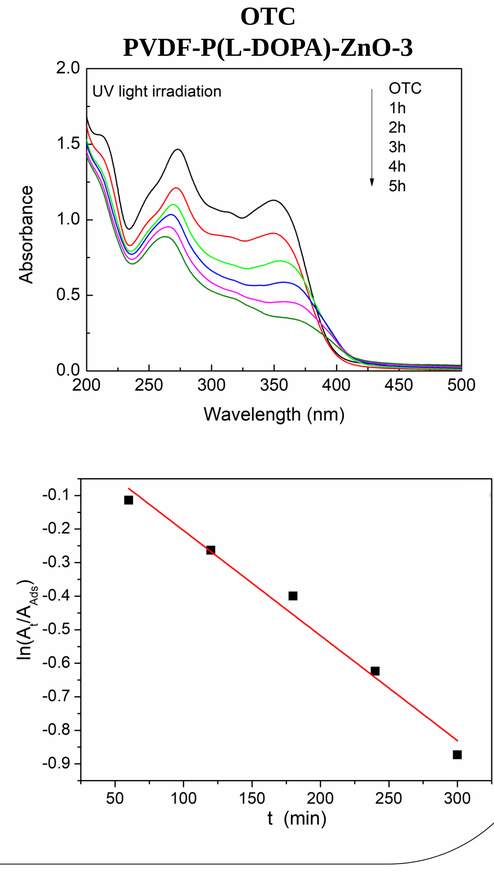
- The contact angle decrease with the increase of ZnO content suggesting the increase of the hydrophilicity.

PHOTOCATALYTIC DEGRADATION





- EPR experimental spectrum (Exp.) measured after 20 min irradiation of PVDF-P(L-DOPA)-ZnO-3 sample and simulated spectrum (SIM) representing a linear combination of following spin adducts: Nitroxide, •DMPO-OCH_3, and •DMPO-O_2^-.



CONCLUSIONS

- The ZnO nanoparticles were grown in situ on a PVDF membrane obtained by phase inversion method using a P(L-DOPA) interlayer which facilitate the nanoparticles binding.
- XRD measurements, sustain the growth of crystalline ZnO nanoparticles with wurtzite structure on membrane surface, and the PVDF polymorphic phases formation was highlighted by FT-IR.
- Through the P(L-DOPA)-ZnO deposition the hydrophilicity of the PVDF membrane was significantly improved.
- The adsorption and photocatalysis are the two processes involved in the removal of Rhodamine B and oxytetracycline.
- The highest RhB removal rate was obtained for PVDF-P(L-DOPA)-ZnO-3, 80% at pH 6. The same sample exhibit 71% removal rate of OTC under UV light irradiation.

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