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Metal peroxide- polymer composites for dye degradation

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Abstract. Semiconductor metal oxides/its composites with polymers have been explored for dye degradation through photocatalytic mechanism; these require UV or visible light for activation. Hence, there is need to develop (photo) catalyst that work in absence/ presence of light. Towards this objective we are exploring metal peroxides and its composites for dye degradation. Here, we report our work on magnesium peroxide and its composites for dye degradation by photochemical pathways. The nanocomposites are synthesized from monomers and peroxides. The synthesized composites have been characterized by IR, DRS and powder XRD. The composites did not degrade dyes in dark.

1. Introduction

The release of dyes effluents in environment is caused of hazardous toxicity in many countries. Organic dyes are mostly used in lather, textile, paint, food, drugs and cosmetic industries. They released these dyes to water bodies resulting high Chemical Oxygen Demand (COD), even after being treated. Dyes like Rhodamine N (RhB) and Methylene Blue (MB) containing C-N and C-S bonds/groups that are resistant toward photolysis. Due to reductive anaerobic degradation it generates carcinogenic products [1]. Now a day, degradation of dyes to non-toxic substances is most important. Reverse osmosis, coagulation, filtration, adsorption chemical oxidation and precipitation required additional treatment [2-4]. COD and BOD are not completely effective for degradation of many textile dyes [5]. The photocatalysis carried out in ambient conditions by using semiconductor metal oxides/its composites with polymers is gaining more importance over the above conventional methods. When H_2O_2 is added to metal oxides, it produces ROS such as hydroxyl radicals to degrade dyes into non-toxic compounds [6].

Here, ZnO_2 and MgO_2 /its composites with polypyrrole (PPY) have been used for Rhodamine B degradation without any irradiation. The magnesium peroxide may generate the ROS under irradiation but without an extra energy like UV or visible light, it did not showing any degradation. The formation of composites with electron rich organic molecules decreased the band gap (E_g) of magnesium from valance band (VB) to conduction band (CB) which leads to easily generation of ROS under ambient condition. This new approach toward this generation of toxic to non-toxic products may replace the old techniques for dye degradation and water treatment at large scale. This method is based on catalytic activity of composites that can be reuse for further water treatment which is time as well as cost effective and environment friendly technique.



2. Experimental section

2.1. Synthesis of ZnO₂

Zn(CH₃COO)₂·2H₂O (1 M) and KOH (2 M) dissolved in 50 ml water separately to get clear solution. KOH solution was added to Zinc acetate drop wise under stirring at room temperature that form zinc hydroxide. 30 ml of 30% H₂O₂ slowly into zinc hydroxide which formed ZnO₂.

2.2. Synthesis of ZnO₂ composites with PPY

After characterization of ZnO₂, 100 mg of magnesium peroxide, 20μL concentrated HCl, 100μL of freshly prepared sodium lauryl sulfate, 100μL pyrrole are added into 10 ml of water and kept at 90 °C overnight in closed container to form respective composites of PPY by *in-situ* polymerization.

2.3. Synthesis of MgO₂

Mg(CH₃COO)₂·4H₂O (1M) and KOH (2M) were dissolve in water separately. The solution of KOH was added drop wise in magnesium acetate under stirring at room temperature to form magnesium hydroxide as white precipitate. 80 ml of 30% H₂O₂ is added slowly into the magnesium hydroxide that from MgO₂.

2.4. Synthesis of MgO₂ composites with PPY

After characterization of MgO₂, 100 mg of magnesium peroxide, 20μL concentrated HCl, 100μL of freshly prepared sodium lauryl sulfate, 100μL pyrrole are added into 10 ml of water and kept at 90 °C overnight in closed container to form respective composites of PPY by *in-situ* polymerization.

2.5. Characterization

In IR (IRAffinity-1 Shimadzu) spectra (Fig.1), (a) ZnO₂ from 1028-1407cm⁻¹ showing stretching frequencies for O₂²⁻ and 404 cm⁻¹ is for ZnO bond.

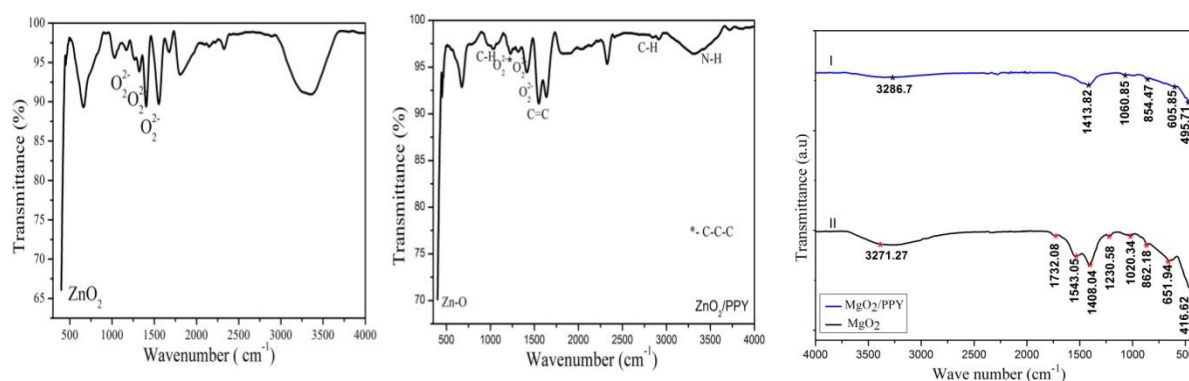


Fig. 1 IR of (a) ZnO₂, (b) ZnO₂/PPY, (c) MgO₂ and (d) MgO₂/PPY

(b) ZnO₂/PPY: 1028 cm⁻¹ is for =C-H (aromatic) bend. 1280-1437 cm⁻¹, this band is for O₂²⁻. The double hump near 1600 cm⁻¹ is due to -C=C- stretching, 2914 cm⁻¹ for Csp³-H stretch. The broad peak at 3300 cm⁻¹ for 2^o amine (N-H cm⁻¹). 1235 cm⁻¹ is for C-N stretching.

(c) The peak at 447 cm⁻¹ in MgO₂ spectrum corresponds to Mg-O bond. For MgO₂/PPY, the broad peak at 3286 cm⁻¹ is for O-H or N-H stretching. 1413cm⁻¹ is for C-N or C-H ring in plane stretching [7]. The band at 1060 cm⁻¹ corresponds to N-H or C-H in plane deform vibrations [8]. The C-H out of plane deformation vibration is at 854 cm⁻¹, and C-C out of plane ring deformation or C-H rocking at 605 cm⁻¹ also observed. The peak at 495 cm⁻¹ in MgO₂ spectrum corresponds to Mg-O bond.

In both spectrum of composites, the band at 1413 cm⁻¹ corresponds to (C₆H₄) - benzenoid ring [9]. The XRD pattern for ZnO₂, (111), (002), (022) and (113) are the indices. ZnO₂/PPY showing

indices (104) for polymerization with PPY. MgO₂ miller indices are observed as (111) at two theta angle 32.010°, (200) at 37.129°, (210) at 41.703°, (220) at 53.519° and (311) at 63.736° has been observed. For both composites, miller indices are same at same angle (Fig. 2). Band gap for ZnO₂ is 3.6 eV, ZnO₂/PPY has 2.86 eV and MgO₂/PANI-I have 1.98 eV shown in Fig 3. $(\alpha h\nu)^n = A(h\nu - E_g)$, where α is absorption, E_g is band gap. Band gap for MgO₂ is 5.19 eV, MgO₂/PPY has 2.07eV and MgO₂/PANI-I have 1.98 eV shown in Fig 3 (Tauc plot) in this figure, the UV-Visible (V-670 JASCO) spectra of ZnO₂ and ZnO₂/PPY have also shown. Crystallite size for ZnO₂ are 52 (111), 53 (002), 46 (022) and 49 nm (113). ZnO₂/PPY, (104) for polymerization with PPY with 58nm. For MgO₂, crystallite size are 54 nm, 56 nm, 61 nm. For MgO₂/PPY, crystallite size are 58 nm, 57 nm.

2.6. Degradation:

Degradation of 10 ppm Rhodamine B without any irradiation using ZnO₂ has been shown in Fig. 4 for 10 ppm, 25 ppm, 40 ppm and 80 ppm, which showing effective degradation under 80 minutes. Fig. 5 is shown for degradation of methylene blue (10ppm) and mixtures of methylene blue, Rh-B and methyl orange using ZnO₂/PPY. Whereas, for Rhodamine B of 10 ppm concentration, MgO₂ and MgO₂/PPY did not showing degradation (Fig. 6).

3. Result and discussion

ZnO₂, ZnO₂/PPY, MgO₂ and MgO₂/PPY have been confirmed by FT-IR and powder XRD (Fig. 1 and 2). Diffuse Reflectance Spectra of all compositions are measured (Fig. 3). Application portion involves degradation of dyes. ZnO₂ and ZnO₂/PPY show good degradation for methyl blue, rhodamine B and mixture of methyl orange, methylene blue and rhodamine B under 80 minutes observation, where as MgO₂ and MgO₂/PPY did show degradation in UV but not under dark (Fig.3-5)

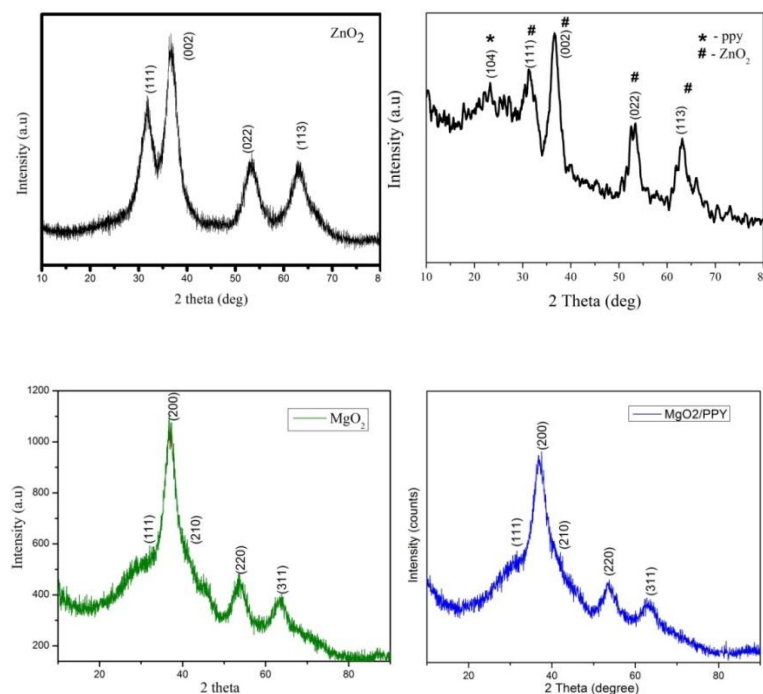


Fig. 2 XRD pattern for ZnO₂, ZnO₂/PPY MgO₂ and MgO₂/PPY

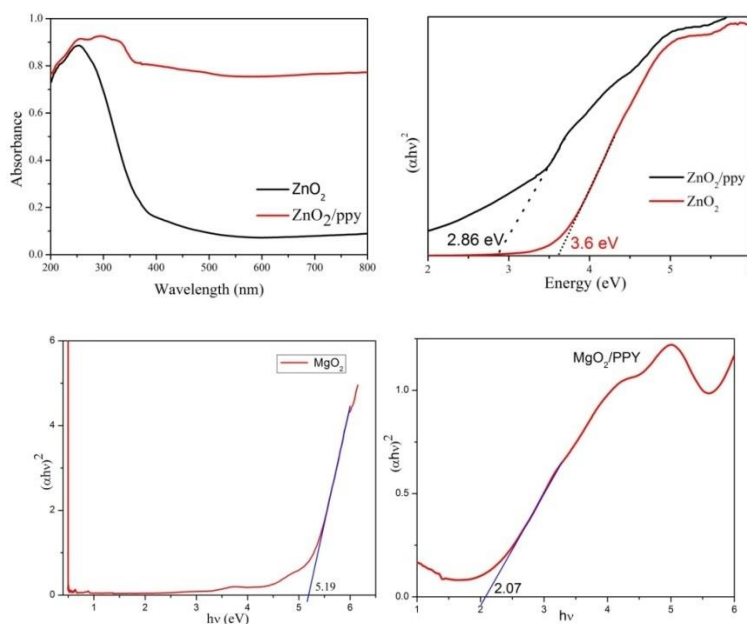


Fig. 3 Tauc plot

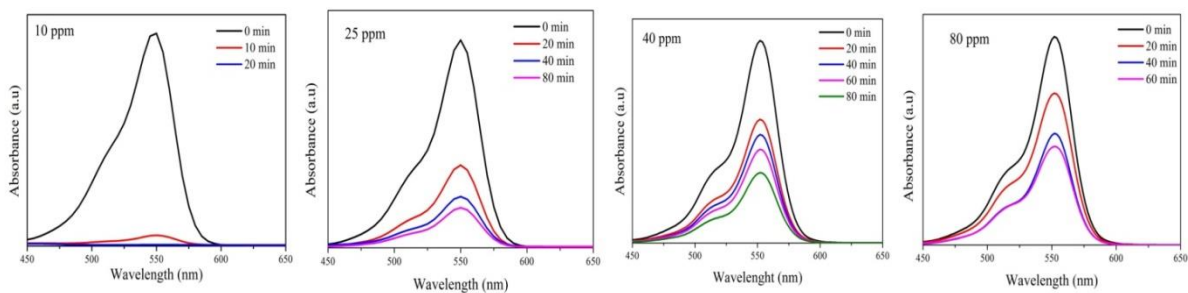


Fig. 4 Degradation of 10 ppm Rhodamine B without any irradiation using ZnO₂

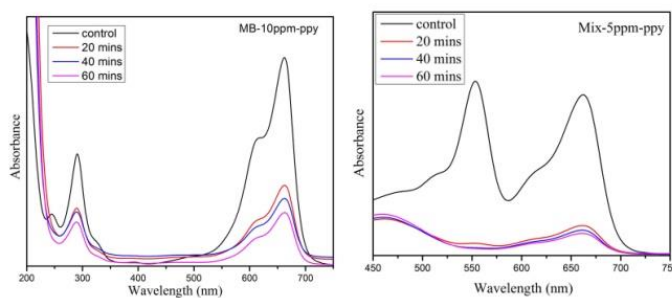


Fig. 5 Degradation of methylene blue and mixtures using ZnO₂/PPY

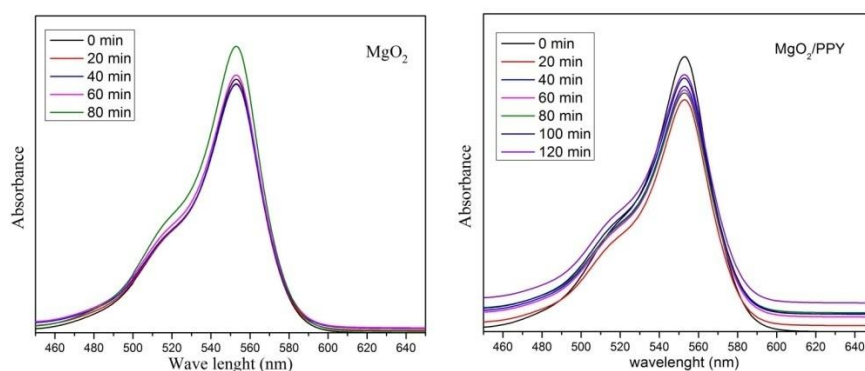


Fig. 6 Degradation of Rhodamine B (10 ppm) using MgO_2 and MgO_2/PPY

4. Conclusion

The generation of ROS is not observed by our compounds in dark and requires irradiation to facilitate the production of ROS. The optimization of ratio of polymers to metal peroxide is underway.

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