One-Step Hydrothermal Synthesis of Al decorated on Manganese oxide: Characterization, and photocatalytic Degradation of malachite Green

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Abstract

Recently, mesoporous transition metal oxides have received enormous attention because of the unique catalytic properties attributed to high surface area and easy accessibility to active sites. A highly crystalline Al decorated Mn_3O_4 nanoparticles were prepared by hydrothermal method. Direct evidence of the decorated of Al in the Mn_3O_4 was observed by the data collected from XRD, FT-IR and UV-Vis techniques. The surface morphology was observed by SEM images. As synthesized nanoparticles act as better photocatalytic activity on Malachite green (MG) dye.

Key Words: Mn_3O_4, Malachite green, photocatalyst.

1 INTRODUCTION

In the last 25 years, heterogeneous photocatalysis over MnO_2 has generated growing interest as a promising technology to degrade chemical substances and inactivate pathogen cells in aqueous solution, since MnO_2 presents suitable features such as low cost and ready commercial availability.[1] Inorganic pseudo capacitive materials such as MnO_2, RuO_2 store charge via redox reactions. Such inorganic electrochemical capacitors use an aqueous electrolyte to reduce the risk of explosion at high temperatures, improve the power density, and show higher efficiency.[2] The photocatalytic activity of MnO_2 is dependent on surface area, charge carrier trapping, particle size and the surface hydroxyl groups may enhance the visible light absorption and they may undergo photodegradation.[3] One more important strategy to improve photocatalytic activity is to tailor the morphology of photocatalysts by using nanotubes, nanorods, nanosheets, nanowires.[4] In this study, we report photocatalytic degradation of Malachite green under visible light irradiation by using synthesized Al decorated manganese oxide.

2 EXPERIMENTAL

Manganese sulfate was purchased from Loba Chemie (AR), Aluminium sulfate and Hexamethylenetetramine was purchased from sigma Aldrich (AR) and sodium nitrate was purchased from Pub Chem (LR) and used as received.

Al decorated Mn_3O_4 were prepared by hydrothermal method. Manganese sulfate, Aluminium sulfate and Hexamethylenetetramine (HMT) in 100 ml solution was maintained at pH 11 using $NaNO_3$. The total molar concentration was $0.01 mL^{-1}$. The mixed solution was poured into an autoclave and heated at 100 ºC for 16h. The brown colored product was washed several times with hot water followed by acetone. Finally the dry product was collected and calcined at 500 ºC for 3h.

Powder X-ray diffraction (XRD) patterns was used to determined the crystal structures and lattice parameters of using a Rich Siefert 3000 diffractometer with Cu $K_{\alpha 1}$radiation (λ= 1.5406 Å). FTIR spectra were recorded using a Perkin Elmer FTIR spectrophotometer on potassium bromide disks in the range 4000 to 400 cm^{-1}. A Carl Zeiss model Ultra 55 FESEM was used to observe directly the morphology of the nanostructures of LDH samples (20 kV). Visible light photocatalytic activities of Al decorated Mn_3O_4 were evaluated through the decolorization of MG solution with an initial dye concentration of 1×10^{-3} M. The photoreactor system employed with a halogen lamp (50 W) providing a light intensity of 185 mW cm^{-2}, was used in this study. In a typical run, 0.30 g of photocatalyst was dispersed in 50 mL of double distilled water using ultrasonic probe for 30 min. The concentration of malachite green substrates was then determined by measuring the absorbance at λmax 618 nm via UV–Vis spectrophotometer (Shimadzu UV-1800).

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3 Results and Discussion

The structural phases and impurity was identified from X-ray diffractogram.The Al decorated manganese oxide can be observed in Fig.1, which represents high crystallinity of the Al decorated manganese oxide, with corresponding formula to $MnAl_2O_4$ (Joint Committee on Powder Diffraction Standard file no: 029-0880).[5] The diffraction value of 30.8, 44.1, 54.7, 58.3 was due to Mn_3O_4 and the peaks at 36.2, 48.3, 64.1 was corresponds to the pure Al. The Al decorated Mn_3O_4 heated at both 100 ºC and 500 ºC were highly crystalline and both of them same phase structure (cubic).

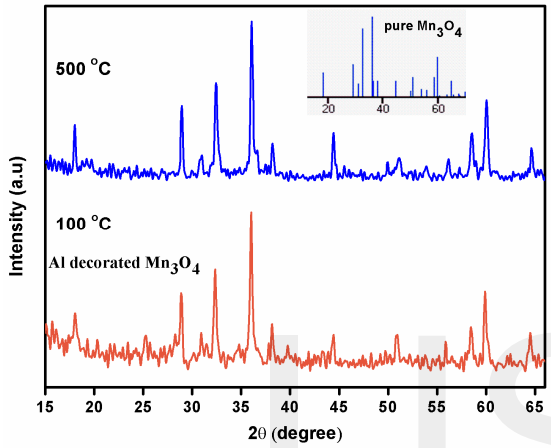

Fig. 1. XRD pattern of Al-Mn3O4 at 100 ºC and 500 ºC

The FTIR spectra of Al decorated Mn_3O_4 As shown in Fig. 2, the samples exhibited similar absorption bands in the recorded spectra. According to the specific frequencies of the absorption peaks, the functional groups existing in the samples can be deduced. Peaks at 3439, 1379, 1120, 619 $cm^{-1}$are present in sample, and are assigned to the H-O-H stretching vibration of adsorbed water, NO^{3-} symmetry stretching vibration (υ1), S=O symmetry stretching vibration (υ1). Peak appears at 739 cm^{-1} was corresponds to AlO-(OH) and peak shows at 535 cm^{-1} was due to Mn-O-Mn.

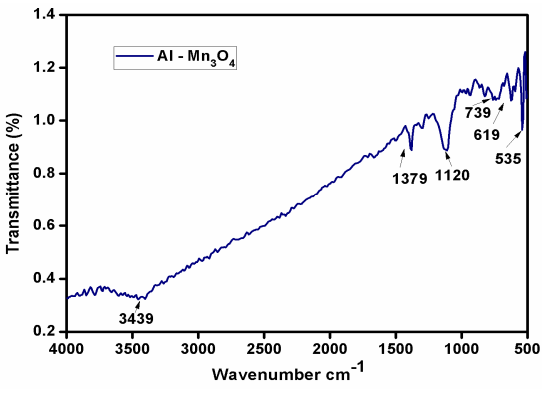

Fig. 2. FTIR spectra of Al decorated Manganese

The FE-SEM image of Al decorated Mn_3O_4 was as shown in Fig. 3a&b. From Fig. 3a clearly form the layered structure and then Al decorated on manganese oxides. The high magnified image shown in Fig 3b.The particle size was ~ 45-110 nm. The manganese oxide surface was attracted by Al due to the van der Waals forces.

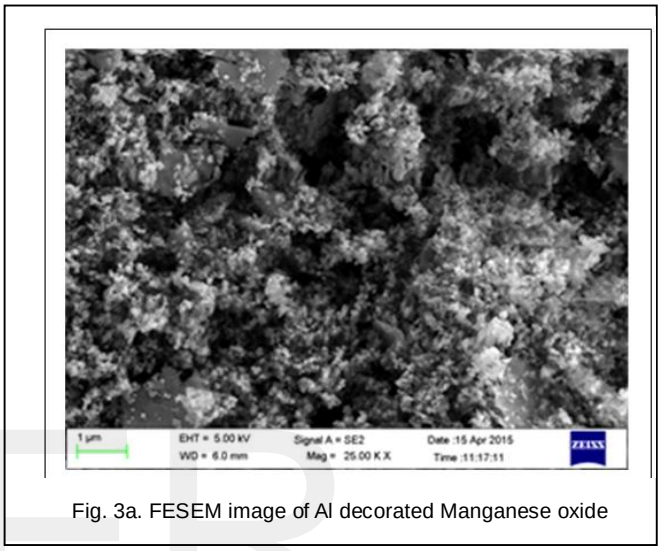

Fig. 3a. FESEM image of Al decorated Manganese oxide

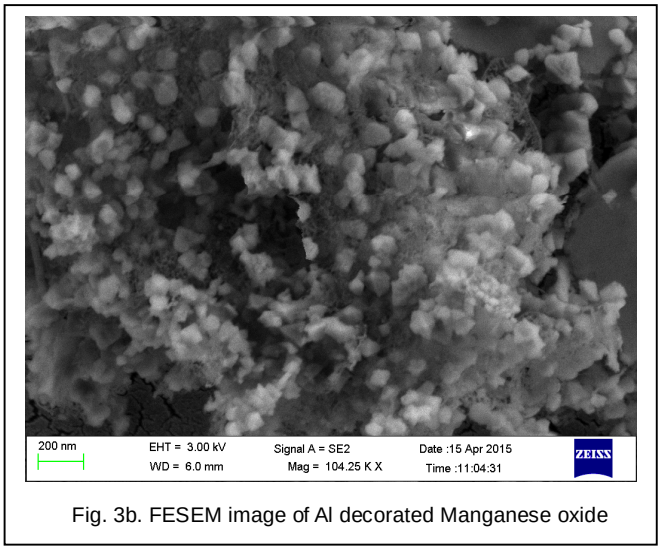

Fig. 3b. FESEM image of Al decorated Manganese oxide

When Malachite Green solutions containing Al decorated Mn_3O_4 nanoparticles were exposed under UV light, decoloration was observed in systems MG/ Al- Mn_3O_4.

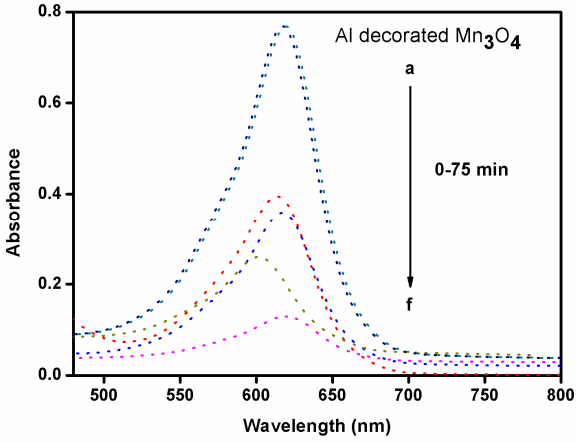

Fig. 4. Photodecolorization of Al decorated Manganese oxide for 0-75 min

The photodegradation could be achieved by OH radicals able to migrate from the Al-Mn_3O_4 surface towards some distance at the bulk solution. This demonstrates that MG oxidation on Al-Mn3O4 is a process, where the interactions between dye and the photocatalyst surface play an important role, the absorption range of MG at 618 nm in visible light region. From the Fig. 4. This implies the photocatalytic degradation of MG and degradation efficiency. The intensity of dark solution was observed at 0.78. The difference between the intensity was near by 0.64. The rapid decrease of the absorption maximum indicates the complete removal of the conjugate structure of the dye. This result indicates the Al decorated manganese oxide was good catalyst against malachite green.

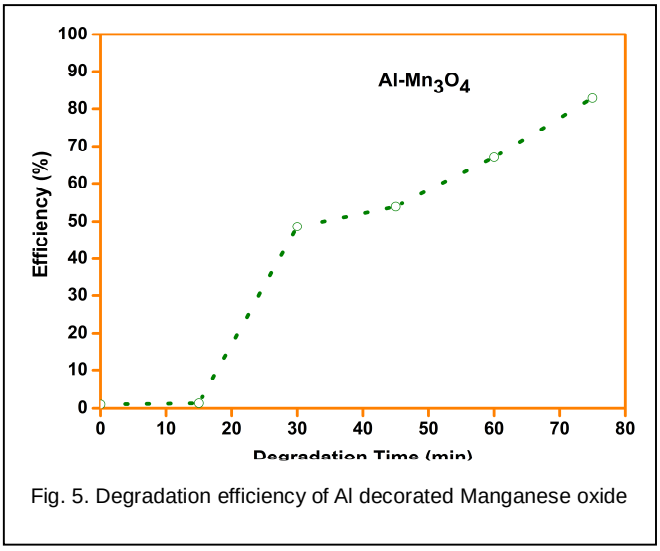

Fig. 5. Degradation efficiency of Al decorated Manganese oxide

4 Conclusion

The results found in this study might suggest that under air saturated atmospheres the photocatalytic degradation of systems MG/ Al-Mn_3O_4 was carried out by visible light process. The photocatalytic degradation efficiency performs to 82%. However, further studies must be done in order to confirm the Al decorated Manganese oxide by using XRD and FT-IR analysis. The morphology which clearly shows the Al decorated on Mn_3O_4.

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