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Preparation and Optical Studies of Layered Double Hydroxides for Photo Catalytic Degradation of Organic Dyes

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ABSTRACT. Over the past decades metal-oxide played in important role in electrocatalyst and photocatalyst. The Mn-Ru layered double hydroxides are prepared by facile one step hydrothermal method. The prepared sample was characterized by variety of techniques. Such as X-Ray Diffract meter was used to determine the phase purity and Crystal structure of the prepared sample. FT-IR is reveals the present of functional groups and DRS UV spectroscopy used to conclude the band gap energy of the prepared materials. The surface morphology was analyzed by using FESEM microscope. The prepared Mn-Ru are layered double hydroxides was further used to photo catalytic degradation of organic dyes.

Introduction. In recent years, most of research efforts have been put into the design and study of different layered double hydroxides (LDHs) for photocatalysis. LDHs, generally also called anionic clays, are known as host-guest layered materials. Though, these contrasts to cationic clays, LDH materials are quite rare in nature [1]. Most of the LDHs are synthetic materials and their structure shows the naturally arising mineral hydrotalcite. LDHs have emerged as a ground breaking photocatalyst group in the fields of energy and environment because of their multy exceptional properties. The fabrication of visible active layered double hydroxide photocatalysts is currently a subject of particular importance because of their significance in both fundamental research and practical applications. Different groups have reported neat LDHs and modified LDHs for the photocatalytic decoloration of organic pollutants and decomposition of water into hydrogen and oxygen, designing a novel visible active LDH photocatalyst for industrial uses is still a great challenge [2]. Manganese oxides (MnOₓ) are eminent resourceful, robust and earth abundant photocatalyst [3]. Moreover, manganese oxides are ubiquitous in nature and environmental responsive that deserve their applications in catalysis, renewable energy and environmental remediation. Although manganese oxides available in various oxidation states of manganese (II, III, IV), Mn₃O₄ (hausmannite) has been found to be an effective and inexpensive catalyst in versatile reactions and we hypothesized that fine MnOₓ nanostructures can scavenge the photo-generated holes utilizing them to oxidize water. Ruthenium is one of the versatile noble metals. It has low bulk resistivity and good physical and chemical stability. These properties make ruthenium appropriate for various applications in photocatalyst and semiconductor device technologies. Ru and RuO₂ consist of 3D structures at the nanoscale and they need a deposition technique that can deliver conformal films on a high aspect ratio framework [4]. Here, Mn-Ru layered double hydroxides synthesized by simple one pot hydrothermal method. The synthesized materials were acts as a very good photocatalyst against Methylene Blue.
The high amount of degradation performs based their wide surface area and electron and hole separation with less activity of recombination.

**Experimental.**

**Materials.** MnCl$_2$.4H$_2$O and RuCl$_3$.4H$_2$O were purchased from Aldrich company. Urea and NaOH were purchased from LOBA chemicals. Ethanol and Acetone solvents were purchased from SRL without purification.

**Synthesis of Mn-Ru layered double hydroxides.** Manganese chloride and Ruthenium chloride was thoroughly dissolved in 100 ml beaker with constant stirring (ratio 1:1). The hydrolyzing agent of 0.1M prepared urea solution was added drop by drop into the metal solution and maintained the base medium using 0.05M NaOH. The mixture of the solution was stirred for 30 min then poured into 100 ml of Teflon steel autoclave. The solution was aged upto 150 °C for 12 h. The product was centrifuged using 4000 rpm, the decanted product was dried an oven at 60 °C.

**Photocatalytic activity.** The photocatalytic activity of the LDH was monitored by the degradation of methylene blue (MB) under irradiation with visible light using a 500 W xenon lamp at room temperature. Typically, a mixture of 50 ml of MB (3.0 mg L$^{-1}$) solution and 175 mg of catalyst was mixed and vigorously stirred for 30 min in the dark in order to establish an adsorption–desorption equilibrium. The reaction solution was then stirred under visible-light irradiation for several hours. At given time intervals, ml aliquots were sampled and filtered to remove the catalysts. The filtrate was analyses by measuring the absorbance at 664 nm using a UV-Vis spectrophotometer. A blank reaction was also carried out using the same procedure, but without adding any LDH catalyst.

**Results and discussion**

**X-ray diffract meter.** Fig. 1a shows the XRD pattern of the prepared Mn-Ru LDH sample. The diffraction peaks indicates the layered material of Manganese and ruthenium was formed as layered material. The cubic structure shows, 2θ at 32.0 (111), 37.2 (200), 53.6 (220) corresponding to RuO$_2$ [JCPDS file no # 50-1428]. The cubic structure of the Mn$_3$O$_4$ peaks appeared 2θ at 18.03 (101), 2809 (112), 31.0 (200), 36.11 (211), 44.4 (220), 49.9 (204), 50.80 (105), 53.9 (312), 56.30 (303), 580. (321), 59.9 (224), 64.6 (400) [JCPDS file no # 80-0382]. The well crystalline peaks due to the manganese oxide homogeneously bind with ruthenium oxides particles. This samples exhibits and highly active catalyst against methylene blue photocatalytic degradation under visible light [5].

**Fourier Transmission Infrared spectroscopy.** The functional groups of the prepared samples revealed from FTIR. Fig. 1b the broad peak and sharp peaks due to –OH stretching and bending vibration of the water molecules at 3404 cm$^{-1}$ and 1620 cm$^{-1}$ respectively. The small peak appears at 1434 cm$^{-1}$ indicates the –NH vibration of the present urea. The two sharp intense peaks corresponding to Ru-OH$_2$ and Ru-O appears at 1328 cm$^{-1}$ and 1256 cm$^{-1}$ respectively [6]. The Mn-O and Mn-O-Mn stretching vibration peak shows at 600 cm$^{-1}$ to 1000 cm$^{-1}$.

**Field Emission Scanning Electron Microscope.** The prepared Mn-Ru LDH particle size and surface morphology analyzed using FESEM. Fig. 1c clearly tells the rod manganese oxides (Mn$_3$O$_4$) were surrounds on the sphere shape ruthenium oxide. The ruthenium oxides were formed regular sphere shape but manganese oxides formed irregular rod shape. Mn-Ru LDH nuclei well growth in base medium using urea and NaOH. The high surface area and many valence state of manganese oxides, induced to act as a superior catalyst. From FESEM image the particle size is ~ 100-140 nm.
**UV-vis spectroscopy.** Fig. 2a, indicates the Mn-Ru LDH of the sample analyzed using UV-vis spectroscopy. Finally, in the Mn and Ru hybrid hydroxides, the electronic transitions of the complexes overlay the transitions arising from the inorganic structures. In the UV region, the charge transfer O→M (M = Mn or Ru) of the inorganic layers is superimposed upon the ligand transitions. The absorption band at about 272 nm and 367 nm is according to the direct charge transfer transitions from O<sup>2-</sup> 2p to Mn<sup>2+</sup> 3d. The energy band structures of RuO<sub>2</sub>-Mn<sub>3</sub>O<sub>4</sub> are generally defined by considering the O 2p orbital as the valence band and the Mn 3d orbital as the conduction band absorption of RuO<sub>2</sub>-Mn<sub>3</sub>O<sub>4</sub> in the UV-visible region can be ascribed to the photo-excited electron transition from the O-2p level into the Mn-3d level.

**Photocatalytic Degradation.** The high surface area enables sufficient interaction between the as-prepared sphere RuO<sub>2</sub>-Mn<sub>3</sub>O<sub>4</sub> nanorods and MB dye molecules, thus making the LDH favorable for the rapid degradation of MB dye molecules, which is illustrated in the following sections. MB dye solution is discolored by the as-prepared RuO<sub>2</sub>-Mn<sub>3</sub>O<sub>4</sub> LDH rapidly, while the color of the MB dye solution shows apparent changes. The results indicate that the layered LDH have much higher oxidation/adsorption ability than general metal oxide nanoparticles. The changes in the UV-Vis spectra demonstrate the discoloration of MB dye solution quantitatively. Fig. 2b shows the successive degradation of MB dye using LDH within 90 min. Fig. 2c&d indicates the efficiency of MB degradation and Percentage of degradation using active prepared LDH layered materials. The possible mechanism of MB dye degradation, the active LDH separates the electron-holes through absorbs the light energy [7]. After electron-holes separation the OH radicals formed, this radical occupy the MB dye sites. Finally, the organic pollutant of MB dye degrades using active prepared LDH layered materials. The degradation percentage reached upto 92%.

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**Fig. 1.** (a) XRD pattern of Mn-Ru layered double hydroxides. (b) FTIR spectrum of LDH (c) FESEM image of layered materials (d) EDX spectrum of the LDH sample.
Summary. The Mn-Ru layered double hydroxides prepared via one-pot hydrothermal method. The LDH materials were characterized using many techniques. XRD, FTIR, UV-vis spectroscopy and FESEM carried out for LDH material. The Ru-MnOx LDH have effectively degrades the organic pollutants of MB dye. The degradation performance reached upto 92%.

References


Cite the paper