Original Article

Characterization, surface morphology and microstructure of water soluble colloidal MnO_2 nanoflakes

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Abstract
In the present work, characterization of water soluble colloidal MnO_2 nanoflakes which act as an oxidizing agent was carried out using UV–visible spectroscopy. Transmission electron microscopy microstructure of colloidal MnO_2 nanoflakes confirms the shape and nature of these particles. Selected area electron diffraction ring indicated that colloidal nanoflakes were amorphous in nature. Surface morphology of synthesized colloidal MnO_2 nanostructure was determined by field emission scanning electron microscopy indicating a crumpled net like arrangement.

Keywords Colloidal MnO_2 · Oxidizing agent · Nanoflakes · UV–visible spectrometer · TEM · FESEM · SEAD

1 Introduction

Transition nonmetal oxides have attracted the attention of chemists and environmentalists due to their broad application in various areas such as antimicrobial activity [1], water treatment [2], food packaging [3], medical devices [4], textile industries [5, 6] and antibacterial activities [7–9]. Manganese dioxide nanostructure materials exhibit novel physical and chemical properties and are widely used in biomedical field as bactericide [10–13] and applied as a coat onto an ultrafiltration membrane to destroy toxins present in drinking water [14, 15]. The performance of nanostructure materials is greatly affected by their morphologies and crystallographic forms. A variety of methods like sol–gel, hydrothermal, electro deposition, combustion, and micro emulsion are applied to synthesize different morphology nanowires, nanoplates, and nanoparticles [16–20].

Water soluble nanoparticles of MnO_2 are good substitute over the insoluble forms due to increased catalytic and oxidizing activities. The adsorption properties of MnO_2 makes it an appropriate choice as a catalyst for redox reactions. Oxidation of formic and oxalic acid in aqueous medium [21, 22], and in micellar medium [23] are noteworthy. Our group is currently engaged in oxidation reactions using water soluble nanoparticles of colloidal MnO_2 in both micellar and aqueous media [24–29] not only because of its broad usage in catalysis, ion-exchange, molecular adsorption, biosensor but also due to its low economical price and eco-friendliness. Solution based base synthesis and use of metal oxide nanostructures is popular due to economically cheap, mild, and viable conditions. It occurs under environmentally safe settings without additional templates and sophisticated apparatus. Synthesis of nanomaterial in the form of colloidal solution provides the possibility of separate nucleation avoiding inter-particle aggregation and controlled growth.

In this paper, we report the characterization, surface morphology and microstructure of water soluble MnO_2 nanoflakes which has not been reported so far in literature.

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2 Experimental

2.1 Materials

$KMnO_4$ (E. Merck, India, 98.5%) and $Na_2S_2O_3$ (s. d. fine, India, 99%) were commercial products and were used as supplied. Deionized water was used as the solvent after double distillation.

2.2 Preparation of water-soluble manganese dioxide nano flakes

Manganese dioxide nano flakes were prepared in aqueous medium using potassium permanganate and sodium thiosulfate as precursors. Standardized $KMnO_4$ (0.1 M) and sodium thiosulfate (0.1 M) were used as stock solutions. To a one-liter volumetric flask filled with 3/4 portions of deionized water, 8 mL $KMnO_4$ stock solution was added. 3 mL stock sodium thiosulfate solution was added to the volumetric flask containing homogeneous $KMnO_4$ solution followed by gentle shaking then its concentration becomes 8×10^{-4} mol dm^{-3} (stock solution of Colloidal MnO_2). The volumetric flask was made up to the mark with deionized water. The resulting solution is a dark brown colloidal system.

$$8KMnO_4 + 3Na_2S_2O_3 + 2H^+ \longrightarrow 8MnO_2 + 6SO_4^{2-} + H_2O$$

3 Results and discussion

3.1 *Characterization of water soluble MnO_2 nanoflakes*

The MnO_2 nanoflakes in colloidal form were characterized by UV–visible spectroscopy scanning from wavelength 200 to 600 nm [2, 4, 10]. Surface morphology of synthesized MnO_2 was determined by field emission scanning electron microscopy (FESEM) (Zeiss SUPRA 40 field emission electron microscope). A small amount of colloidal solution drops casted on a clean aluminum foil and dried at 50 °C to remove the solvent (water). Thin film of MnO_2 formed on aluminum foil coated with gold and used for FESEM analysis. Microstructures of nanoflakes were determined by transmission electron microscopy (TEM) analysis (Tecnai FEI G^2 transmission electron microscope operated at 200 kV). Select area electron diffraction (SAED) was taken on the nanoflakes during the TEM analysis. Samples for TEM measurement was prepared by placing a drop of MnO_2 sol on a holey carbon-coated standard copper grid (300 mesh).

3.2 Surface morphology and microstructure

Field emission scanning electron microscopy image of colloidal MnO_2 was taken in a Ziss Supra 40 FESEM operated under 5 kV accelerating voltage. The colloidal solution of MnO_2 was drop casted on a carbon tape and dried at 60 °C for 6 h. Further, the sample deposited carbon tape was mounted on the sample holder of FESEM and coated with a thin film of gold. TEM image was captured in a FEI Techni G2 TEM operated at 200 kV accelerating voltage. The colloidal solution was drop casted on a carbon coated Cu TEM grid and allowed to stand at room temperature for overnight. Finally, the grid was used for TEM study.

Surface morphology of synthesized colloidal MnO_2 nanostructure was determined by FESEM analysis as shown in Fig. 1. Low magnification micrograph showed aggregated nano structures with a net like morphology.

Magnified image clearly revealed that netlike aggregates were composed with very thin flakes of MnO_2. Thickness of each flake was found to be about 2–4 nm. TEM was used to analyze the morphology and particle size of colloidal nanoflakes as shown in Fig. 2.

The image shows that nanoflakes are found in aggregates and are stacked one over the other, crumpled and assembled to form net like arrangement. Selected area electron diffraction (SAED image 2 (Fig. 2) reveals a diffused ring pattern. This diffused SEAD ring indicated that colloidal nanoflakes were amorphous in nature.

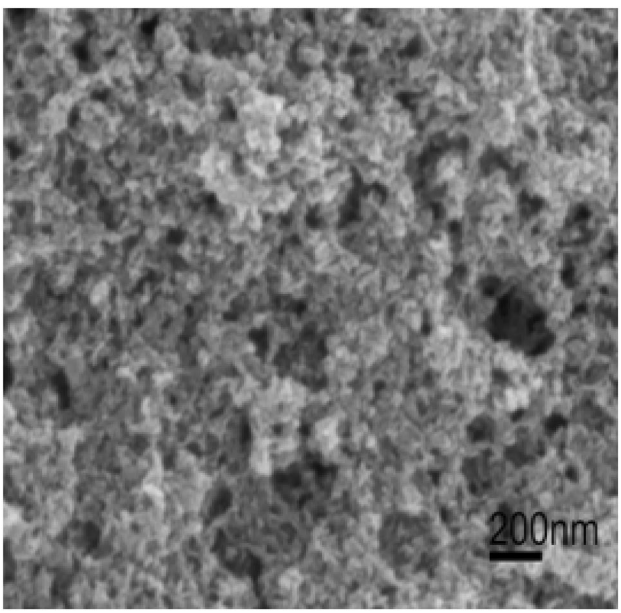

Fig. 1 FESEM micrograph of colloidal MnO_2

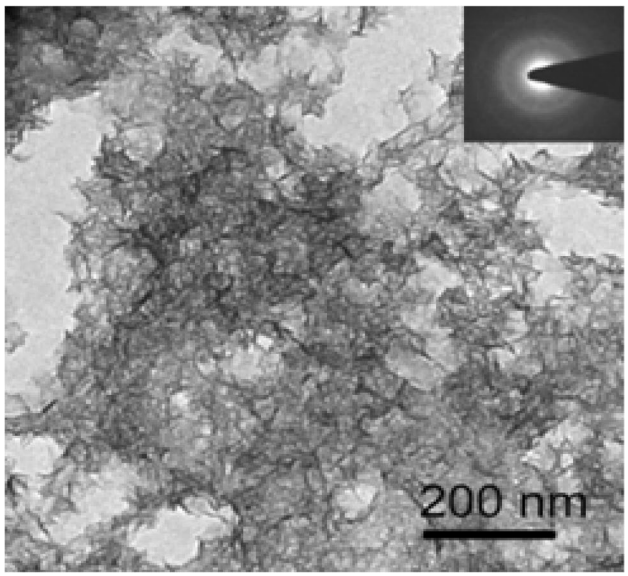

Fig. 2 SAED micrograph of colloidal MnO_2

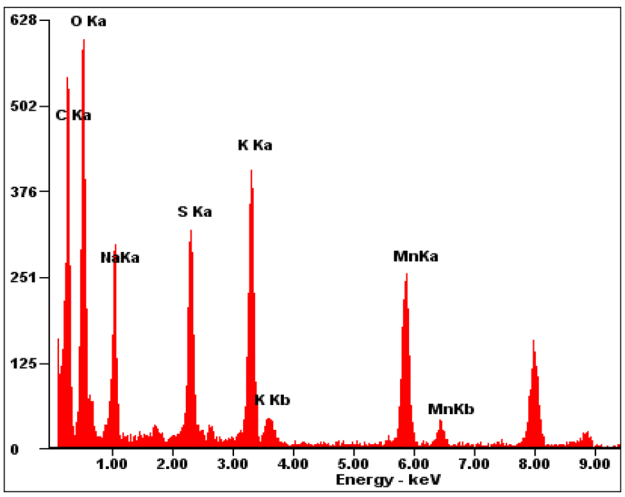

Fig. 3 EDX spectrum of colloidal MnO_2

Elemental analysis was done with the help of energy dispersive X-ray (EDX).

Figure 3 shows the constituent element of colloidal nanostructures. Presence of manganese and oxygen confirms the formation of manganese dioxide which was further supported by UV–VIS spectra of colloidal MnO_2 [24–30]. The UV–visible spectra of water soluble colloidal MnO_2 nanoflakes showed λ_{max} at 390 nm. For this wavelength (λ_{max}) Kabir Ud-Din et al. [24–28] and Kabir Ud-Din and Iqubal [29, 30] had worked and suitable for kinetic observations.

4 Conclusion

In summary, the author has successfully reported the surface morphology and microstructure of water soluble colloidal MnO_2 nanoflakes. TEM microstructure of colloidal MnO_2 nanoflakes confirm that the particles are spherical and amorphous in nature. It is conducted with economically cheap and readily available reagents. The reaction occurs under mild and under environmentally safe conditions. Thus, it is believed that the present work is a major breakthrough in the area of nanomaterials.

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Data availability statement Data will be made available upon request.

Declarations

Conflict of interest No conflict of interest.

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