Short communication

MnO$_2$ nanostructures of different morphologies from amino acids–MnO$_4^-$ reactions in aqueous solutions

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ABSTRACT

In this paper, we describe a simple method for the synthesis of MnO$_2$ nanostructures (quantum dots) by permanganate oxidations of methionine and cysteine. Upon addition of permanganate to a solution of reductant (methionine and/or cysteine), yellow-brown color species appears within the time of mixing which was stable for several weeks. The UV–vis spectroscopy and transmission electron microscopy (TEM) techniques were used to characterize the nature of color formed. TEM images show that the MnO$_2$ sol consists of aggregated spherical nonoparticles (size in the range $ca \leq 7$ nm) of various forms. In addition, we observed the different morphologies of the MnO$_2$ nanostructures (MnO$_2$ nanoparticles, nanosheet, and fiber-like aggregated nanostructures) under different experimental conditions. The effect of various parameters, such as [H$^+$], [MnO$_4^-$], and [reductants] was also investigated.

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1. Introduction

Synthesis of anisotropic inorganic nanomaterials (nanosheets, nanowires, nanotubes and nanorods) has been the subject of various researchers because of their potentials applications in information technology, electronics and transport [1–6]. Manganese dioxide (MnO$_2$; brown substance insoluble in water) is one of the most attractive inorganic materials not only because of its wide range of applications in molecular sieves, catalysis, ion-exchange, biosensor and particularly energy storage but also because of its low cost and environmentally benign nature [7–10]. Due to general recognition that their performance is highly dependent on their morphologies as well as crystallographic forms, a variety of synthetic strategies (radiation-, chemical-, photo-, and electro-chemical) have been described for the preparation of water-soluble and water-insoluble colloidal and/or nanoparticles of manganese dioxide [11–15].

Manganese(VII) is an effective oxidant in bringing about the oxidation of inorganic and organic reductants in acidic, neutral, and alkaline media. Its reduction product is almost invariably Mn(II), where as Mn(VI), Mn(V), Mn(IV), and Mn(III) are formed as an intermediate(s) [16,17]. The stability and color of these species depends on the pH of the working solutions as well as on the nature of the reducing agents [18,19]. In weakly acidic solution Mn(VII) changes to Mn(IV). It has been reported on several occasions that the intermediate (Mn(IV)) could be H$_2$MnO$_4^{2-}$, H$_2$MnO$_3$, colloidal MnO$_2$ or a phosphate complex [20,21]. Different morphologies of MnO$_2$ nanostructures (nanotubes, nanowires, hollow nanoshells, nanorods and nanosheets) have been synthesized by a large number of researchers [13,15,22–24]. Generally, polymers, surfactants, ligands and solid matrices have been used as stabilizers for the synthesis inorganic nanomaterials in aqueous media. Solution-based synthesis and use of metal oxide nanoparticles, however, require special mention due to their low cost, convenience and use without additional templates and apparatus. As such, the small metal particles in solution has been found advantageous over the water-insoluble forms because UV–vis spectrophotometric methods can be used to monitor the optical changes that accompany the surface reactions (solutions of nanometer large particles are transparent and the scattering of light can be neglected [25,26].

Our goal of research was to find out the suitable S-, N-, and O-containing biomolecules (reducing agents) for the preparation and reduction of water-soluble colloidal MnO$_2$ [27,28]. As far as we know, no TEM measurements has been carried out to determine the size and shape of MnO$_2$ formation in the reduction of permanganate by sulphur containing amino acids in absence of any stabilizers. In the present paper, the reduction of Mn(VII) is carried out under conditions where all permanganate is reduced in presence of methionine and cysteine. Under these conditions, only MnO$_2$ particles (yellow-brownish color) are formed; the aggregation of these particles is studied. To the best of our knowledge,

different nanostructures of MnO_2 (quantum dots, nanosheets and other aggregated structures) were prepared by a facile route for the first time in absence of any stabilizers.

2. Experimental

2.1. Materials

Amino acids (glycine, alanine, methionine and cysteine), oxidant (potassium permanganate), sulphuric acid and ethanol (all 99% Merck, India products) were used as received. The solvent used was water, previously doubly distilled, deionized and CO_2 free for the preparation of all reagents solutions. Permanganate solutions were stored in a dark glass bottle and standardized by titration against oxalate.

2.2. Preparation of MnO_2 nanoparticles

The preparation of perfectly transparent sol of MnO_2 was carried out as follows: $5.0\,cm^3$ of permanganate solution ($0.01\,mol\,dm^{-3}$) was added to a solution of methionine ($15\,cm^3$, $0.01\,mol\,dm^{-3}$) and $30\,cm^3$ of water (total volume $50\,cm^3$). This mixture was shaken well for a couple of minutes. The color of the solution changed rapidly from purple to yellow-brown, indicating the formation of MnO_2 sol. The as-prepared MnO_2 sol was used directly for the TEM measurements. On the other hand, permanganate solution immediately leads to the formation of a brownish precipitate of MnO_2 in presence of cysteine ($3.0\,cm^3$ of $0.01\,mol\,dm^{-3}$) at room temperature. The resulting precipitate was collected and washed with distilled water for several times to remove the impurities. The sol and the solid were very stable over extended periods of several months. We did not observe the appearance of yellow-brown color and/or any significant changes in the UV–vis spectrum of permanganate ($1.0 \times 10^{-4}\,mol\,dm^{-3}$) in presence of glycine and alanine ($1.0 \times 10^{-3}\,mol\,dm^{-3}$), which rules out the any role of $-COO^-$ and $-NH_3^+$ in the reduction of Mn(VII) into MnO_2 under the present experimental conditions. These observations suggest that the presence of sulphur atom in methionine and cysteine is responsible for the fast formation of yellow-brown color MnO_2.

2.3. TEM measurements

Transmission electron microscope (JEOL, JEM-1011; Japan) was used to determine the shape and size of MnO_2 particle. Samples were prepared by placing a drop of MnO_2 sol on a carbon-coated standard copper grid (300 mesh) operating at 80 kV. For the solid MnO_2, sample was first dissolved in ethanol and then deposited on the working grid.

3. Results and discussion

3.1. UV–vis spectral studies

The spectrum of the reaction product of methionine and permanganate has been recorded after ensuring complete reduction of the Mn(VII). The absorbance spectrum of the sol containing $[MnO_4^-] = 1.0 \times 10^{-4}\,mol\,dm^{-3}$ and $[methionine] = 1.0 \times 10^{-3}\,mol\,dm^{-3}$ are given in Fig. 1. Absorbance spectrum of MnO_4^- is also given for comparison (Fig. 1(●)). The absence of peak at 525 nm characteristic of reduced Mn(VII) (Fig. 1(○)), indicates the complete reduction of Mn(VII) to Mn(IV) (this Mn species commonly involved in the permanganate oxidation of organic reductants). The Mn(IV) sol covers the whole visible region of the spectrum and is deep yellow-brown in color (Fig. 1(○)). These are similar to the results reported for colloidal MnO_2 by Perez-Benito el
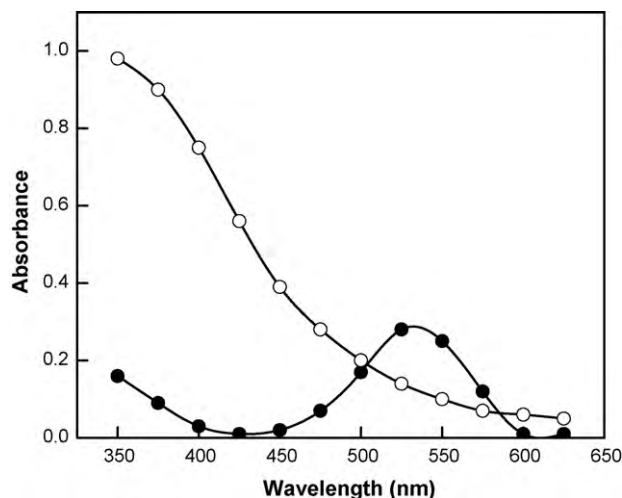

Fig. 1. Absorption spectra of aqueous solution of MnO_4^- only and MnO_2 sol formed after the complete reduction of permanganate ($1.0 \times 10^{-4}\,mol\,dm^{-3}$) by methionine ($3.0 \times 10^{-3}\,mol\,dm^{-3}$) at 25 °C.

al. [29] and Tuncay et al. [30]. The shape of the spectra gives information about the size, shape, the size distribution and the surface properties of the metal particles. The nature of the MnO_2 sol spectra was unsymmetrical indicating the presence of aggregated particles (polydispersity).

Nature of reducing agents and pH of the working solutions are the important parameters for the formation of stable and transparent water-soluble colloidal MnO_2 (yellow color) particles and the colloidal MnO_2 can exist in aqueous-neutral media. A series of experiments were performed in presence of different $[HClO_4]$ (1.0×10^{-6} to $1.0 \times 10^{-2}\,mol\,dm^{-3}$) at constant $[methionine] = 1.0 \times 10^{-3}\,mol\,dm^{-3}$ and $[MnO_4^-] = 1.0 \times 10^{-4}\,mol\,dm^{-3}$. Interestingly, at higher $[HClO_4]$ ($\geq 1.0 \times 10^{-3}\,mol\,dm^{-3}$), the formation of yellow color was not observed. On the other hand, yellow color was stable at higher $[methionine]$ ($\geq 3.0 \times 10^{-3}\,mol\,dm^{-3}$) where as formation of this color was not observed in excess of $[cysteine]$ ($\geq 4.0 \times 10^{-4}\,mol\,dm^{-3}$) in absence of $HClO_4$. Therefore, in presence of $HClO_4$ and/or excess of $[cysteine]$, the intermediate Mn(IV) is unstable and undergoes acid hydrolysis. Due to the stability of Mn(VI) in alkaline solution, therefore, it should be emphasized here that reaction were studied with out adding $HClO_4$ and NaOH. Thus, we may safely conclude that the reactivity of methionine towards permanganate is much lower than the cysteine because the reactive site (sulphur) is partially blocked by a methyl group in methionine.

Some experiments were also performed in order to see any change in the pH of the working in presence of methionine and/or cysteine. The pH values was found to be nearly constant with increasing the concentrations of both amino acids (pH = 5.12 ± 0.4 at [amino acids] values of 0.5, 1.0, 1.5, 2.0, and $2.5 \times 10^{-4}\,mol\,dm^{-3}$). These result suggests that methionine and cysteine (weak acids; $pK_1 = 2.28$; $pK_2 = 9.21$ and $pK_1 = 1.71$; $pK_2 = 8.33$; $pK_3 = 10.78$ for methionine and cysteine, respectively) acts as a reducing as well as buffering agents which control the pH of the working solutions.

3.2. TEM studies

In order to determine the size and shape of MnO_2 particles, a series of TEM measurements were preformed. The observed results are given in Figs. 2–5 for MnO_2 (sol and solid) prepared during the reduction of permanganate by methionine and cysteine, respectively. The TEM images indicates the MnO_2 particles are nearly spherical and the average particles size ranges between 2 and 7 nm
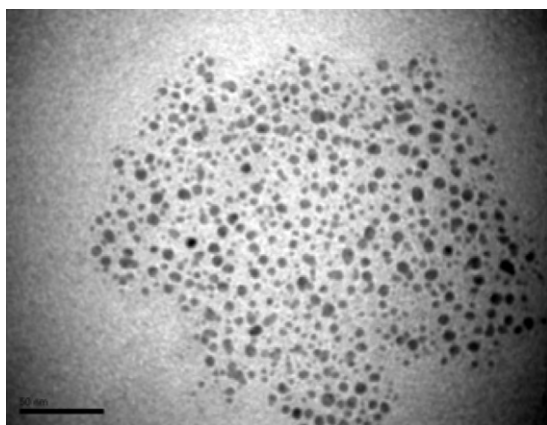
Fig. 2. TEM pictures showing the size, shape, and distribution of MnO$_2$ particles at 25 °C. *Reaction conditions*: [MnO$_4^-$] = 1.0 × 10^{-3} mol dm^{-3}; [methionine] = 3.0 × 10^{-3} mol dm^{-3}.
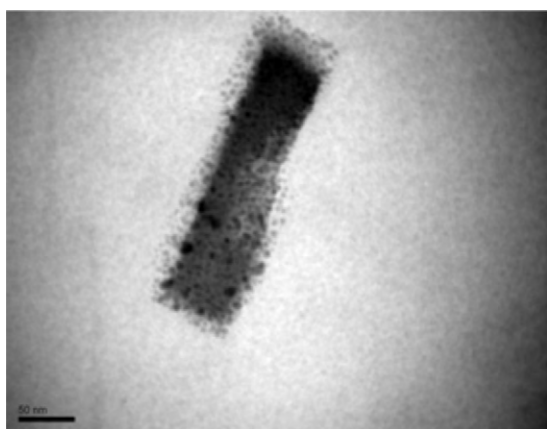

Fig. 3. TEM pictures showing the aggregation of MnO$_2$ nanoparticles in the form of nanosheet. Reaction conditions are the same as in Fig. 2.

with the maximum close to 3.5 nm (Fig. 2). The TEM images in Fig. 3 indicate clearly the regular and irregular aggregations, respectively, of MnO$_2$ nanoparticles and finally MnO$_2$ nanostructures of different morphologies are formed. TEM image also confirmed the self-aggregation of MnO$_2$ particles in an ordered particle matrix leading to the formation of a larger tabular particle (nanosheet) in which nanosize subunits of MnO$_2$ attached at their edges (Fig. 3). In fact, there are several processes such as slow generation of MnO$_2$,
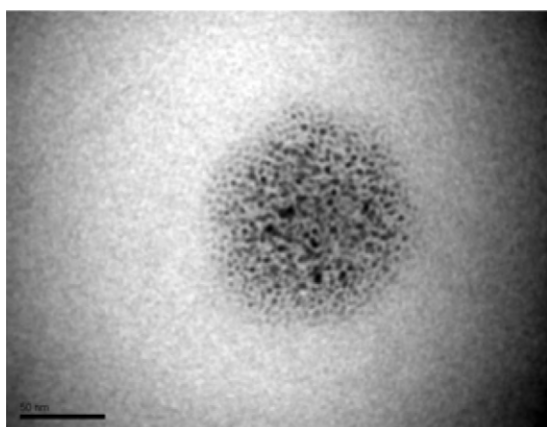

Fig. 4. TEM pictures of MnO$_2$ nanostructures formed after the reduction of permanganate (1.0 × 10^{-3} mol dm^{-3}) by cysteine (6.0 × 10^{-4} mol dm^{-3}).
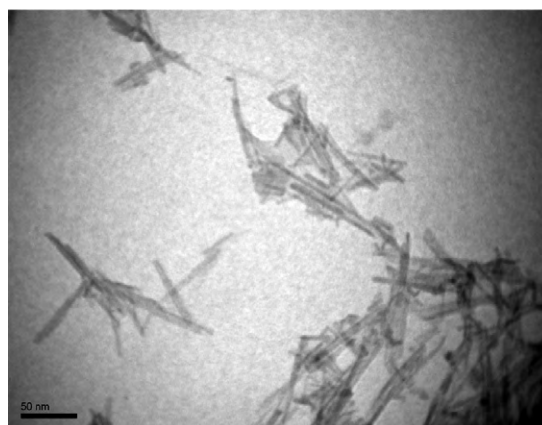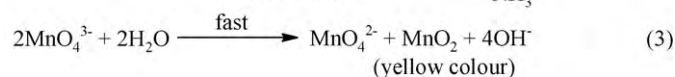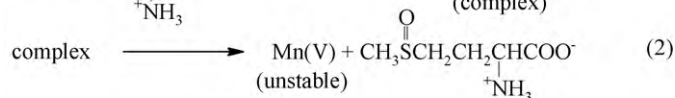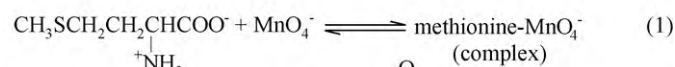

Fig. 5. TEM pictures of MnO$_2$ nanoparticles from a colloidal dispersion in ethanol. Reaction conditions are the same as in Fig. 4.

preferential aggregation and incorporation of nanosize MnO$_2$ into the larger anisotropic particles are responsible for the formation of crystal-like tabular sheet under our experimental conditions (reduction of permanganate by methionine) [31]. On the other hand, TEM picture shows the aggregation and simultaneous precipitation of MnO$_2$ aggregated nanoparticles in presence of cysteine (Fig. 4). Formation of precipitate noticed within the several minutes after cysteine addition, indicating that generation, aggregation, incorporation and precipitation are rapid. Fig. 5 is a typical TEM image of MnO$_2$ nanorods (fiber-like aggregated structure) synthesized by the cysteine reduction of permanganate (*vide supra*). The individual fibers are likely built from nanosize particles of MnO$_2$.
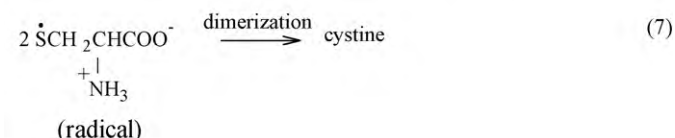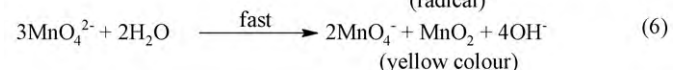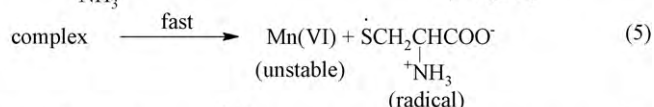
3.3. Mechanism

Before attempting to propose the mechanisms for the reduction of MnO$_4^-$ by sulphur containing amino acids, it is necessary

(i) Mechanism for methionine oxidation

$$CH_3SCH_2CH_2CHCOO^- + MnO_4^- \rightleftharpoons \text{methionine-MnO}_4^- \quad (1)$$
$$\underset{+NH_3}{|} \qquad \qquad \text{(complex)}$$

$$\text{complex} \longrightarrow \underset{\text{(unstable)}}{Mn(V)} + CH_3SCH_2CH_2\overset{O}{\overset{\|}{C}}HCOO^- \quad (2)$$
$$\underset{+NH_3}{|}$$

$$2MnO_4^{3-} + 2H_2O \xrightarrow{\text{fast}} MnO_4^{2-} + MnO_2 + 4OH^- \quad (3)$$
$$\text{(yellow colour)}$$

(ii) Mechanism for cysteine oxidation

$$HSCH_2CHCOO^- + MnO_4^- \rightleftharpoons \text{cysteine-MnO}_4^- \quad (4)$$
$$\underset{+NH_3}{|} \qquad \qquad \text{(complex)}$$

$$\text{complex} \xrightarrow{\text{fast}} Mn(VI) + \overset{\cdot}{S}CH_2CHCOO^- \quad (5)$$
$$\text{(unstable)} \qquad \underset{+NH_3}{|}$$
$$\text{(radical)}$$

$$3MnO_4^{2-} + 2H_2O \xrightarrow{\text{fast}} 2MnO_4^- + MnO_2 + 4OH^- \quad (6)$$
$$\text{(yellow colour)}$$

$$2\,\overset{\cdot}{S}CH_2CHCOO^- \xrightarrow{\text{dimerization}} \text{cystine} \quad (7)$$
$$\underset{NH_3}{\overset{|}{+}}$$
$$\text{(radical)}$$

Scheme 1.

to discuss the oxidation products of methionine and cysteine. It is well known that CO_2, ammonia, and corresponding aldehydes are the oxidation products of amino acids by permanganate. Interestingly, under our experimental conditions, ammonia and CO_2 were not detected as the oxidation products of methionine and cysteine where as N-benzoylmethionine sulphoxide and cystine were identified the oxidation products by the reported method [27]. Eqs. (1)–(7) can be taken into account for the formation of MnO_2 sol (Scheme 1).

 (i) Mechanism for methionine oxidation
(ii) Mechanism for cysteine oxidation

In Scheme 1, Eqs. (2) and (5) represents the formation of Mn(V) and Mn(VI) as an intermediate in a one-step two- and one-electron oxidation–reduction mechanism, respectively. Finally, Mn(V) and Mn(VI) may hydrolyses to Mn(IV) species (Eqs. (3) and (6)).

4. Conclusions

In this paper, we used four amino acids (glycine, alanine, methionine and cysteine) for the preparation of MnO_2 nanoparticles. It is found that the shape, the size distribution, aggregation, and stability of MnO_2 nanoparticles strongly depend on the nature and concentration of the reducing agents. TEM results suggest that the synthesis of MnO_2 nanomaterials (nanosheet and fiber-like nanostructure) could be performed by controlling the pH and the rate of electron transfers. This study provides the evidence that the presence of methyl group in the side chain of methionine, retarding the formation, deposition and/or precipitation of MnO_2 by decreasing the reducing nature of methionine, and stabilizing the nanoparticles.

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