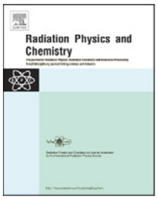
Radiation Physics and Chemistry 85 (2013) 152–160

Contents lists available at SciVerse ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Gamma radiation induced formation and characterization of the nano-oxides of manganese

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HIGHLIGHTS

- Nano - crystalline oxides of Mn were formed by γ-radiolysis of MnO_4^-.
- The oxides formed were characterized using by XRD, Raman, XPS, SEM and AFM.
- Broad XPS and Raman spectra suggested existence of Mn^{3+} and nano-sized particle.
- SEM images confirmed existence of nano-rods of very narrow width distribution.
- Plausible mechanism for formation of Mn in different oxidation states is proposed.

ARTICLE INFO

Article history:
Received 6 June 2012
Accepted 17 December 2012
Available online 25 December 2012

Keywords:
Nano crystalline oxides
γ-Radiolysis
Photoelectron spectroscopy
Laser Raman
SEM

ABSTRACT

Nano-crystalline oxide powders of manganese were formed by the radiolytic reduction of permanganate (MnO_4^-) at ambient temperature and pressure in (i) acid (ii) neutral and (iii) alkali mediums. Gamma radiolysis generated brown/black precipitates of manganese oxides were analyzed by X-ray powder diffraction, Raman spectroscopy, XPS, AFM and SEM. The influence of oxygen on the nature of oxides formed was studied. Permanganic acid ($HMnO_4$), at low concentrations (2.5 mM) and irradiated to 123 kGy, produced λ-MnO_2 with an average crystallite size of 30 nm whereas at high concentrations (8 mM) and absorbed dose of 300 kGy, MnOOH was formed. The XRD pattern of the oxide powder obtained in all other cases showed broad peaks indicating nano-crystalline nature. The results of nitrogen adsorption–desorption experiments showed high specific surface area of ~53 m^2/g corresponding to ~5 nm average pore size for the oxide obtained from 8 mM $HMnO_4$ irradiated to 300 kGy. Atomic force microscopy (AFM) indicated a minimum particle size of ~13 nm for the same oxide whereas the SEM images showed presence of nano-rods.

1. Introduction

The MnO_2/Zn and MnO_2/Li couple are the basis of widely used Leclanche and alkaline primary batteries due to their tunnel and layered structure and relative arrangements of oxygen and manganese atoms within the tunnels of [MnO_6] octahedral unit (Balachandran, 2003; Kim et al., 2006). Nanocrystalline oxides of manganese are expected to show better capacitive property (Lee and Goodenough, 1999). MnO_2 is inexpensive, non-toxic, abundant and exists in a wide variety of allotropic forms, natural or synthetic such as: pyrolusite (β-MnO_2), nsutite (γ-MnO_2), birnessite (δ-MnO_2), ramsdellite, cryptomelane (α-MnO_2), ε-MnO_2 and λ-MnO_2 (Schlörb et al., 1997). Among these, only the λ-form has a structure related to spinel (Hunter, 1981). Apart from ramsdellite and pyrolusite all other forms are formed by a random intergrowth of ramsdellite and pyrolusite (Kohler et al., 1997). Nanosized γ- and λ-MnO_2 powder can also be used as pH electrode due to the ion exchange properties of surface adsorbed OH groups. A linear pH–potential curve, over the pH range of 2–13 with a sensitivity of −78.3 mV/pH was reported for thin film of MnO_2 coated electrode (Teixeira et al., 1999; Qingwen et al., 1999). The MnO_2 micro-fibers with secondary nanostructure may be found to have potential applications in the areas of catalysis, ion-sieve for cations, and molecular adsorption etc. due to their porous nature (Cao and Suib, 1994; Chen et al., 1997; Feng et al., 1999).

The design, synthesis, and characterization of nano-scale materials (characterized by a grain size of <100 nm) have been the subject of recent research due to significant differences in their properties with their micro-grain sized counterparts and a variety of methods like hydrothermal, co-precipitation, sol–gel and inert gas condensation are being used. Each method has

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http://dx.doi.org/10.1016/j.radphyschem.2012.12.018

its advantages and limitations. Radiolytic method is simple, reproducible due to absence of introduction of any impurities during the process and often small particles are formed under ambient conditions. The particle size can be easily manipulated by altering total absorbed dose, dose rate and experimental conditions for obtaining the required distribution of particle size. Irradiation with high energy ionizing radiations like γ-rays or electrons are found to be very effective in synthesizing nanoparticles of noble metals (Belloni et al., 1998; Henglein and Giersig, 1999; Ni et al., 2002; Shimou et al., 2005), non-noble metals (Marignier et al., 1985) and also metal oxides (Dey et al., 2006; Gracien et al., 2006; Hu et al., 2006; Liu et al., 1996; Liu et al., 1997; Lume-Pereira et al., 1985; Yadav et al., 2009).

Lume-Pereira et al. (1985) reported the synthesis of MnO_2 colloids by radiolytic reduction of 1×10^{-4} M $KMnO_4$ (irradiated to a dose of 4 kGy) in air-saturated solution at pH 10. Variation in particle size and their shape can easily be controlled by varying dose, concentration of the solute and the matrix. Radiolytic production of colloids in the size range 3–5 nm was formed for a dose of 0.4 kGy (0.4 mM $KMnO_4$, pH=10, aerated), whereas using stabilizers like sodium dodecyl sulphate (SDS) and polyvinyl alcohol (PVA), a narrow particle size distribution with a minimum particle size of 6 nm was observed for a dose of 2 kGy (Liu et al., 1996, 1997). Mn_2O_3 was reported (Liu et al., 1996) to be formed on gamma radiolysis when the pH of the solution was above 9.5 and it was irradiated to higher doses (45–60 kGy) whereas nano-crystalline MnO_2 was formed in the pH range of 6.5–8.5 (Liu et al., 1997). More recently, formation of nano-rods (~50–100 nm length and 2–3 nm thickness) of MnO_2 in the radiolytical reduction of N_2 saturated $KMnO_4$ containing *tert*-butanol as OH and H scavenger is reported along with nanosheets from the oxidation of $Mn(SO_4)_2$ at pH 10 (Yadav et al., 2009).

Permanganate based reagents such as alkaline permanganate, nitric acid permanganate and permanganic acid ($HMnO_4$) are also used as pre-treatment reagent in the oxidative step during decontamination of chromium containing alloys such as stainless steels, Incoloy-800 and Inconels (Segal and Swan, 1983) and are part of CORD process (Herrald and Horst-Otto, 2000). During the decontamination process, these decontaminants get exposed to continuous radiation field and generate manganese oxide in the form of crud which has a chance of re-deposition at low flow regions and crevices. Thus, clear knowledge about the nature of oxides formed is of importance for their reductive dissolution and effective removal in subsequent steps. Enhancement of the reactivity of oxides upon irradiation was also reported due to incorporation of permanent structural changes like grain size etc. (Roth et al., 2006).

In the present work, manganese oxides were prepared by the radiolysis of permanganate system at different pHs, both in aerated and de-aerated conditions, without any organic stabilizer or radical scavenger. These were comprehensively investigated by XRD, Raman, XPS and SEM to understand their phase chemistry and microstructures.

2. Material and methods

All the chemicals used were of high purity grade and used as such without any further purification. Purified water (resistivity 18.7 MΩ/cm) from Sartorius water system Germany (consisting of a UV lamp and several micro porous ultra filters) was used to prepare all solutions. Permanganic acid ($HMnO_4$) solution was prepared by passing $KMnO_4$ solution through nuclear grade cation resin column (Tulsion from Thermax Private Ltd., India, in H^+ form). De-aerated solutions were prepared by bubbling ultra high purity argon gas through these. High purity NaOH and HNO_3 were used for adjusting pH. The Nicolet Evolution 500- UV–visible spectrophotometer from Thermo Electron Corporation, UK was used for determining permanganate solution concentration (mM) from its absorbance at 536 nm. The pH of the solutions was measured using radiometer analytical ION Check 65 Multi Parameter Instrument, France.

2.1. Gamma irradiation

γ-Irradiations were performed with a Gamma Chamber 5000 supplied by Board of Radiation and Isotope Technology (BRIT), DAE Mumbai, India, having dose rate of about 5.14 kGy h^{-1} (as determined by the Fricke dosimeter). All the samples were irradiated to high dose to ensure complete degradation. A high concentration of MnO_4^- was used to get sufficient quantity of oxide products for analysis. About 200 ml of 30 mM $KMnO_4$ solutions was used for neutral, acidified (with HNO_3 to pH 3), alkaline (250 mM NaOH) conditions and 8 mM $HMnO_4$ were irradiated to a dose of 300 kGy. $HMnO_4$ of lower concentration (2.5 mM) was also irradiated to a lower dose (till complete decomposition) for observing the concentration and dose effects. Direct interaction of the radiation with the solute is negligible and is not taken into account in this study. The brown/black precipitate of manganese oxides formed in all the cases were filtered, washed with de-ionized water and dried at 60 °C in an oven and compared with commercially procured MnO_2 supplied by Himedia, India.

2.2. XRD analysis

X-ray diffraction studies were carried out on all the samples using Cu-K_α line with a Philips spectrometer. The particle size of oxide obtained from the radiolysis of permanganic acid was measured from micrographs and determined from XRD patterns according to the Scherrer formula:

$$L = K\lambda/\beta \cos\theta$$

where L is average particle size, K is the Scherrer constant related with the shape and index ($h\,k\,l$) of crystals (Langford and Wilson, 1978), λ is the wavelength (1.5418 Å) of X-ray, and β is obtained from the Warren and Biscoe equation (Wagner and Aqua, 1964),

$$\beta^2 = B^2 - b^2$$

where B and b are the full width at half maxima (FWHM) for the sample under investigation and a standard sample, respectively. Analytically pure, crystalline Si powder has been used as the standard sample.

2.3. X-ray photoelectron spectroscopic analysis

X-ray photoelectron spectroscopic (XPS) studies were carried out in a UHV chamber with a pressure of 1.7×10^{-10} mbar, using VG ESCA Lab MK 200X, UK, equipment with 150 mm hemispherical analyzer and dual X-ray source. The spectra were collected using Al K_α X-ray (energy 1486.6 eV) as the exciting source for photoelectrons and with 20 eV pass energy of the analyzer. C 1s peak was taken at 285.1 eV for correction of charging effects due to any carbon contaminants.

2.4. Laser Raman spectroscopic analysis

Raman spectra were recorded on the sample using HORIBA Jobin Yvon HR 800 spectrometer, France, with 514.5 nm Ar^+ ion laser from 100 to 1500 cm^{-1}. Laser power was optimized to 0.5 mW on