Sonochemical Synthesis and Characterization of Turbostratic MnNi(OH)$_2$ Layered Double Hydroxide Nanoparticles for Supercapacitor Applications

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In this research, Manganese and Nickel transition metal layered double hydroxide nanoparticles (MnNi(OH)$_2$) with a size of ~100 nm have been successfully prepared by sonochemical irradiation method for the supercapacitor applications. X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) analyses clearly indicate the formation of MnNi(OH)$_2$ nanoparticles. Scanning and Transmission electron microscopic images identify the layered double hydroxide structure formation. MnNi(OH)$_2$ layered double hydroxide nanoparticles were tested as a supercapacitor material which exhibits specific capacitance 160 Fg$^{-1}$ at a current density of 1 mAcms$^{-2}$ at the potential range from 0.0 to 1.0 V in 1 M Na$_2$SO$_4$ solution.

1. Introduction

Layered double hydroxides (LDHs)$^{1-4}$ consist of stacked array of positively charged layers of mixed metal hydroxides with charge balancing exchangeable anions in the interlayer have found many uses in both electrochemical detection (chemical sensors and biosensors) and energy-storage devices (alkaline or lithium batteries and supercapacitors). In general, such LDHs have a generic formula [M$^{2+}_{x}$A$^{n+}_{y}$X(OH)$_{2}$](A$^{n+}$)$_{n/2}$·mH$_2$O, where M$^{2+}$ = Mg, Co, Ni, Cu, Zn, Mn, Ca; A$^{n+}$ = Al, Fe, Cr, Ga, V; A$^{n+}$ is anion such as CO$_3^{2-}$, NO$_3^-$, SO$_4^{2-}$, etc; and x = 0.25 – 0.33 and the most common mineral of this class found in nature is hydrotalcite having the composition M$_2$Al$_2$(OH)$_6$CO$_3$·4H$_2$O which consist of Mg$^{2+}$ as divalent cation and Al$^{3+}$ as trivalent cation.$^{8,9}$ In addition, such LDHs also resemble the structure of mineral brucite, Mg(OH)$_2$, with Mg$^{2+}$ ions octahedrally surrounded by 6 OH$^{-}$ ions and the octahedra share edges to form infinite sheets.$^{9,12}$ Such brucite-like sheets can be stacked either with hexagonal symmetry of two layers or rhombohedral symmetry of three layers per unit cell.

Lots of progresses have been achieved in the synthesis of LDHs with new compositions and morphologies through several approaches, which include co-precipitation, urea method, sol gel method, microwave irradiation method, sonochemical method, and the alkali metal method, allowing improved applications in many areas over the past few years.$^{13-17}$ For example, Yeh, et al.$^{18}$ followed hydroxide co-precipitation method to synthesize a new material Li[(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)$_{0.96}$Al$_{0.02}$B$_{0.02}$]O$_{1.98}$F$_{0.02}$, via a liquid-solution transition approach which avoids the precipitated transition metal hydroxide to be readily oxidized in the aqueous solution. Kamath, et al.$^{19}$ prepared LDH of mixed Ni(II) and Co(II) transition metal hydroxides even though it did not have any trivalent cations in the lattice which would account for the inclusion of anions as well as water molecules in the interlayer space and in addition they proposed partial protonation of the hydroxyls giving rise to a net positive charge on the α-hydroxide layers. In this regard, we here attempt to synthesize and characterize Manganese and Nickel transition metal layered double hydroxide nanoparticles (MnNi(OH)$_2$) through sonochemical approach because such material also does not have any trivalent cations and in addition such materials may store more electrochemical energy by reversible surface faradic (redox) reactions compared to pristine transition Manganese hydroxide nanoparticles.$^{20,21}$ The advantages of manganese and nickel layered double hydroxides are their low cost and relatively environment friendly nature. In addition, the sonochemical method has received much attention in the synthesis of inorganic and organic nanostructured materials because of its non-hazardous property, rapidity in reaction time, and selectivity performance of the reaction. In addition, such approach has led to high activity in catalysis due to their particle size and high surface area than those reported by other methods.$^{17,22}$

Experimental Details

Chemicals
All chemicals were of the highest purity available and were used as received without further purification. Typically, 0.2 M of Manganese(II) nitrate tetrahydrate (5.02 g) was dissolved in 100 ml of distilled water and subsequently 3 g of urea (0.5 M) was added as fuel/reducing agent and stirred for 15 minutes (Solution A). Similarly, 0.2 M of Nickel(II) nitrate hexahydrate (5.81 g) was dissolved in 100 ml of distilled water and subsequently 3 g of urea (0.5 M) was added as fuel/reducing agent and stirred for 15 minutes (Solution B). Solution B was then added to solution A and then 0.1 g PVP as stabilizer was added into the above mixture and stirred for 30 minutes at room temperature under Argon gas atmosphere. After stirring for 30 minutes, the resultant solution was irradiated with high-intensity ultrasonic horn (Ti-Horn, 20 kHz, 100 W/cm²) in Argon atmosphere for 2.5 h. The significance of PVP here is to control particle size and morphology. On completion of sonication, the solution turned straw yellow color (see photo image, inset of Fig 1A). The precipitate was centrifuged and washed with distilled water followed by ethanol for several times and dried under vacuum at 80°C for about 6 h. For comparison, pristine manganese (II) hydroxide (Mn(OH)₂) nanoparticles (brown color) were synthesized by following the above procedure without nickel nitrate hexahydrate. 

Results and discussion

In order to obtain more information about the formation, chemical composition, and major functional groups of the Manganese and Nickel layered double hydroxide (MnNi(OH)₂) nanoparticles, Fourier Transform Infrared (FTIR) analysis was recorded in the region 550–4000 cm⁻¹ on a Thermo Nicolet iS5 FTIR spectrophotometer (Fig. 1A). The observed characteristic broad absorption bands in the range from 3400-3550 cm⁻¹ and a shoulder peak around 1620 cm⁻¹ (hydroxyl stretching vibration and the corresponding deformation mode) can be attributed to absorbed water molecules on the surface of the nanoparticles. In addition, peaks around 2200 cm⁻¹ are due to C–N stretching, 1390-1170 cm⁻¹ are due to the intercalated nitrate anions in the Metal-OH layer, and a peak around 650 cm⁻¹ are associated with Metal-OH functional group. Absence of MO₂ peaks supports that the prepared samples are purely metal hydroxides M(OH)₂.

The crystallinity and crystal phase of MnNi(OH)₂ nanoparticles were characterized by XRD (using Rigaku diffractometer, Cu-Kα radiation, Japan) (Fig. 1B). MnNi(OH)₂ shows intense peaks positioned at 20 values 24, 31, 36, 51 and 60, which match well with the Mn(OH)₂ JCPDS value (JCPDS file no. 73-1133) and in addition some other peaks noticed at 20 values 12.3 and 24.7 could be assigned to the (003) and (006) planes of Ni(OH)₂. Furthermore, an asymmetric nature of reflection plane at 20 value 37.7 indicates that the formed MnNi(OH)₂ may have some special turbostratic structure. Further to support the formation of MnNi(OH)₂ nanoparticles, XPS analysis were performed (using Physical Electronics PHI 5600 XPS spectrophotometer with monochromatic Al-Kα (1486.6 eV) excitation source) and the survey plot for MnNi(OH)₂ nanoparticles is shown in Fig. 2A. The XPS spectra of MnNi(OH)₂ nanoparticles show main peaks characteristic for Manganese (Fig. 2B) (Mn (2P½) and Mn (2P½) at 641.2 eV and 652.8 eV), and Nickel (Fig. 2C) (Ni (2P½) and Ni (2P½) at 855 eV and 872.4 eV) respectively. In addition, a satellite peak noticed around 861 eV indicates the occurrence of Nickel as Ni²⁺ only and not Ni⁰. Further, the mixed MnNi(OH)₂ nanoparticles show a single peak for oxygen (O (1s)) at 531 eV, which indirectly indicates the presence of M-OH bonding (Fig. 2D).
LDH), which was stacked regularly to form a dancing like morphology structure (Fig. 3D). The width of the sheets was in the range 80-100 nm. In addition, MnNi(OH)$_2$ nanoparticles also reveal similar morphology under TEM analysis. Under lower magnification, it looks like microsphere-like or sea urchin-like morphology (Fig. 3E), whereas at high magnification it looks like layered sheet-like structure (Fig. 3F). In HRTEM image, both Mn (101) and homogeneous nucleation and crystallization of LDH materials. That is, Mn(OH)$_2$ nuclei generally evolve into nanorods by preferential c-axis ([002] direction) oriented 1D growth. Further when the crystal growth along the [002] direction is suppressed, nanoslices can be obtained due to quasi 1D growth. Finally, when multiple nanoslices grow further, LDH can be formed by self-assembled growth.

Ni (101) lattice planes are found (Fig. 3G) and also SAED pattern (Fig. 3H) confirms the same. EDX analysis (Fig. 3I) corresponding to such HRTEM image shows the presence of manganese, nickel, and oxygen as elements in the nanoparticles. In general, the progressive hydrolysis of urea or sonolysis makes the solution alkaline (see reactions 1-4) and induces CO (NH$_2$)$_2$ + H$_2$O $\rightarrow$ 2NH$_3$ + CO$_2$  
NH$_3$ + H$_2$O $\rightarrow$ NH$_4^+$ + OH$^-$  
Mn$^{2+}$ + 2OH$^-$ $\rightarrow$ Mn(OH)$_2$  
2Mn(OH)$_2$ + xNi$^{2+}$ + yOH$^-$. + zH$_2$O $\rightarrow$ MnNi(OH)$_2$  

The prepared MnNi(OH)$_2$ layered double hydroxide nanoparticles.
n nanoparticles were tested as active electrode material for supercapacitor applications. For this, cyclic voltammetric response of graphite substrate electrode modified using MnNi(OH)₂ nanoparticles (working electrode area is 0.5 cm²) was recorded in an aqueous solution of 1 M Na₂SO₄ vs Ag/AgCl at different scan rates (5-160 mV s⁻¹) in the potential range of 0.0 to 1.0 V. The drop coating was carried out on graphite substrate (5×5 mm²), electrode grade, EDM-200, POCO Graphite Inc.) followed by drying at room temperature for 24 h and heat treated at 250 °C in air for 1 h. The weight of the heated-treat sample is around 0.008 mg. The observed rectangular shape of voltammogram without any redox current peaks indicates the ideal capacitive behavior of mixed Manganese and Nickel hydroxide nanoparticles (Fig. 4A). Furthermore, the size of the voltammogram increases with an increase in the sweep rates (5-160 mV s⁻¹), indicating the high power characteristics of MnNi(OH)₂ layered double hydroxide nanoparticles.

Further, charge–discharge tests for the Manganese and Nickel hydroxide nanoparticles containing 1 M Na₂SO₄ at an applied current density of 1 mA cm⁻² in the potential range from 0.0 to 1.0 V are shown in Fig. 4B. The linear profile of charge and discharge curves (Fig. 3B) exhibit good electrochemical reversibility without apparent deviations in each cycles, revealing good capacitive characteristics of the MnNi(OH)₂ layered double hydroxide nanoparticles. The calculated specific capacitance values based on equation \[ C_{sp} = \frac{i\Delta V}{m} \] where \( i \) = current density, \( t = \) discharge time in seconds, \( \Delta V = \) is the potential window, and \( m = \) mass of the electro-active material were found to increase for MnNi(OH)₂ layered double hydroxide nanoparticles (160 F·g⁻¹) while compared to pristine Mn(OH)₂ nanoparticles (128 F·g⁻¹).  

Since the good cycling stability is important requirement for real supercapacitor application, a long cycling stability of the MnNi(OH)₂ layered double hydroxide nanoparticles was studied by charge – discharge cycling at a current density of 1 mA cm⁻² in 1M Na₂SO₄ as electrolyte and the variation of calculated specific capacitance as a function of cycle number is given in Fig. 4C. After 1200 cycles, more than 85% of the initial capacitance was retained, indicating that the prepared electrode using MnNi(OH)₂ layered double hydroxide nanoparticles exhibit a good electrochemical stability and hence capacitance retention capability. Further, the energy and power densities are important parameters for supercapacitor applications. It can be calculated using eqn (5) and (6):

\[
E = \frac{(1*V\cdot t) / (7.2*M)}{Wh/kg} \quad (5)
\]

\[
P = \frac{3.6E}{t} \quad W/kg \quad (6)
\]

where \( E \) and \( P \) is the energy and power density respectively. \( I \) is the applied current (mA), \( t \) is the discharge time of the active material (s), \( V \) is the potential window (V) and \( M \) is the mass of the active material (mg). It is observed that energy density decreases with increasing power density (See Ragone plot; Fig. 5). The \( E \) values are high, being 15-18 W h kg⁻¹, while the \( P \) values are in the range 60-63 W kg⁻¹. The high energy density without significant loss of power density is a key to be considered as smart supercapacitor electrode materials. The overall results show that the sonochemically prepared MnNi(OH)₂ might be a good candidate for electrochemical capacitor applications. In summary, MnNi(OH)₂ layered double hydroxides has been successfully synthesized by sonochemical irradiation method to explore its ability as high energy density pseudocapacitor electrode and its properties. This methodology could be used for synthesizing a number of various mixed transition metal hydroxides with diverse structural morphology. The present work, however, may serve as a preliminary step towards further studies on the electrochemical storage devices under scrutiny in our laboratory at present.
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References

Graphic Abstract