



Synthesis of $\text{Cu}^{2+}/\text{Ce}^{3+}$ Layered Oxides by Hydrothermal Method and Their Characterization

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Abstract -Layered oxides (LO) or anionic clays are a class of synthetic two-dimensional lamellar compounds with positively charged layers and charge-balancing anions located in the layer region. Layered double hydroxide (LDH) materials are mixed metal hydroxides represented by the general chemical composition $[\text{M}_{(1-x)}^{2+}\text{M}_x^{3+}(\text{OH})_2]_n\text{A}_{x/n}^{n-} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} stands for divalent and trivalent cations respectively, occupying octahedral sites within the hydroxyl layers forming brucite type layers; x is equal to the $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ ratio and includes values over the range of 0.20 to 0.50; and A^- is an exchangeable interlayer anion. Then it was refluxed with 10 h under nitrogen gas atmosphere at 80-110°C to form LO. We have prepared $\text{Cu}^{2+}/\text{Ce}^{3+}$ LO through precipitation method of an aqueous solution of divalent copper and trivalent cerium ions using hexamethylenetetramine (HMT) as hydrolysis agent under nitrogen gas atmosphere at 80-110°C. The presented strategy is simple for synthesizing the LO with layer thickness of about micrometer. The synthesized samples were characterized by XRD, SEM, FTIR and HRTEM. Furthermore, the possible formation mechanisms of layered oxide nanosheets were proposed.

Key words: Layered oxides, Hexamethylene tetraamine, Hydrolysis.

I. INTRODUCTION

“Layer-engineered” oxides of the 3d and 4f metals have been widely recognized as candidates for the next-generation electronics materials. A compound with layered structure has interesting chemical properties in fields such as intercalation, photocatalysis, ion-exchange, photoluminescence, and electrochemistry [1]. Their properties largely change with the kinds of ions and/or molecules existing in the interlayer. In general, the layered oxides consisting of Ti, Nb and Ta have high photocatalytic activity for water photolysis [2]. However, thus far the electrochemical and photoelectrochemical properties of these layered oxides in aqueous solution have not been known, because it is difficult to prepare a ceramic-type electrode for their oxides due to poor electrical conduction [3]. A variety of ordered mesoporous materials have been synthesized

using the supramolecular assembly of surfactant molecules as a template. These materials have a range of framework compositions, morphologies, and porous structures. This approach to mesostructured materials has been extended to non-silica oxides, which might promise applications involving electron transfer, magnetic interactions, photocatalysis, and catalyst support [4].

A novel pillaring procedure to convert dense layered metal oxides and silicates into high surface area molecular sieves with large interlayer separations. The procedure is applicable to a wide variety of layered phases and allows for the engineering of micro porous materials with diverse compositions and physical properties [5]. In the present work, we have synthesized layered oxides of $\text{Cu}^{2+}/\text{Ce}^{3+}$ like layered double hydroxides (LDH). The $\text{Cu}^{2+}/\text{Ce}^{3+}$ LDH were further refluxed with 80°-110°C for 10 h to form CuO and CeO₂ as good microstructures. The crystal structure, morphology of the obtained layered oxide (CuO/CeO₂) nanostructures was characterized using XRD, FESEM, and HRTEM.

II. EXPERIMENTAL

Materials

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and Ammonium Ceric Nitrate (CAN) were purchased from Sigma Aldrich. Hexamethylenetetramine (HMT) was purchased from Fluka A. R.

Preparation of Layered Oxides of CuO/CeO₂

All the $\text{Cu}^{2+}/\text{Ce}^{3+}$ LDH with NO_3^- anions as counter ions in the interlayers were synthesized using a hexamethylenetetramine by hydrolysis method. The total metal cation concentration was 0.01 M and the molar ratio of HMT/Ce was controlled to be 1.5. In brief, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and ammonium ceric nitrate, hexamethylenetetramine, and sodium nitrate were dissolved in double distilled (DD) water under nitrogen gas protection. The aqueous solution was refluxed with 80-110 °C to 10 h with continuous stirring. After being

aged, the products were filtered, washed with DD water and finally dried in air vacuum.

Characterization Techniques

The formation of phase was verified using the X-ray powder diffraction (XRD) technique by Seifert X-ray powder diffractometer using Cu-k α_1 radiation ($\lambda = 1.5406 \text{ \AA}$) with quartz monochromator. The average crystallite size was determined from Reflection of the XRD pattern using Scherrer formula. The Fourier transformed infrared (FT-IR) spectra were recorded in the wave length range of $4000\text{-}400 \text{ cm}^{-1}$ using KBr pellets with Shimadzu FT-IR 8300 instrument. Synthesized nanomaterial topography and size were observed by HITACHI SU6600 (FE-SEM) field-emission scanning electron microscopy coupled with EDAX and HR-TEM using a FEI TECNAI G2 model T-30 at accelerating voltage of 250 kV.

III. RESULT AND DISCUSSION

a) XRD study

The crystal structure, phase formation and the crystallite size calculation of the CuO/CeO₂ were analyzed using powder XRD measurements confirm the phase formation of CuO/CeO₂, which could be slightly amorphous in nature due to the limited temperature.

The resulted diffraction patterns were well matched with the slightly crystalline structure of monoclinic CuO (JCPDS No.89-5899). This result indicates that some secondary phase of CeO₂ could be obtained by the addition of the Cu/Ce with the ratio of 3:1 at the co-precipitation reaction. From Fig. 1, it could be notice that the diffraction pattern showed the characteristic peaks of CuO/CeO₂ ($2\theta = 32.5, 35.4, 35.5, 38.7, 38.9$ and 48.2 and marked plane indices corresponds to (110), (002), (-111), (111), (200), and (-112) respectively. The broadening of all recorded peaks in the pattern indicates the presence of nanoscale crystallites [6]. The average crystallite size of the LO was calculated using Scherrer relation and the size was $\approx 32 \text{ nm}$. The above details confirm the successful formation of CuO/CeO₂ LO.

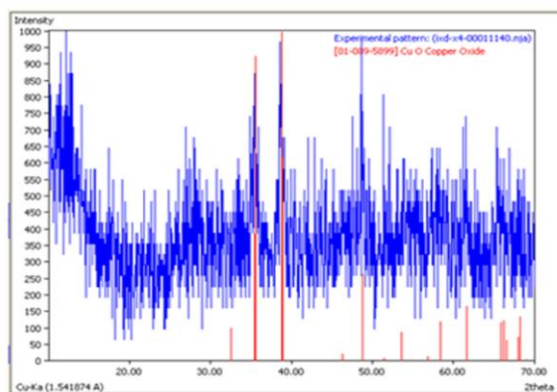


Fig.1. XRD patterns of CuO/CeO₂

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b) FT-IR Transmission Spectroscopy

Fourier-transform infrared (FT-IR) spectrum of CuO/CeO₂ were shown in Fig 2. the FTIR spectrum of CuO/CeO₂ provides the details about the groups such as, metal-oxygen (M-O) stretching vibration observed in the region of 600 to 1000 cm^{-1} and the broad band observed at 3441 cm^{-1} was assigned to the OH stretching mode of water molecules chemically associated with CuO. The OH bending peak appears at 1628 cm^{-1} .

The peak observed at $1504, 1557 \text{ cm}^{-1}$ were relates to the NO and NH respectively, this could be attributed due to the intercalated NO₃⁻ ion and the HMT species. The corresponding bending, wagging of CH₂ vibrations are at $1411, 1339 \text{ cm}^{-1}$ respectively[7].

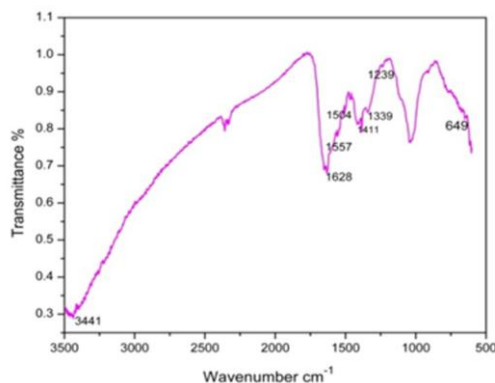


Fig. 2. FT-IR spectrum of CuO/CeO₂

c) Field Emission Scanning Electron Microscopy (FESEM) morphology

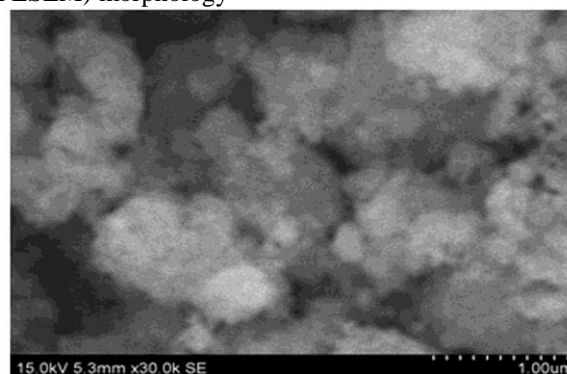


Fig.3. FESEM image of CuO/CeO₂

The FESEM image of the CuO/CeO₂ was shown in the Fig. 3. The most commonly observed particle morphology was that of aggregated spherical-shaped

nanostructure. The CuO/CeO₂ layered oxide like nanostructure resulting the homogeneity, and nanoscale size with the small aggregation due to the thermal heating were observed. The size of the CuO/CeO₂ was about 95 nm.

d) HR-TEM images

The HRTEM images of CuO/CeO₂ were shown in Fig.4 revealed that the aggregated layer-like nanosheets. The HR-TEM images of CuO which are in good agreement with the results from FE-SEM. Also the HRTEM images reveal the homogeneous size distribution of nanoparticles by the pillaring, which may due to presence of HMT that prevents the agglomeration of two layers [8].

e) LO Growth mechanism

The nanosheets of CuO/CeO₂ layered oxide possible mechanism proposed below: HMT undergo the hydrolysis to produce the ammonia and formaldehyde [9]. Ammonia can form a complex with metal ions, which decrease the free metal ion concentration, and reduce the rate of the crystal growth, while the reaction precedes more HMT hydrolyze leading to the increase of the concentration of OH⁻¹ in the solution.

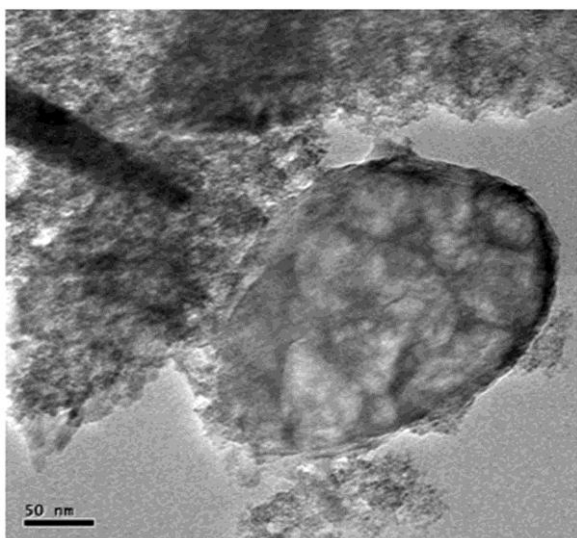


Fig.4. HRTEM image of CuO/CeO₂

The enough basic medium produced by HMT leads to the formation of layered hydroxide. During the thermal process, layered hydroxides undergo oxidation to the CuO/CeO₂ LO. The gradual and controlled sodium nitrate common ion was added for slow dissociation. At the same time, the unreacted HMT may selectively adsorb on certain facets of CuO/CeO₂ nanoparticles due to their high binding capacity resulting in the formation of nanosheets.

IV. CONCLUSION

A series of mixed CuO/CeO₂ layered oxide nanostructures were simply prepared by hydrothermal co-precipitation method. They also appeared to be quite stable under reaction conditions. They very finely

dispersed Cu²⁺/Ce³⁺ layered oxides are responsible for the high activity in low temperature. The possible growth mechanism of LO was also proposed from the morphology of layered oxides found from FE-SEM and HRTEM images.

V. ACKNOWLEDGEMENT

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