Exfoliation-free Nanosheet Synthesis of Transition-metal Hydroxynitrate and Its Transformation to Oxide Particulate Nanosheet

Hongtao Cui, Marcos Zayat, and David Levy*
Instituto de Ciencia de Materiales de Madrid, C.S.I.C 28049 Cantoblanco, Madrid, Spain

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A new strategy, epoxide-assisted precipitation route presented in this work, allows the exfoliation-free nanosheet synthesis of $Ni_3(NO_3)_2(OH)_4$ by the control of dynamics of the precipitation reaction. The mechanism of growth limitation in the third direction can be explained by the bonding of the molecule resulting from the ring-opening reaction of the epoxide to the surface of primary nanosheets, preventing the thickening of the layer.

Layered metal hydroxides including layered double hydroxides (LDHs) and layered basic metal salts (LBMSs) are a kind of compounds composed of alternately stacked hydroxide and intercalated species (anions or water) layers with 2D structure. The exfoliation of the layers can be achieved by reducing the interaction of layers, controlling the intercalation species to increase the interlayer distance. Due to their unique microstructure, physical and chemical properties, layered metal hydroxides have obtained a wide spectrum of useful properties including high catalytic activity, absorbing efficiency, bioactivity as an inorganic carrier, electroactivity and photoactivity.[1] The recently reported magnetic properties of layered basic transition-metal salts,[2] $M(OH)_{2-n}X_n{\cdot}zH_2O$ (M^{II} = Cu, Co, and Ni; X = inorganic or organic anion), are one of the most fascinating findings among the investigations on the magnetic materials due to their tunable magnetic properties induced by their special 2D structures.

In order to maximize their usage or promote their performance in a variety of applications, it is necessary to minimize the thickness of this kind of layered metal hydroxide into the nanometric range (nanosheet). However, their preparations by usual routes do not produce nanosheets directly due to the difficulty of control of their continue growth in the third dimension. The only way is to exfoliate their layers by inserting other species into the interlayer space to destroy the weak interaction of the layers. The main disadvantage of exfoliation is the affinity between the layers of the compound, which is main impediment for the delamination process. Therefore, the simplest way is to synthesize the nanosheet directly avoiding the exfoliation step. However, the realization of this idea is still a challenge, because the 2D anisotropy growth of hydroxides remains a difficult issue needing to be solved.

An epoxide route for the synthesis of metal oxide offers an alternative solution for the synthesis of hydroxides nanosheets due to the unique chemistry of the epoxide-assisted precipitation reaction. In this route the epoxide has been successfully used as a gelation agent to prepare metal oxide nanoparticles and aerogels.[3] Due to the low acidity of some metal ions in the solution, the addition of the epoxide often results in the precipitation of hydroxides after long reaction times, instead of the formation of a gel. This issue, however, offers an opportunity to control the structure and morphology of the precipitated hydroxide particles and then the morphologies of the oxide nanostructure after calcination.

In this work, an epoxide-assisted precipitation route was reported for the one-step direct synthesis of nickel hydroxynitrate nanosheets by the control of the dynamics of the precipitation reaction. The nanosheets can be transformed to NiO particulate nanosheets through the heat treatment. Bulk NiO is a two-sublattice antiferromagnetic material with NaCl crystal structure and Néel temperature of 523 K. However, when the particle size of antiferromagnetic materials including NiO reaches the nanoscale range, the particles show ferromagnetic properties.[4,5] The especially interesting point is that the surface anisotropy of their nanometric particles gives the main contribution to the effective anisotropy, which may give rise to excellent magnetic properties.[5] These new findings initiate a branch of investigation on magnetism and make this kind of antiferromagnetic material a promising candidate for applications.

The obtained precipitate precursor resulting from the reaction between $Ni(NO_3)_2$ and propylene oxide was identified by XRD as $Ni_3(NO_3)_2(OH)_4$ (JCPDS 22-0752). The structure of the precursor remains unchanged until it is converted into NiO (JCPDS 44-1159) during the calcination at 300 °C. The particles after the heat treatment at 400 °C grow larger, as can be concluded from the sharpening of the XRD diffraction lines. A representative TEM image of the precursor $Ni_3(NO_3)_2(OH)_4$ is shown in Figure 1a. It is very interesting to note that the entire sample consist of very thin nanosheets with undefined width from several hundreds of nanometers to a few microns. $Ni_3(NO_3)_2(OH)_4$ is a hydroxynitrate compound with layered structure, previously prepared by the thermal decomposition of $Ni(NO_3)_2{\cdot}6H_2O$. From the structural point of view, the hydroxynitrate is derived from the metal hydroxide having a layered CdI_2 structure. Part of the hydroxy groups are substituted by the nitrate groups, which induce an increase of the interplanar distance. This kind of layered hydroxy compounds, obtained by traditional routes, usually shows irregular morphologies and very thick thickness.[6,7] To obtain the nanosheets from the thick layered precursor, the exfoliation of the layers should be carried out.[7] However, it is very fascinating that very thin nanosheets of $Ni_3(NO_3)_2(OH)_4$ can be obtained directly by the epoxide-assisted precipitation.

Propylene oxide acts as an acid scavenger through the protonation of its oxygen and the subsequent ring opening by the nucleophilic anionic conjugate base. It consumes protons from the hydrated nickel ion complexes, which promotes the hydrolysis of the complexes. In the solution, the acidity of the +2 metal ion aquo complexes $[Ni(H_2O)_6]^{2+}$ is much lower than that of other ions with higher charge, which slows down the protonation of the propylene oxide and then the hydrolysis rate of $[Ni(H_2O)_6]^{2+}$. This slow hydrolysis process can not consume the hydrated water in $[Ni(H_2O)_6]^{2+}$ completely, which makes

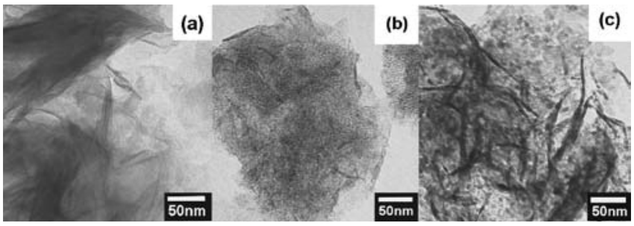

Figure 1. TEM images of $Ni_3(NO_3)_2(OH)_4$ (a) and the NiO samples obtained by the calcination at 300 °C (b) and 400 °C (c).

the NO_3^- group enter into the structure and form the layered $Ni_3(NO_3)_2(OH)_4$ structure at last. The reaction process can be expressed in eq 1. It is reasonable to assume that the continuous growth of $Ni_3(NO_3)_2(OH)_4$ in the third dimension is limited by $C_3H_6(OH)(NO_3)$, anchored through hydrogen bonds, to the surface of the formed primary nanosheet particles (The $C_3H_6(OH)(NO_3)$ is produced during the ring-opening reaction of propylene oxide as shown in eq 1).

A TEM image of the NiO sample obtained after calcination of the precursor nanosheets at 300 °C is shown in Figure 1b. The morphology of the nanosheet is maintained, although the sample is decomposed from $Ni_3(NO_3)_2(OH)_4$ to NiO during the calcination. The thin nanosheets are composed of a monolayer of closely assembled NiO nanoparticles with size of a few nanometers. As shown in Figure 1c, the sample still keeps the nanosheet morphology after treatment at 400 °C. However, the NiO nanoparticles in the sheet grow further to about 8 nm. The sheets are lightly curved and self-tangled, which seems that their flexibility is higher than those calcined at lower temperature.

$$\begin{aligned}&[Ni(H_2O)_6]^{2+} + NO_3^- + C_3H_6O\\ &\quad\rightarrow [Ni(H_2O)_5OH]^+ + C_3H_6(OH)(NO_3)\\ &\quad\xrightarrow{NO_3^-} Ni_3(NO_3)_2(OH)_4\end{aligned} \tag{1}$$

The addition of $NiCl_2{\cdot}6H_2O$ into the solution of $Ni(NO_3)_2{\cdot}6H_2O$ changes the structure and morphology of the obtained precursors. The XRD pattern of the sample prepared with $Ni(NO_3)_2/NiCl_2 = 5$ shows a $Ni_3(NO_3)_2(OH)_4$ structure. However, its diffraction lines are slightly shifted to lower values of 2θ as compared with those of samples synthesized without $NiCl_2$. This demonstrates that the layered structure of $Ni_3(NO_3)_2(OH)_4$ (d spacing = 0.75 nm)[8] is slightly distorted due to the partial replacement of NO_3^- by Cl^-. Increasing the Cl^-/NO_3^- ratio in the initial solution results in a progressive loss of the structure to obtain amorphous nickel hydroxide.[9] The change of the structure of the precipitate precursors with the different nickel salt used for its preparation is accompanied with a change in their morphologies as shown in Figure 2. The sample prepared with $Ni(NO_3)_2/NiCl_2 = 5$ (Figure 2a) shows much more self-tangled and curved morphology as compared with that synthesized from $Ni(NO_3)_2$, keeping the same nanosheet morphology. Although the sample prepared with $Ni(NO_3)_2/NiCl_2 = 1$ is amorphous (Figure 2b), it gives a completely different morphology from that synthesized from the $NiCl_2$ solution (Figure 2c), keeping the nanosheet morphology, however in a more agglomerated form. However, the sample prepared from the $NiCl_2$ shows just an agglomeration of randomly arranged particles of a few nanometers. Although there is no very clear explanation to this phenomenon, it is reasonable to assume that the NO_3^- group helps to hold the layered structure of the precipitate even when the precipitate is amorphous.

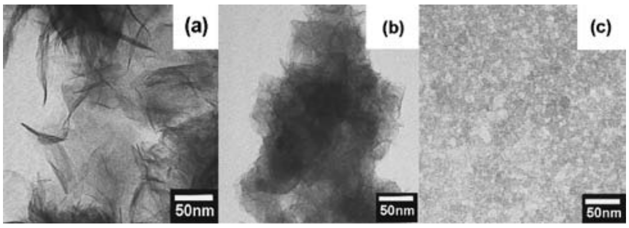

Figure 2. TEM images of the sample (heat treated at 100 °C) obtained from mixture solutions with $Ni(NO_3)_2/NiCl_2 = 5$, (a); 1 (b); and 0 (c) respectively. The molar Ni/propylene oxide ratio is 10 in all cases.

The exfoliation-free synthesis of $Ni_3(NO_3)_2(OH)_4$ nanosheets has been successfully carried out through an epoxide-assisted precipitation route. The growing of the layered compound is limited in the direction of the third dimension, resulting in the formation of nanosheets. The mechanism of growth limitation can be explained by the bonding of the molecule resulting from the ring-opening reaction of the epoxide to the surface of primary nanosheets, preventing the thickening of the layer. The $Ni_3(NO_3)_2(OH)_4$ nanosheets can be used as a self-template to synthesize the NiO particulate nanosheet by phase transformation during calcination. Usually, the transition-metal hydroxides and basic hydroxide salts exhibit a layered structure. Taking advantage of the unique chemistry of the epoxide-assisted precipitation route to depress the growth of the compounds in the third dimension, nanosheets of different metal ions may be prepared in future works to establish a general synthetic route for the preparation of transition-metal hydroxide and the corresponding oxide nanosheets.

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References

1 B. Sels, D. De Vos, M. Buntinx, F. Pierard, A. Kirsch-De Mesmaeker, P. Jacobs, *Nature* **1999**, *400*, 855; P. C. Pavan, G. D. Gomes, J. B. Valim, *Microporous Mesoporous Mater.* **1998**, *21*, 659; J. H. Choy, S. Y. Kwak, Y. J. Jung, J. S. Park, *Angew. Chem.* **2000**, *39*, 4041; A. Sugimoto, S. Ishida, K. Hanawa, *J. Electrochem. Soc.* **1999**, *146*, 1251; R. Sasai, N. Shin'ya, T. Shichi, K. Takagi, K. Gekko, *Langmuir* **1999**, *15*, 413.
2 S. Park, C. Lee, *J. Phys. Chem. B* **2005**, *109*, 1118; R. Sasai, N. Shin'ya, T. Shichi, K. Takagi, K. Gekko, *Langmuir* **1999**, *15*, 413.
3 H. Cui, M. Zayat, D. Levy, *J. Non-Cryst. Solids* **2005**, *351*, 2102; D. Suh, T. Park, W. Kim, I. Hong, *J. Power Sources* **2003**, *117*, 1.
4 M. Ghosh, K. Biswas, A. Sundaresan, C. N. R. Rao, *J. Mater. Chem.* **2006**, *16*, 106.
5 E. Winkler, R. D. Zysler, M. V. Mansilla, D. Fiorani, *Phys. Rev. B* **2005**, *72*, 1324091.
6 M. Ogawa, S. Asai, *Chem. Mater.* **2000**, *12*, 3253.
7 J. Miao, M. Xue, H. Itoh, Q. Feng, *J. Mater. Chem.* **2006**, *16*, 474.
8 M. Taibi, S. Ammar, N. Jouini, F. Fiévet, P. Molinie, M. Drillon, *J. Mater. Chem.* **2002**, *12*, 3238.
9 A. E. Gash, J. H. Satcher, Jr., R. L. Simpson, *J. Non-Cryst. Solids* **2004**, *350*, 145.

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