Preliminary Mechanism of Tubular Nano-Mg(OH)$_2$ Formation

W. Zhou$^1$ & J. Zheng$^{1,*}$

$^1$School of Medical Technology and Engineering, Henan University of Science and Technology, Luoyang City, Henan Province, China

ABSTRACT: Since the discovery of tubular nano-scale materials in 1990s, they have been considered as the ideal materials for a variety of applications due to their unique mechanical, ferromagnetic properties for spintronics, magnetic, chemical and biological properties. In our previous work, nano-tube structured magnesium hydroxide has been discovered in solution phase under the normal atmospheric pressure. The present work focus on discussing the effects of reaction concentration, temperature, reaction time, crystal shape control agent dosage on the tubular nano-Mg(OH)$_2$ formation initially. The crystal shape control agent plays an important template role in inducing Mg(OH)$_2$ crystal nuclei forming tubular nano-Mg(OH)$_2$ during the synthesis process. The resulting tubular nano-Mg(OH)$_2$ implies its potential expanded applications in many research areas like the papermaking industry, fertilizer additive, pharmacy, biomaterials and etc.

1. INTRODUCTION

Magnesium hydroxide (Mg(OH)$_2$) has been an important inorganic material owing to its wide use in pharmacy, catalysis, plastic rubber, fire retardants, wood pulp bleaching, neutralization of acid waste water, etc. (Suihkonen et al., 2012). In biomedical fields, Mg(OH)$_2$ is an approved drug and food additive for its non-toxicity (Zhou et al., 2014). Specifically, it is often used as antacid to help neutralize stomach acid. In addition, Mg(OH)$_2$ is the most important precursor for industrial production of magnesium oxide (Nowak & Carter, 2009).

Since the birth of tubular nano-scale materials in 1990s, they are becoming more and more attractive owing to the unique microstructure, and the consequent unique electrical, mechanical, magnetism, chemical and biological properties (Zheng & Zhou, 2014). Compared with the familiar nano-scale materials with lamellar-like, wire-like, rod-like or needle-like structure, the iconic nanotube structured materials have much higher porosity and larger surface area. Therefore, tubular nano-scale magnesium hydroxide would expand unpredictable applications in

* Corresponding author. E-mail address: zhengjun288@hotmail.com (J. Zheng).
various areas. For example, it may be a promising candidate as nano-carrier that applied to drug
delivery, gene therapy, targeting therapy, tissue engineering and etc.

In our previous work, large quantity of Mg(OH)$_2$ nanotubes have been discovered in solution
phase under mild conditions. But the formation mechanism of tubular nano-Mg(OH)$_2$ has not
been concerned. The present work preliminary discussed several factors including the reaction
concentration, temperature, reaction time and crystal shape control agent that had impacts on the
formation of nano-Mg(OH)$_2$ morphologies

2. EXPERIMENTAL

2.1 Materials

The starting materials were MgCl$_2$·6H$_2$O, Mg(NO$_3$)$_2$, NaOH, NH$_3$·H$_2$O, Polyethylene Glycol
(PEG) that purchased from various suppliers and without further purification. Deionized water
was employed for all experiments.

2.2 Preparation of nano-Mg(OH)$_2$

According to our former studies, tubular Mg(OH)$_2$ nano-crystals were synthesized in solution
phase under the normal atmospheric pressure. In short, adding the NH$_3$·H$_2$O (or NaOH) solution
to MgCl$_2$·6H$_2$O (or Mg(NO$_3$)$_2$) slowly under manual stirring. After that, certain amount of
crystal control agent (PEG) was added to the suspensions. During the reaction process, the pH
was maintained between 9~12. When the reaction ended, the slurries were filtered, washed with
deionized water for 3 times, and dried at 180 °C.

2.3 Characterization

The phase identification of Mg(OH)$_2$ nanoparticles was conducted by X-ray diffraction (XRD)
method (D8 ADVANCE, Bruker AXS, Germany). The XRD patterns of the deposited film were
measured on a Rigaku D/max II diffractometer with Cu Kα radiation (λ=1.54056 Å, 40 kV, 80
mA). The interplanar spacing of the resultant film was determined from the diffraction peak
position / patterns with a structural analysis software. Morphology and microstructure of tubular
nano- Mg(OH)$_2$ were observed by Transmission electron microscope (TEM, JEM–2100, JEOL
Ltd., Japan). The samples were dispersed in ethanol and loaded onto copper grids supporting
formvar film.
3. RESULTS AND DISCUSSION

3.1 Characterization of Nano-Mg(OH)$_2$

The figure 1 exhibits XRD pattern of Mg(OH)$_2$ nanoparticles. All diffraction peaks can be indexed as the hexagonal structure magnesium hydroxide (JCPDS file number 7-239). The significant peak broadening indicates that the resulting Mg(OH)$_2$ has a very small grain size. No evidences of impurities could be found in the XRD pattern that implies the high purity of Mg(OH)$_2$ nanoparticles obtained through this preparation method.

![X-ray diffraction (XRD) patterns of Mg(OH)$_2$.](image)

Figure 1. X-ray diffraction (XRD) patterns of Mg(OH)$_2$.

The typical TEM picture and SAED pattern of tubular nano-Mg(OH)$_2$ are given in Figure 2. Studies of TEM reveal that the Mg(OH)$_2$ nanocrystals are of homogeneous dispersion without obvious aggregation. All the Mg(OH)$_2$ nano-crystals display open-ended tubular morphology with a length of 80-150 nm. And the widths of these nano-tube magnesium hydroxide are in the range of 5-10 nm. Combined with the results of the XRD study, the selected area electronic diffraction (SAED) results demonstrate that the final product is high-quality hexagonal crystal system nanocrystals.

![TEM picture and SAED pattern of tubular nano-Mg(OH)$_2$.](image)

Figure 2. TEM picture and SAED pattern of tubular nano-Mg(OH)$_2$. 
3.2 Formation mechanism of tubular nano-Mg(OH)$_2$

The control of precipitation reaction play a key role in the liquid phase of nano-Mg(OH)$_2$ preparation. In the process of precipitation reaction, when the concentrations of Mg$^{2+}$ ions and OH$^-$ ions above a certain value, Mg$^{2+}$ ions connected with OH$^-$ ions. Firstly, the nucleation generates, and then grows sustainably to form the precipitation particles. In the process of precipitation reaction, the crystalline solids form when the growth units align orientation to certain crystal lattice; the amorphous solids form when the precipitation particles aggregate loose. Experiments indicate that the advisable reaction conditions are: OH$^-$ ions concentration is excessive to Mg$^{2+}$ ions concentration (0.5-1.5 mol/L), and the pH value of the reaction suspension maintained above 9.

The ionic energy is low when the temperature is very low. Even if the supersaturation of ionic liquid is very high, the grain’s growth rate is still low. With the temperature rise, the grain’s growth rate can reach maximizing. Then with the increasing of temperature, the supersaturation decreases, the situation are not conductive to formation of stable grains. And the grain’s growth rate drops instead. Research also shows that the temperature range of the maximizing nucleation is lower than that of the nuclei growth. The advisable reaction temperature range is 50-90 °C.

In theory, the shorter reaction time results in the smaller size of grain, and the narrower particles size distribution. But the shorter reaction time is detrimental to the growth of tubular nanocrystallines. For this reason, specific reaction time is needed. In the actual reaction process, the appropriate reaction time is in the range of 30~50 minutes.

Crystal shape control agent refers to a small amount of foreign additives which has nothing to do with crystalline materials. The crystal shape control agent has diverse effects on crystal growth in solution. It can influence the solubility of material and the nature of the solution, and even make changes to the crystallization habits, significantly. The selective adsorptions of crystal shape control agent on different crystal surfaces often occur, owing to the crystalline anisotropic. These adsorptions usually block crystal growth, change the relative crystal growth rate of every crystal surface. So the controlling of the crystal morphologies is achieved. The crystal shape control agent can adsorption on the crystal surface, steps or twist and fold of magnesium hydroxide, and replace the lattice ions, prevent the adsorption or migration of the lattice ions, consequently inhibit the crystal growth of magnesium hydroxide. If the crystal shape control agent is added to the reaction suspensions, it can adsorp on the surface of Mg$^{2+}$ ions to form a complex. Then OH$^-$ could interaction with Mg$^{2+}$ ions in certain angles to form semi-stable hexagonal structured magnesium hydroxide nuclei. In the theory of crystal growth
kinetics, the crystal shape control agent can be considered as the energy of changing the crystal growth process.

The volume of crystal shape control agent applied has a significant effect on magnesium hydroxide crystal morphologies. In general, the amount of crystal shape control agent should be strictly controlled in a certain range. Less amount of crystal shape control agent could not meet the requirement. More amount of crystal shape control agent can affect the performance of products, such as the white degree, dispersion, or even fail to obtain certain crystalline shape. The former studies indicated that the volume of crystal shape control agent has an direct effect on particles size of nano-Mg(OH)$_2$ samples.

4. SUMMARY

In conclusion, the present work discuss the preliminary formation mechanism of tubular nano-Mg(OH)$_2$ in solution phase. Based on the former work, typical tubular nano-Mg(OH)$_2$ with lengths of 80-150 nm, widths of 5-10 nm were successfully synthesized. Explorations of X-ray diffraction (XRD) and selected area electronic diffraction (SAED) exhibit that the product is high-quality hexagonal crystal system nanocrystals. The reaction concentration, temperature, reaction time and crystal shape control agent dosage are the important factors that affect the formation of the tubular nano-Mg(OH)$_2$. Especially in the biomedical field, the unique morphology of open-ended tubular magnesium hydroxide nanostructure have great potential applications in drug delivery, inorganic anti-bacterial agents and other biomedical fields.

ACKNOWLEDGMENT

This work was financially supported by the university-level Youth Foundation (No. 2015QN045) and the Doctoral Initiating Scientific Foundation from Henan University of Science and Technology. The corresponding author is Dr. Jun Zheng.

REFERENCES

