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Chapter 9

The Synthesis of Nano-Crystalline Metal Oxides by Solution Method

Xuejun Zhang and Fuxing Gan

Additional information is available at the end of the chapter

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1. Introduction

The performance of materials in many of their uses in industries and scientific researches is directly dependent on their crystal structure, which correlates to the chemical and physical properties of the materials. And also, as the size of crystal particles decrease to nanometer scale, nanocrystals exhibit some unexpected properties that are evidently different in physics and chemistry from their bulk crystals and their cluster compounds as well.

One of the most important applications of nano-materials is as catalyst to be widely used in petroleum and chemical industries, which has been a hot research area attracting high attention from researchers around the world. A lot of nanomaterials that have shown highly catalytic activity are nano-sized metal oxide crystals or doped metal oxide crystals. As well known, the nature of semiconductor is one of major features for solid catalyst, especially for solid photo-catalyst. The properties could exhibit or work as catalysts only when the metal oxide bears crystal structure. Therefore, the crystallization of oxide or doped oxide is a key step in the preparation of catalyst.

Nowadays the current processes of preparing metal oxide nanocrystal are mainly involved in sol-gel method and some modified sol-gel methods. The products synthesized by the methods, however, are metal hydroxides, which have to undergo a firing treatment (at over 350 °C) in order to have them crystallized and to be endowed with semiconductive and catalytic properties. But, the formation of oxide crystals in the roasting process involves a phase transition process, in which a new grain boundary forms and expands at high temperature, leading to size increase of the particle obtained in solution synthesis or even to a new matrix element phase from which the doping element is excluded. In addition, the process of phase transformation in calcination is unfavourable for the preparation of nuclear-shell structure of nano materials such as a magnetic nuclear coated with TiO₂, SiO₂ or SnO₂, resulting in tow-phase separation and a failure of coating on magnetic nuclear. For
the synthesis of nano-crystalline metal oxides with alterable valence, the calcination in the air causes the valence of metal to rise by oxidation and the original crystalline structure to change. And also, on the surface of the directly synthesized metal oxide nanocrystals without high-temperature burning there exist a large number of hydroxyl groups, which are more conducive to water molecules, organic solvents, or organic compounds compatible and to surface modification and functionalization of nanocrystals. See Section 4.4.

A modified sol-gel method, “precipitation–condensation with non-aqueous ion exchange (P-CNAIE)”, associating with a drying method, “azeotropic drying of iso-amyl acetate (AD-IAA)”, was put forward in 2005 (Zhang 2005), that is, in ethanol a strongly basic anion-resin was used as an exchanger to remove by-product Cl⁻ and as a reactant to provide OH⁻ for hydrolysis. The high-purity metal hydroxide tends to dehydrate in an intermolecular manner with the assistance of super water-absorbable ethanol to form crystal.

2. Method of synthesis

The solution chemistry method, usually referred to sol-gel method, is a significant process to synthesize the precursors of many nanoscale metal oxides. The method is widely used for it can achieve uniform doping of multi-elements no matter whether at atomic, molecular or nanometer levels at the gelatination phase. Generally, sol–gel processes have associated problems, such as difficulty in removing chlorine, and in accurate and repeated doping.

The new solution chemistry method proposed by us involves a precipitation–condensation process, with non-aqueous ion exchange in ethanol used for the removal of chlorine and for providing hydroxyl ion. (Zhang, 2005; Zhang et al., 2006, 2008; Yang et al. 2007).

2.1. The underlying principle of the hydrolysis method

The method involving P-CNAIE for removal of chlorine is based on a reaction that occurs in low-polar solvents containing limited water under a slightly alkalinity condition. Generally, as the soluble metal salts dissolved in water the solution become acidic and metal ions are hydrolyzed. Such tendency is much stronger for high valence metal ions because the acidity of high valence metal ions is stronger than that of low valence metal ions. This means the $K_{sp}$ of hydroxides of high valence metal ions are much smaller than that of low valence metal ions. Different kind of metal ion or the metal ions with different valence state have different $K_{sp}$, $M(O\text{H})_n$, which results in a part precipitation of the metal ion with low $K_{sp}$, $M(O\text{H})_n$ in aqueous solution. That a limited amount of water is added in the organic solvent will control the hydrolysis degree of metal ions, and in this case, addition of a limited amount of ammonia water instead can both control the hydrolysis degree and avoid part precipitation of a metal ion as a doped nano-material is synthesized.

Here $\text{MCl}_4$ is referred to as matrix metal chloride and $\text{NCl}_3$ as metal dopant. In the synthesis, the hydrolysis takes place limitedly under the assistance of ammonia water in absolute alcohol. The acidification is attributed to the HCl coming from $\text{MCl}_4$ and $\text{NCl}_3$, being caused by the first-order hydrolysis of $\text{MCl}_4$ and $\text{NCl}_3$. 
The Synthesis of Nano-Crystalline Metal Oxides by Solution Method

The product of the second-order hydrolysis of $\text{MCl}_4$ and $\text{NCl}_3$ is generally a white suspended precipitate. In an organic solvent, the polar product is precipitated much more readily, and the size of the particles is smaller because of the solubility of polar compound in organic solvent is much lower than that in water. (Wuhan U. 2000) The limited amount of ammonia water controls the rate of hydrolysis and the pH of the solution to slightly alkaline, preventing a part precipitation of either $\text{MCl}_4$ or $\text{NCl}_3$:

$$\text{MCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{M(OH)}_2\text{Cl}_2 \downarrow + 2\text{HCl} \quad (3)$$

$$\text{NCl}_3 + 2\text{H}_2\text{O} \rightarrow \text{N(OH)}_2\text{Cl} \downarrow + 2\text{HCl} \quad (4)$$

The third- and fourth-order hydrolysis of $\text{MCl}_4$ and $\text{NCl}_3$ is very weak. From the third-order hydrolysis on, the pH of the solution is almost maintained at around 7 (if $\text{pH} > 9$, the products might be $(\text{NH}_4)_2\text{MO}_3$ and $(\text{NH}_4)\text{NO}_2$, instead of $\text{M(OH)}_4$ and $\text{N(OH)}_3$, for some amphoteric elements). The third- and fourth-order hydrolysis is reversible.

$$\text{M(OH)}_2\text{Cl}_2 \downarrow + 2\text{H}_2\text{O} \rightleftharpoons \text{M(OH)}_4 \downarrow + 2\text{HCl} \quad (5)$$

$$\text{N(OH)}_2\text{Cl} \downarrow + \text{H}_2\text{O} \rightleftharpoons \text{N(OH)}_3 \downarrow + \text{HCl} \quad (6)$$

To maintain reactions (5) and (6) and prevent the formation of $(\text{NH}_4)_2\text{MO}_3$ and $(\text{NH}_4)\text{NO}_2$, chlorine has to be removed under neutral or slightly alkaline conditions. This is often performed by repeatedly using a fresh neutral solvent to wash the precipitate. This process consumes considerable amount of solvent and time. However, in the process of hydrolysis using anion-exchange resin, because the affinity of the anion-exchange resin for $\text{Cl}^-$ is over 25 times (Luliang et al., 2000) that for $\text{OH}^-$, the resin readily exchanges $\text{Cl}^-$ and supplies $\text{OH}^-$ for the hydrolysis.

$$\text{Resin} - \text{OH}^- + \text{Cl}^- \rightleftharpoons \text{NH}_4^+ \downarrow \text{Resin} - \text{Cl}^- + \text{OH}^- \quad (7)$$

This speeds up the hydrolysis and shortens the duration of time for formation of hydroxides of $\text{M(IV)}$ and $\text{N(III)}$.

The reaction for hydrolysis associates with anion resin can be written as

$$\text{MCl}_4 + 4\text{Resin} - \text{OH}^- \rightleftharpoons \text{NH}_4^+ + 4\text{Resin} - \text{Cl}^- + \text{M(OH)}_4 \downarrow \quad (8)$$

$$\text{NCl}_3 + 3\text{Resin} - \text{OH}^- \rightleftharpoons \text{NH}_4^+ + 3\text{Resin} - \text{Cl}^- + \text{N(OH)}_3 \downarrow \quad (9)$$

Instead of complete dispersion, the hydroxides of $\text{M(IV)}$ and $\text{N(III)}$ showed a tendency to dehydrate, and formed condensates. (D’Souza et al., 2000) Starting from the second-order
hydrolysis, when the monomer hydroxide has two condensable functional groups, \( f = 2 \), more and more linear condensates are formed. From the third-order hydrolysis, the average functionality of the monomer becomes more than two, \( f > 2 \). This allows cross-linking between linear condensates, and also gelation.

### 2.2. The operation of the method

In an airtight flask containing 200 mL anion-exchange resin (say the DOWEX Monosphere 550A UPW(OH), Dow Chemical Company, Midland, MI), 100-200 mL alcohol, and 10–15 mL of ammonia water, 200-300 mL ethanol solution containing \( \text{MCl}_4 \) (15-25%, w/v), or/and \( \text{NCl}_3 \) (desired%, w/v) are added dropwise with fast stirring. \( \text{NH}_3 \) gas was aerated in the reaction solution to catalyze the hydrolysis. The reaction apparatus is shown as Fig. 1.

The reaction solution is held close to neutral, pH 6-8, by adjusting the speed of addition. After the addition is complete, a solution containing a white suspended precipitate is separated with resin through a glass-sand funnel or a 120 mesh stainless steel screen. The filtrate reacts repeatedly with 50-100 mL fresh anion-exchange resin on a shaker, to continue removal of chlorine and promote further hydrolysis for five or six times until the upper solution does not become clear upon standing and Cl\(^-\) in solution is not detected by More Essay. The final chlorine-free (checked by \( \text{AgNO}_3 \) solution) colloid solution is held idle on a bench for ca. 48–72 h and separated into an upper lightly turbid solution and a lower dense precipitate. The upper, lightly turbid solution is then removed and kept aside for final recovery of all precipitate. Iso-amyl acetate (70–100 mL) is added to the lower dense precipitate solution to make a co-boiling system. A dispersive fine powder is obtained by co-distilling off water absorbed on the colloid and solvents, or azeotropic drying.

![Figure 1. The glass apparatus for preparation of doped nanocrystal by hydrolysis of \( \text{MCl}_4 \) and/or \( \text{NCl}_3 \).](image)

All the exchanged ion-exchange resins are combined and repeatedly washed with fresh solvent to collect any residual precipitate on the surface of the resin. The washed solvent is applied to a short column of ion exchange to remove any remaining chlorine, and is then combined with the upper lightly turbid solution. The resulting dried powder is then
dispersed in the combined solution on a shaker, and a chlorine-free solution containing powder is distilled to separate the solvent and leave behind the hydrolysis product, as a high-dispersively fine powder.

2.3. The drying of nano-crystalline metal oxides

To coupling with the method “P-CNAIE”, a drying method of “azeotropic drying of iso-amyl acetate (AD-IAA)” was presented in 2005 (Zhang, 2005; Yang et al., 2007). Although the solution chemistry method is a significant process to synthesize many nanoscale metal oxides, the drying methods plays a key role in the successful preparation of nanoparticles. If the surface tension is not reduced (Sun & Berg, 2002) during the drying process of precipitate colloids, the colloid particles will aggregate to form rigid gel pieces in the end. It has been known that gels can be formed either through the condensation of polymers or through the aggregation of particles (Diao et al., 2002). According to cluster–cluster growth models, clusters stick together randomly with a certain probability upon colliding (Brinker & Scherer, 1990). It is found that cluster–cluster growth resulting from colliding may occur easily at the drying stage. Although dried gel bulks can be ground to powder, the mechanical force cannot crush them into the powder as fine as the particles synthesized. In addition, the ground powder displays structural features different from the original colloid-precipitated particles. Thus, along with the synthesis process, the drying process is critical in determining the dispersivity and size of the final dried products in the solution chemistry process (Richards & Khaleel, 2001).

Several drying methods, such as supercritical drying (Boujday et al., 2004; Park et al., 2002), freeze drying (Vidal et al., 2005; Shlyakhtin et al., 2000), microwave drying (Hwang et al., 1997), and azeotropic distillation (Hu et al., 1998; Frazee & Harris, 2001; Luan et al., 1998) have been developed to remove the trace of water adsorbed on the surface of colloid particles in order to prevent or reduce aggregation caused by shrinkage of water films between precipitated particles. The water film is formed by adsorbing water on the surface as colloid particles contact. See Scheme 1. Supercritical, freeze, and microwave drying methods reduce agglomerates by eliminating or reducing the surface tension of the water films between colloids. Azeotropic distillation, however, removes the adsorbed water on the surface as colloids disperse in an azeotropic solution, thereby preventing the formation of water films between colloids and aggregation of particles. Some surfactants can prevent colloids from aggregating, but they have a high boiling point and are adsorbed on the dried powder so tightly that it is hard to be removed by the normal drying process.

Scheme 1. Particles come close up as water films between particles shrink at final drying stage.
The synthesis of nano-crystalline metal oxides by solution method is discussed. It is noted that compounds similar to that without azeotropic treatment (Fig. 2A) play the same roles as water molecules, leading to semi-transparent xerogel pieces (Figs. 2A and B). The rigid gel is formed through aggregation (Brinker & Scherer, 1990). Even though the dense precipitate solution is shaken with TCE or n-BuE vigorously, once shaking is stopped, the mixture immediately separates into a colloid precipitate phase and a clear solvent phase, implying that solvents with functional groups –Cl and –O– cannot form stable H-bond with surface water molecules or surface –OH (see Table 1). When the mixtures are dried under an infrared lamp, grinding can disperse wet agglomerates into small particles and dried fine dust is obtained (see Fig. 2H), but the wet agglomerates become hard dried agglomerates without grinding (see Fig. 2G). The sedimentation experiments of colloid particles in other solvents have demonstrated that colloid particles can disperse well in these organic solvents with –OH or/and –COO–, suggesting that there are stable H-bonds between the functional groups and water molecules or –OH on the surface of the colloid.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Molecular Wt.</th>
<th>Characteristics of dried product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g/mL)</td>
<td>Color Agglomerates Hardness</td>
</tr>
<tr>
<td>Ethanol</td>
<td>78 –OH</td>
<td>29.06 +++++ +++++ +++++</td>
</tr>
<tr>
<td>1,4-Butanediol</td>
<td>1.016 235</td>
<td>56.10 +++++ +++++ +++++</td>
</tr>
<tr>
<td>EGMMeE</td>
<td>0.964 –OH,–O–</td>
<td>43.09 ++++ +++++ ++++</td>
</tr>
<tr>
<td>TCE</td>
<td>1.622 4 –Cl</td>
<td>24.02 +++ ++++ ++++</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>0.810 –OH</td>
<td>57.11 +++ +++ +++++</td>
</tr>
<tr>
<td>n-Pentanol</td>
<td>0.815 –OH</td>
<td>71.14 +++ +++ ++</td>
</tr>
<tr>
<td>i-Amyl alcohol</td>
<td>132</td>
<td>–OH 71.14 ++ ++ +</td>
</tr>
<tr>
<td>n-Butyl acetate</td>
<td>0.881</td>
<td>–COO– 84.16 + ++ +</td>
</tr>
<tr>
<td>n-Butyl ether</td>
<td>0.769</td>
<td>–O– 114.23 ++ + + +</td>
</tr>
</tbody>
</table>

Table 1. Characters of products azeotropicly dried by different solvents

The characteristics of the dried products prepared using n-pentanol, i-AmAl (i-Amyl alcohol), or n-BuA as an azeotropic agent have some differences, which, it is assumed, result from the differences in their molecular structures. Although compared with n-pentanol, i-AmAl is a more effective azeotropic agent and the obtained dried product is fluffier. However, the dried product treated by n-BuA is fluffier than that treated by i-AmAl. These results indicate that the improvement of fluffiness results from the molecular steric structure. n-BuA has the highest steric effect. Its two side chains stretch out and cover more surface area of colloid particles to prevent the particles from contacting each other. All of these suggested that the capacity of the azeotropic agent to remove water adsorbed on the surface of the colloid depends not only on its boiling point but also on its ability to replace the surface water molecules and indicated that the dispersivity and fluffiness of the dried product are controlled by the steric effect of the azeotropic agent. In this case, an effective azeotropic drying agent may be called an azeotropic dispersing agent.
and (C) are similar to that without azeotropic treatment (Fig. 2(A)), meaning that they play
the same roles as water molecule, leading to semi-transparent xerogel pieces (Figs. 2(A) and
(B)). Here, the rigid gel is formed through the aggregation (Brinker & Scherer, 1990).

Even though the dense precipitate solution is shaken with TCE or n-BuE vigorously, once
shaking is stopped, the mixture immediately separates into a colloid precipitate phase and a
clear solvent phase, implying that the solvents with functional groups –Cl and –O– cannot
form stable H-bond with surface water molecules or surface –OH (see Table 1). When the
mixtures are dried under an infrared lamp, grinding can disperse wet agglomerates into
small particles and dried fine dust is obtained (see Fig. 2(H)), but the wet agglomerates
become hard dried agglomerates without grinding (see Fig. 2(G)). The sedimentation
experiments of colloid particles in other solvents have demonstrated that colloid particles
can disperse well in these organic solvents with –OH or/and –COO–, suggesting that there
are stable H-bonds between the functional groups and water molecules or –OH on the
surface of the colloid.

Table 1. Characters of products azeotropically dried by different solvents a (Zhang, 2005)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>D. (g/mL)</th>
<th>BP  °C</th>
<th>Groups</th>
<th>Molecular Wt. (no groups)</th>
<th>Color</th>
<th>Agglomerates</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>1.016</td>
<td>235</td>
<td>–OH</td>
<td>29.06</td>
<td>++++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>1,4-Butanediol</td>
<td>0.964</td>
<td>124</td>
<td>–OH,–O–</td>
<td>43.09</td>
<td>++++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>TCE</td>
<td>1.622</td>
<td>122</td>
<td>–Cl</td>
<td>24.02</td>
<td>++++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>0.810</td>
<td>117</td>
<td>–OH</td>
<td>57.11</td>
<td>++++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>n-Pentanol</td>
<td>0.815</td>
<td>138</td>
<td>–OH</td>
<td>71.14</td>
<td>++++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>i-Amyl alcohol</td>
<td>0.881</td>
<td>132</td>
<td>–OH</td>
<td>71.14</td>
<td>++</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>n-Butyl acetate</td>
<td>0.769</td>
<td>142</td>
<td>–COO–</td>
<td>84.16</td>
<td>++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>n-Butyl ether</td>
<td></td>
<td></td>
<td>–O–</td>
<td>114.23</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
</tbody>
</table>

a: Five plus indicates that colour is the deepest, agglomerates are the most, and hardness is the highest.
The trends of dispersivity and fluffiness of the dried products changing with the functional groups and molecular structures of azeotropic solvents are shown in Fig. 3. Some empirical rules for selecting an azeotropic agent are drawn as follows: (1) the solvent molecule should contain at least one oxygen as the H-bond acceptor to form H bonds with the surface –OH of the polymer particle; (2) the H-bond acceptor should locate in the middle of the alkane chain rather than on the terminal so that the alkane can stretch out and cover more surface area; and (3) solvents should have a higher boiling point (~140°C) to reduce the time of azeotropic distillation and the residual amount of azeotropic agent.

Figure 3. The variation of dispersivity and fluffiness of dried products with the groups and molecular structures of azeotropic solvents. (Zhang, 2005)

2.3.2. Iso-amyl acetate as an azeotropic agent (Zhang, 2005; Yang et al., 2007)

The empirical rules and Fig. 3 guide us to find some other new organic azeotropic solvents for both drying and dispersing. Except for 2-hexanol, the other three organic solvents in Table 2 should have similar capacities of drying and dispersing colloid particles. The i-AmA (iso-Amyl acetate) is chosen as azeotropic solvent for it is commercially available and cost-effective among the three solvents. The behaviors of mixtures combining i-AmA with dense precipitate solution are monitored and measured carefully. (Yang et al., 2007).

The analysis of specific surface area of dried product is conducted for further substantiating the effects of i-AmA on the dispersivity. The adsorption isotherms are displayed in Fig. 4. The BET nitrogen surface areas are obtained by applying the BET equation to a relative pressure range of 0.05–0.3 on the adsorption isotherm. It can be seen that the BET surface area increases from 234.75 to 286.43 m²/g as the azeotropic solvent changes from the often-used n-butanol to i-AmA, and the dispersivity of the dried powder increases by 22%. Before the adsorption measurement, the dried product, large pieces of dried agglomerates,
obtained with n-butanol has to be ground. However, the dried product from i-AmA is a highly dispersed powder such that it does not need further grinding, see the TEM images in Fig. 8. The IR spectrum of the dried powder derived from i-AmA shows lower residual organic compounds. XRD patterns and TEM images suggest a high mono-dispersivity of dried powder. These findings indicate that i-AmA is a much better azeotropic agent than other organic solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Structure</th>
<th>Group</th>
<th>MMWt.</th>
<th>b.p.(℃)</th>
<th>D.(g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-Amyl acetate</td>
<td>-COO-</td>
<td>98.19</td>
<td>143</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>n-Amyl acetate</td>
<td>-COO-</td>
<td>98.19</td>
<td>149</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>2-Hexanol</td>
<td>-OH</td>
<td>85.17</td>
<td>140</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>Propyl butyrate</td>
<td>-COO-</td>
<td>98.19</td>
<td>142</td>
<td>0.88</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Structures and physical properties of the selected organic solvents. (Zhang, 2005)

Figure 4. Nitrogen adsorption isotherms for dried Sb-doped SnO₂ powder on the SA3100 made by Becjman-Coulter co. USA. (Yang et al., 2007)
3. The formation of crystal particle in the process of synthesis (Zhang, 2008)

3.1. Functions of anion-exchange resin

The anion-exchange resin accelerates the hydrolysis of metal chloride, which is quite significant for the hydrolysis of the third- and fourth-order hydrolysis of MCl₃ and NCl₃ because the hydrolysis is reversible. However, if the removal of chlorine from hydrolyzate is carried out by washing with water or organic solvent, the hydrolysis will be a slow and a long-term process. When the number of group —OH borne by an atom M or N is more than two, condensation will take place between molecules by inter-molecularly dehydrating, or even gelatination occurs. The gelatination has the polycondensate form, a space network structure. The structure hinders the complete removal of fourth- or even third-order chlorine from gel and, therefore, can not lead to the formation of crystal of metal oxide because the remained chlorines block the condensation. See Scheme 2 A.

Scheme 2. The condensation of hydrolysis product.

The anion-exchange resin has a much higher affinity for Cl⁻ than for OH⁻, if once bonding a chloride ion to itself and a hydroxyl ion is given off to keep a constant concentration of OH⁻. Due to anion-exchange resin can remove Cl⁻ completely from solution, in this case, the hydrolysis product is high purity, which is of great advantage for the condensation of metal hydroxide to form crystal or assume a crystalline structure. See Scheme 2 B.

Another important function of ion-exchange resin is to crush masses of gel to nanoparticles like small balls in the Ball Grinder as the removal of chlorine is carried out on a shaker. In this way, the removal of chlorine from nanometer-sized particles is easy, fast, and efficient, which provides the condensation and crystallization with metal hydroxides bearing high purity. And also the function of the ion-exchange resin pellet analogous to that of ball milling results in a synthesized product with a nano-meter size and a very narrow size distribution.

Moreover, the removal of chlorine by ion-exchange resin instead of by repeated changing fresh solvent is of great importance to be used for accurate and repeated doping and for preparing nanocrystals with a narrow size distribution.

3.2. Functions of ethanol as solution medium

In the synthesis, the absolute ethanol is selected as a solution medium. Generally, metal salts, especially high valence metal salts, hydrolyzes evidently when they are dissolved in water, contributing to a acid reaction solution that cause part precipitation (segregation) of
some metal salts as the doping is conducted. In addition, since a lot of metal salts have fast hydrolytic reaction rate, the use of water as solvent leads to an uncontrollable hydrolysis speed and a great deal of hydrolyzate settlement and agglomeration in a short time, which increases the difficulty of complete removal of chlorine from solid precipitates. A limited amount of water can control the hydrolytic rate under the ammonia as a controller of pH and the strongly anion exchange resin as a donor of \( OH^- \).

The crystallization process in the solution synthesis of nanocrystal of metal oxide is essentially an inter-molecular dehydration process of metal hydroxides. A large quantity of water existing in the reaction system will definitely slow or even stop inter-molecularly dehydrating of the hydroxides. Ethanol, as well known, is born with a strongly hygroscopic property and will pull water away from metal hydroxide to have it form oxide crystal. The water as a carrier of \( OH^- \) between metal salt and ion-exchange resin, see reaction formula (8) and (9), is limited, whereas a large excess of ethanol plays an important role in promoting the crystallization by seizing water molecules from metal hydroxides, especially the promotion effect of ethanol is highly effective as the hydrolysis product is milled to nanometer size by ion-exchange resin balls on a shaker.

3.3. Behaviours of hydrolysis products and the crystal forming process in synthesis

The hydrolysis of many metal salts using the method of “P-CNAIE“ follows some regularity. The stability of hydrolysis product colloid and the solution viscosity are related to the remains of chlorine in the hydrolysis solution, as shown in Fig. 5 and 6, which show the behaviours of the hydrolysate produced from \( SnCl_4 \), doped with \( SbCl_3 \) and from \( ZnCl_2 \) doped with \( SbCl_3 \). The left ones in both figures are the settlement ratio of hydrolysate in 2 h and right ones are the variation of the relative viscosity of solution containing hydrolysate.

We believed that the process of synthesizing nanocrystal undergoes three stages as shown in Fig. 7. At the first stage the sol, or linear molecule, is formed since where the sol is just the product of the first- and second-order hydrolysis of \( MCl_4 \) and \( NCl_3 \), which corresponds to the A to B in left figures of Fig. 5 and 6. The sol particles grow as the third- and fourth-order hydrolysis of \( MCl_4 \) and \( NCl_3 \) occurs and settle down at the bottom of the container at the second stage, corresponding to the line CD in the left figures in Fig. 5 and 6. Whereafter, the obtained precipitate is kept on reacting with ion-exchange resin to remove the remained chlorine and the precipitate re-suspends in ethanol solution at the third stage, as line EF in the left figures in Fig. 5 and 6. Here a further condensation takes place, leading to the contraction inward of particles and formation of nanocrystal in their central core.

Fig. 7 indicates that when the surface of precipitates bears a same material or electric charge (chlorine or water) precipitates become colloids suspending in solution. The phenomena are more evident for high valence metal than low valence metal. But for the alkali rare metal (such as Lanthanum) the hydrolyzate is unstable and readily settles down.

The variation of viscosity is evidence that substantiates the growth of sol in the synthesis of nanocrystal. The increase of the relative viscosity, \( \eta_r \), of reaction solution shows the increase
of the internal friction of hydrolysate, thus indicative of the increase of polymerization degree, or molecular weight, of hydrolysate. The successive ion exchanging does not add the molecular weight but cause the hydrolysate condensate inwards and internal friction decrease, contributing to relative viscosity drop. The inward condensation of particles accompanied by the dehydration between linear polymers is the crystallization process of colloid particles.

Figure 5. The stability of colloid in solution, see the left, and the solution relative viscosity, \( \eta_r \), see the right, vary with [Cl\(^{-}\)] in hydrolysis of SnCl\(_4\) doped with SbCl\(_3\). (The low limit of More Essay is 9×10\(^{-6}\) mol/L for Cl\(^{-}\)).

Figure 6. The stability of colloid in solution, see the left, and the solution relative viscosity, \( \eta_r \), see the right, vary with [Cl\(^{-}\)] in hydrolysis of ZnCl\(_2\) doped with SbCl\(_3\). (The low limit of More Essay is 9×10\(^{-6}\) mol/L for Cl\(^{-}\)).

Figure 7. The three stages in the hydrolysis process of MCl\(_4\) (or mixed with NCl\(_3\)).