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Benzyl alcohol-based synthesis of oxide nanoparticles: the perspective of S_N1 reaction mechanism†

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In this paper, we describe a class of benzyl alcohol-based reactions for the synthesis of a series of inorganic oxide nanoparticles. Benzyl alcohol served as both the solvent and the reagent to interact with various metal chlorides for the synthesis of a series of metal oxides and compound oxides. Typical metal(IV) oxides, like TiO_2, metal(III) oxides, like Fe_2O_3, and metal(II) oxides, like ZnO, with uniform size and special dispersibility, have been prepared through these reactions. The reaction can be illustrated from the perspective of S_N1 reaction mechanism attributed to the easier formation of benzyl carbocation and unique reactivity of benzyloxy group with nucleophilic agents. By adjusting the experimental conditions, it was found that this type of reaction is available for the synthesis of many inorganic oxides.

Introduction

As has been well-known, alcohol is one of the most widely used organic solvents in many fields attributed to its low cost, easy accessibility, low biotoxicity, and other versatile physicochemical properties. Recently, alcohol-mediated synthesis of nanomaterials has attracted a lot of attention.[1–9] According to different criteria, such as the number of hydroxyl groups, the type of alkyl group, or the form of α-carbon atom, alcohols can be classified into many categories, such as primary alcohol, secondary alcohol, tertiary alcohol, polyols, aromatic alcohols, *etc.* Depending on their diverse molecular structures, all kinds of alcohols usually exhibit considerably distinct properties. In a variety of alcohols, there exist some special kinds of alcohols, which present stronger carbon–oxygen dissociative tendency attributed to their better stability of carbocation derived from more effective distribution of positive charge in non-hydroxyl group. In general, this type of alcohols included tertiary alcohols, 2-en-1-ols and certain alcohols containing heteroatoms.[10–12] Due to better forming ability of carbocation, compared to common aliphatic alcohols, these alcohols are easier to form hydroxyl leaving group to provide oxygen sources to metal ions for the generation of metal oxides. In organic chemistry, this type of alcoholic reaction involving the generation of carbocation intermediates and the substitution of hydroxyl group by other nucleophilic groups was named as S_N1 reaction.[13] The typical reaction case is their reaction with haloid acid, such as Lucas reagent, to generate alkyl halide and water, in which chloride ions act as nucleophilic agent to replace hydroxyl group. Starting from the case, it is easy to suggest, another type of substance that can be considered as Lewis acid, such as metal chloride, chloride alkoxides, with similar functional groups with haloid acids may play the similar role and be able to react with this type of alcohol, to generate metal oxide instead of water in the aforementioned reaction with haloid acid. Obviously, the reaction is unique and attractive. First of all, metal chlorides are cheap and easy to access in most chemical labs. Second, some metal chlorides easy to hydrolyze can be well dissolved by alcohol for the more clean synthesis and structure control of the desired products. In addition, in place of the effect of the proton of water provided, carbocation intermediates may play the role of capping agent to avoid the introduction of other surfactants for the simplification of reaction system.[14,15] In fact, this type of reaction can also be deemed as alcoholysis reaction involving the dissociation of carbon–oxygen bond, although different from conventional alcoholysis reaction involving the dissociation of oxygen–hydrogen bond. Herein, in order to better classify this reaction and present the difference from common aliphatic alcohol-mediated reaction, we will adopt the concept of S_N1 reaction mechanism that has been well-established in organic chemistry to describe the reaction and display their uniqueness. However, it has to be mentioned in here, S_N1 can only be a relative concept to S_N2 because a clear-cut distinction between the two mechanisms is impossible due to a gradual transformation of an S_N2 into an S_N1 mechanism.[16,17]

In our work, benzyl alcohol (B_ZOH), a special 2-en-1-ol, was employed as a representative alcohol to react with metal chlorides. Benzyl alcohol is a kind of aromatic alcohol with benzene

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ring on α-carbon. Due to the direct bonding of benzene ring with α-carbon, the positive charge of carbocation can be effectively distributed onto large benzyl group attributed to p–π conjugation to improve the stability of carbocation and thus to enhance the forming ability of carbocation intermediate. Consequently, in contrast to common alcohol, benzyl alcohol is easier to ionize and attacked by a nucleophilic agent. Metal chlorides are cheap and common precursors without oxygen, and thus can provide metal sources while to exclude the interference of oxygen on the synthesis of oxides for better study of reaction mechanism.

As we know, oxide nanomaterials have been studied for decades attributed to their promising applications in multiple fields, and many solution-based methods have been employed for their synthesis.[18–21] Alcohol-based synthesis is one of the most used methods, in which oxides were usually obtained *via* the thermolysis of organometallic precursors. However, little attention was paid to the reaction of metal chlorides and alcohol for the preparation of oxides. As a matter of fact, the reaction between metal chlorides and alcohols had been discovered decades ago. Vioux *et al.* reported the reactions of some high-valence metal chlorides with benzyl alcohol and tertiary alcohol for the preparation of several oxides, such as TiO_2, SiO_2, Al_2O_3, *etc.*[22–24] Subsequently, Niederberger *et al.* further developed this approach for the preparation of other high-valence metal oxides and compounds. They especially paid more attention to so-called "benzyl alcohol routes".[25,26] In this route, benzyl alcohol was used as the solvent to react with metal chlorides,[27–30] metallic alkoxides, acetates, acetylacetonates and other metal organic complexes to fabricate various metal oxides.[31–34] However, in above-mentioned investigations about the reaction of benzyl alcohol and metal chlorides, only some high-valence metal chlorides were involved, and the reaction of low-valence metal chlorides with benzyl alcohol were rarely mentioned. In this work, following their steps, we continue to employ benzyl alcohol as the solvent attributed to its special reactivity, good thermal stability, low biotoxicity and excellent ability to dissolve inorganic salts, to investigate their reaction with not only high-valence but also low-valence metal chlorides so as to expand the application area of the reaction as well as to better study and classify the reaction mechanism. It is worth to say that benzyl alcohol-based reaction with metal chlorides is just a representative of one type of alcohol-based reactions involving alcoholic solvent with strong ionization tendency of hydroxyl group that can directly supply oxygen sources. Some other alcohols with the similar properties could also play similar role. For example, earlier than this work, tertiary alcohol-based reactions with metal chlorides for the synthesis of oxides have also been investigated by us.[35] It was found that tertiary alcohol can also supply oxygen sources for the preparation of metal oxides. However, different from benzyl alcohol-based synthesis, in tertiary alcohol-based synthesis, E1 reaction was found to be the leading reaction to induce the formation of metal oxides because tertiary carbocation is easy to eliminate a proton and become an alkene. The elimination reaction of benzyl carbocation is hard to happen due to the better stability of benzene rings. Therefore, in benzyl alcohol, in place of E1 reaction, S_N1 reaction became the first choice. This paper just wants to show the reasonableness and applicability of S_N1 reaction mechanism in describing this kind of benzyl alcohol-based synthesis and better broaden this concept from organic synthesis to inorganic synthesis, although the concept had been mentioned roughly by others.[36–38] Distinct to some previous reports by other researchers, we successfully broaden the application range of this kind of reaction from high-valence metal chlorides to low-valence metal chlorides and make it a more available synthetic strategy for the preparation of metal oxides with special structure, morphology and properties.

Results and discussion

As was investigated, the reaction activities of these metal chlorides with different kind of alcohols were quite different. Even at room temperature, the dissolving phenomena also present the diversity. For example, $TiCl_4$ can be mildly dissolved by primary alcohol at room temperature to obtain light yellow transparent solution, but when dropped into secondary alcohol, like cyclohexanol, it will immediately make the solution turbid and viscous, which can become clear again by heating, and when added into tertiary alcohol or benzyl alcohol, violent reaction will occur and there even appeared solid precipitates and suspensions. From these phenomena, we can see that different types of alcohols exhibit considerably different reactivity with metal chlorides, and generally tertiary alcohol and benzyl alcohol are more active than secondary alcohol, which is more active than primary alcohol.

By increasing the temperature, the reactivity of benzyl alcohol can be further enhanced due to endothermic nature of carbon–oxygen dissociative reaction. Based on this characteristic, by adjusting the reaction temperature, many metal chlorides were found to be able to react with benzyl alcohol. Herein, we will take several typical examples to describe the reaction and show its availability in the synthesis of different metal oxides.

The reactions of metal(IV) chlorides and benzyl alcohol

In the experiments, we firstly investigate the reactions of several tetravalent metal chlorides, such as $TiCl_4$, $SnCl_4$, $SiCl_4$, in benzyl alcohol. As we know, metal tetrachloride was usually thought of as molecular compounds with intermolecular van der Waals' force. Attributed to unoccupied atomic orbital of metal and strong polarization effects, high-valence metal ions were attacked more easily by nucleophilic agent and present strong reactivity. In protic solvents, such as water, alcohol, amine, the chloride ions are easy to be replaced by other nucleophilic groups.[39,40] In the case of benzyl alcohol, $TiCl_4$, $SnCl_4$ and $SiCl_4$ may react with benzyl alcohol to firstly generate corresponding ester and then form oxides. The reaction of $SnCl_4$ and benzyl alcohol, and $TiCl_4$ and benzyl alcohol have been intensively investigated by Niederberger *et al.*[27,29,41]

Similar experiments were also carried out by us. It was found that ultra-small crystalline tin dioxide (Fig. 2a) and titanium dioxide nanoparticles (Fig. 2b–e) can be synthesized in relatively low temperature through the reaction. Fig. 1 showed their XRD patterns. However, in the method, as-prepared TiO_2 particles tended to form the aggregates adhered by a lot of organics, as showed in Fig. 2b and c. From HRTEM image presented in the inset of Fig. 2b, we can see some particles have even grown into one-dimensional structures. These aggregates were very hard to dissociate into individual particles due to the difficulties in the removal of thick organic coating although the aggregate as a whole can present good dispersion in many solvents. In order to obtain monodisperse TiO_2 particles, we investigated the features of TiO_2 products in some mixed solvent reaction system, such as DCMA–BzOH, acetone–BzOH, ethanol–BzOH, but the phenomena of particles aggregation cannot be eliminated. However, it was found that the introduction of amines or amides can obviously improve the monodispersion of TiO_2 nanoparticles. For example, by introducing dodecylamine into this reaction system, we found TiO_2 nanoparticles show much better monodispersion than for pure benzyl alcohol in polar solvent like DMF (Fig. 2d). It was also found that TiO_2 particles synthesized in certain mixed reaction systems can be even well dispersed in water, such as for the products obtained from *n*-pentanol–BzOH (ESI Fig. S1†). Furthermore, when we use NMP to dissolve $TiCl_4$ firstly and then add benzyl alcohol, a large amount of quasi-one-dimensional structure of TiO_2 can be obtained (Fig. 2e). As investigated by us, crystalline TiO_2 can even be synthesized in benzyl alcohol at 80 °C within several hours, which appear to be much faster than common aliphatic alcohol. A series of control experiments were done to investigate the differences of the reactivity between common aliphatic alcohol and benzyl alcohol. It was found that TiO_2 cannot be generated in *n*-butanol within 12 h when the temperature is 80 °C. Even at 100 °C for 12 h, TiO_2 colloids cannot still be obtained, although Woodfield *et al.* report that TiO_2 can be formed in ethanol by baking at 87 °C for 3 days.[42] When using *n*-octanol as the solvent, at 140 °C, TiO_2 particles can be generated but with much bigger size. As was investigated, TiO_2 obtained from benzyl alcohol are typically nanoparticles with the diameter of several nanometers, and the diameter of TiO_2 particles from *n*-octanol can achieve several hundreds of nanometers (ESI Fig. S2†). Evidently benzyl alcohol played a role in limiting the size and controlling the morphology of nanoparticles may be attributed to carbocation effect. In addition, secondary and tertiary alcohol appear to play similar roles in controlling the size of TiO_2 particles. $SiCl_4$ can also react with benzyl alcohol to form a transparent gel, and by dilution with ethanol and centrifugation, we can collect white amorphous powders. EDX indicated the products mainly contain silicon and oxygen, which should correspond to amorphous silica.

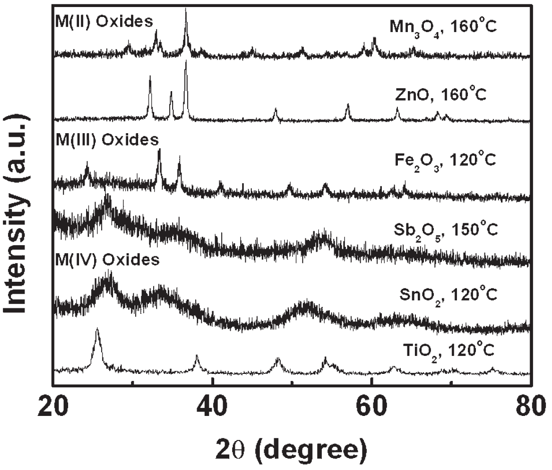

Fig. 1 XRD patterns of as-prepared different oxide nanoparticles under different conditions.

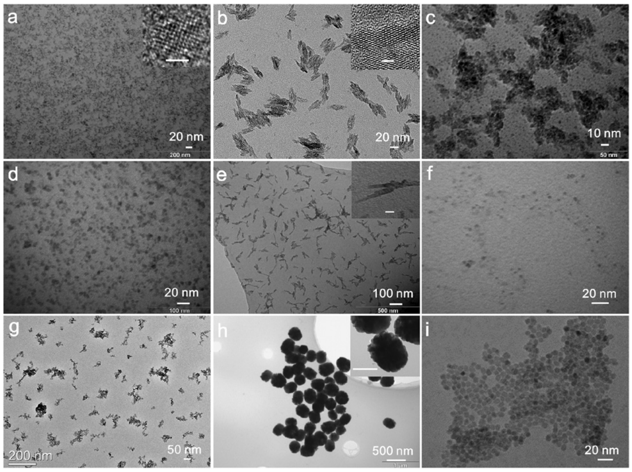

Fig. 2 TEM and HRTEM images of as-prepared oxide nanoparticles, (a) SnO_2 synthesized at 120 °C, insert: scale bar is 2 nm; (b) TiO_2 synthesized at 120 °C in the mixed solvent of DCMA–BzOH, insert: scale bar is 2 nm; (c) TiO_2, 120 °C, acetone–BzOH; (d) TiO_2, 120 °C, dodecylamine–BzOH; (e) TiO_2, 120 °C, NMP–BzOH, insert: scale bar is 5 nm; (f) Fe_2O_3, 120 °C; (g) Sb_2O_5, 150 °C; (h) ZnO, 180 °C, dodecylamine–BzOH, insert: scale bar is 200 nm; (i) Mn_3O_4, 160 °C, dodecylamine–BzOH.

The reactions of metal(III) chlorides and benzyl alcohol

Compared to tetravalent metal chlorides, the reactivity of trivalent metal chlorides with benzyl alcohol seems to be a little weaker due to weaker polarization effect of metal ions. In the experiments, some typical trivalent metal chlorides, such as $FeCl_3$, $SbCl_3$, $AlCl_3$, were used to react with benzyl alcohol. It is found that, in specified temperatures, the reactions can occur. Among them, $FeCl_3$ is relatively easier to react with benzyl alcohol to generate crystalline metal oxides maybe attributed to better low-temperature crystallization performance of iron oxide than alumina and stronger polarization force of Fe^{3+} than Sb^{3+} for the alcoholysis. In this reaction, we can also consider $FeCl_3$ as a kind of Lewis acid, and benzyl alcohol as Lewis base owing to better stability of carbocation and thus easier leaving of hydroxyl group. As a result of strong electrophilicity of Lewis acid, $FeCl_3$ can interact with hydroxyl group to help its leaving from benzyl group, and then chloride ions can attach to benzyl group to stabilize benzyl carbocation, which can also be supported by the formation of FeOCl (ESI Fig. S3†). Further substitution reaction will result in the formation of stable ferric oxides. XRD pattern showed the crystalline α-Fe_2O_3 was formed, and electrospray ionization-mass spectra (ESI-mass) and gas chromatography-mass spectra (GC-MS) both indicated the generation of benzyl chloride in the reaction solution. Some control experiments were also done. It was found that common aliphatic alcohols have weaker reactivity with $FeCl_3$ than benzyl alcohol. For example, $FeCl_3$ cannot nearly react with *n*-butanol at 80 °C within 12 h, but for benzyl alcohol, the reaction is easy to proceed and a lot of FeOCl precipitates can be formed at the bottom of the glass bottle (ESI Fig. S3†). We further investigated the influence of the temperature on the phase and morphology of the products in benzyl alcohol. When the temperature was increased to 100 °C, instead of FeOCl, Fe_2O_3 will be the dominant products and small Fe_2O_3 nanoparticles will be generated. Further increased reaction temperature and time will result in the growth and aggregation of Fe_2O_3 nanoparticles. In addition, we also found that, in high $FeCl_3$ concentration, high reaction temperature and long reaction time can result in the polymerization of benzyl alcohol solution, which was probably attributed to the formation of polybenzyls by hydrogen–chlorine elimination of benzyl chloride under the assistance of $FeCl_3$.[43,44]

The reaction of $SbCl_3$ and benzyl alcohol to obtain pure antimony oxide is more difficult than $FeCl_3$. As was investigated, when the concentration of precursor $SbCl_3$ is high, antimony oxychloride is the preferred product. XRD pattern indicate that $Sb_4O_5Cl_2$ phase can be formed when the concentration of $SbCl_3$ is high (ESI Fig. S3†). As-obtained $Sb_4O_5Cl_2$ particles are obviously large and have a poor dispersion in the solvent. With decreasing the concentration of $SbCl_3$, antimony oxides will be gradually the main products. It was found that, when the reaction temperature was set at 150 °C and the concentration of $SbCl_3$ is 0.02 M, and antimony oxide can be formed. XRD pattern indicated that antimony trichloride was oxidized into Sb_2O_5 but with poor crystallinity (Fig. 1). HRTEM was hard to obtain clear crystal lattice images. Until the temperature was increased to 180 °C, the crystallinity will be improved a little (ESI Fig. S4†). $AlCl_3 \cdot 6H_2O$ can also react with benzyl alcohol to generate a transparent gel. Through dispersing and diluting the gel with ethanol and then collecting the products by centrifugation, we can obtain white products. EDX results and XRD pattern indicate that the products should be amorphous alumina.

The reactions of metal(II) chlorides and benzyl alcohol

It is easy to find that, in all above-mentioned chemical reactions for the generation of corresponding oxides, metal ions almost have high valence states, trivalent or above, which impart them strong ability to grasp oxygen attributed to high ion charge. But for metal ions with lower valence state, such as divalent ions, the ability will become weaker and make the reaction proceed more difficultly. In order to further broaden the application range of this kind of reaction in the synthesis of inorganic oxides, we continue investigating some reactions between benzyl alcohol and some divalent metal chlorides with obvious features of ionic compounds, like $ZnCl_2$, $CoCl_2$ and $MnCl_2$. It is found that corresponding metal oxides were hard to form merely through simple reaction of benzyl alcohol and metal chlorides. Even at 180 °C for 24 h, we cannot obtain metal oxides, probably because the weaker interaction between low-valence metal ions and oxygen is easy to be broken by chloride ions. Starting from this opinion, we try to affect the interaction through introducing some other chemicals, such as amines. In our experiments, dodecylamine was used to play this role, and finally it was found that, in this situation, chloride ions of metal chlorides can be replaced by oxygen and thus result in the formation of metal oxides. It is really an interesting experimental phenomenon. We thought that, in this process, on the one hand, amine can coordinate with metal ions to weaken the interaction of metal ions and chloride ions; on the other hand, amine can capture proton and chloride ions to form amine hydrochloride thus to facilitate the combination of metal ions with benzyloxy groups. However, it is worthwhile to note that, amine is not the only reason that render the generation of metal oxides, because in the case of $ZnCl_2$, in the same conditions, when using ethylene glycol or *n*-octanol as solvent, we cannot obtain metal oxides at all, which indicate the uniqueness of benzyl alcohol in providing oxygen sources. GC-Mass spectrometry cannot detect benzyl chlorides in amine-involved reaction, which, however, can be found in the reaction of benzyl alcohol alone and zinc chlorides, which indicate that amine seem to play a role to trap chlorine. The composition of the liquid products was complicated maybe attributed to the reaction of benzyl alcohol and amines because we found that a lot of hydroxyl groups of benzyl alcohol have been replaced by amino groups through GC-MS. Therefore, it was thought that in this reaction, the formation of metal oxides should still be attributed to the easier dissociation of carbon–oxygen bonds and the stabilization of benzyl carbocation by the attachment of nucleophilic agent onto benzyl group. In addition, when amine was introduced into this reaction, the polymerization of benzyl alcohol did not occur any longer even under high temperature and high precursor concentration, which indirectly prove our previous deduction about the polymerization resulting from the hydrogen–chlorine elimination between benzyl chlorides. From TEM images, we can see ZnO particles appeared to present much bigger sizes than other oxides, but further high-magnification SEM images indicated these particles are still composed of small-sized particles, which will be elaborated in the following specific case of amine-assisted synthesis of ZnO. Similarly, Mn_3O_4 and Co_3O_4 nanoparticles can also be synthesized through amine-assisted benzyl alcohol route (Fig. 2i and ESI Fig. S5†), and cannot be obtained in the absence of amine.

In the same way, this reaction could also be used to prepare some compound oxides, such as antimony-doped tin oxide (ATO), which have been investigated by Niederberger *et al.*[45] We also did some investigations in this topic. $SnCl_2 \cdot 2H_2O$ and

$SbCl_3$ were employed as the precursors. It was found that small ATO nanoparticles can be formed (ESI Fig. S6†). In the preparation process, we found that the addition of $SbCl_3$ can accelerate the reaction obviously and facilitate the generation of compound oxides. Here, the works will not be described in detail, this is just a small showing to prove the wide applicability of this method in materials synthesis.

Case analysis: amine-assisted shape control of ZnO nanostructures

As was above-mentioned, we have synthesized several typical divalent metal oxides by introducing dodecylamine into this reaction system. It was found that dodecylamine cannot only facilitate the formation of metal oxides but can also help the control of the morphology of oxides. For example, in the case of ZnO synthesis, by adjusting the concentration of amine, the structures of ZnO can be well tuned.

Fig. 3 showed SEM images of ZnO products under different amine concentrations. When without amine introduced, ZnO cannot be obtained even at 200 °C. A small amount of amine can obviously change the kinetics of this reaction. Even at a low amine concentration, such as 0.005 mL mL^{-1} (volume ratio of amine to benzyl alcohol), ZnO can be generated, but with a low yield ratio. Fig. 3a showed the products have irregular structure. When increasing the amine concentration to 0.01 mL mL^{-1}, the yield of ZnO can dramatically increase, and the products have changed into uniform spheres but still with a small amount of irregular bulks (Fig. 3b). High-magnification SEM images show these ZnO spheres are composed of small nanoparticles. In Fig. 3c, we can find some hollow spheres with outside layers consisting of small nanoparticles. Further increasing the concentration to 0.05 mL mL^{-1}, the morphology of ZnO products did not change a lot. Spherical assembled structures have been the dominant products. From Fig. 3d and 3e, we can see the products are very uniform and clean, and also composed of small nanoparticles. When the amine concentration was increased to 0.1 mL mL^{-1}, the morphology of the product changed dramatically and uniform brick-like structures were formed. From the magnified images (Fig. 3g), we can see they have rough surfaces. It was thought that this kind of structure may be induced by the etching of amine hydrochlorides. There might be a dynamic process of generation and dissolution of ZnO attributed to high concentration of amine, which was also supported by subsequent experiments. Because when the amine concentration was further increased to 0.25 mL mL^{-1}, the formation of ZnO became difficult obviously. Even sometimes, ZnO cannot be generated within 48 h at 180 °C. It apparently violates the rule that we try to obtain that is increasing amine concentration will result in increasing yield ratio of ZnO. In fact, when the amine concentration is high enough, the formation of ZnO, however, becomes more difficult. Hence, we think that ZnO may be dissolved by certain substances. In consideration of the inherent dissolving ability of amine hydrochlorides to ZnO, we thought the amine hydrochlorides should be the intermediate products of this synthetic reaction. The formation of brick-like structure with rough surfaces should be attributed to the etching of amine hydrochlorides on the surface of ZnO. From Fig. 3h and 3i, we can see that in high amine concentration, the products are some hexagonal pillars with larger size than for low amine concentration. Grounded on the same consideration, we think that only large enough particles can stand the etching of high-concentration amine hydrochlorides, and small particles are easily dissolved, and thus the products are generally large. Therefore, in this case, the formation of ZnO should be mainly attributed to the roles of amine in grasping protons to facilitate the combination of zinc ions and benzyloxy groups and in stabilizing benzyl carbocation by the attachment of amino group onto carbocation. In addition, the easy dissociation of carbon–oxygen bonds in benzyloxy groups was an important factor that resulted in the formation of ZnO.

Fig. 4 showed the photoluminescence (PL) spectra of as-prepared ZnO particles with different morphologies. It was found

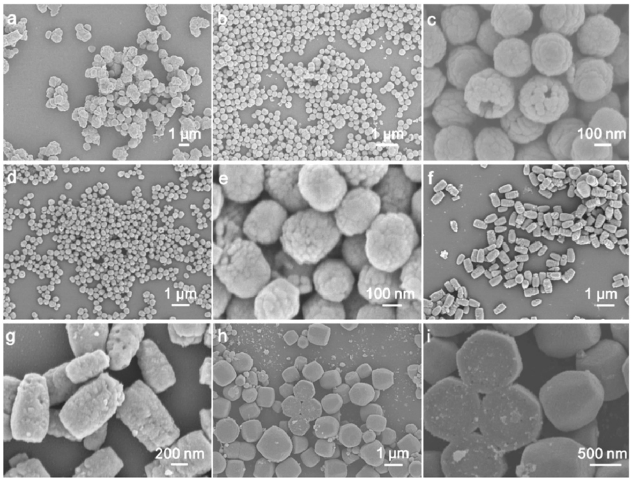

Fig. 3 SEM images of ZnO nanostructures through benzyl alcohol-mediated synthesis in different concentrations of dodecylamine. (a) C_A = 0.005 mL mL^{-1}; (b, c) C_A = 0.01 mL mL^{-1}; (d, e) C_A = 0.05 mL mL^{-1}; (f, g) C_A = 0.1 mL mL^{-1}; (h, i) 0.25 mL mL^{-1}.

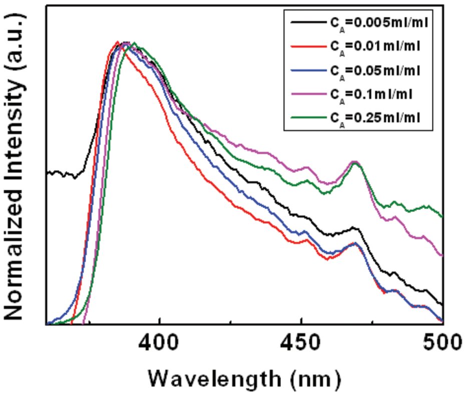

Fig. 4 Photoluminescence spectra of as-prepared zinc oxide nanostructures, and C_A represents the concentration of dodecylamine.

that the strongest emitting peaks of PL spectra slightly blue shift from 391 nm to 384 nm and another emitting peak of 469 nm basically keep unchanged, which may be attributed to the size and assembly effect of ZnO. Except for the lowest amine concentration, under other amine concentrations, we can find that, with amine concentration decreasing, the strongest peak of PL spectra move towards short wavelength gradually, which indicated PL spectra of ZnO can be controlled by adjusting experimental parameters.

Then the photocatalytic performance of as-prepared hollow ZnO nanoparticles synthesized under the amine concentration of 0.05 mL mL^{-1} was also investigated in consideration of the large surface area and good conductivity of such assembled structures (Fig. 5). It was found that methylene blue (MB) can nearly be degraded completely within 40 min in the presence of as-prepared ZnO particles without any heat treatment. The performance appeared to be better than many other ZnO nanostructures reported by others.[46,47] The better photocatalytic activities of as-prepared ZnO particles might arise from the special synthetic method-induced structures, crystallinity and even possible doping effects. For comparison, we also investigated the degradation of methylene blue in the presence of P25 and without catalyst. It was found that, under the same conditions, when without catalyst, the degradation of methylene blue is not obvious within 40 min. Although as-prepared ZnO particles have a poorer photocatalytic activity in contrast to P25, the performance could be expected to improve by further treatment in the future work. In a word, the above-mentioned result indicated that as-prepared ZnO particles through our method have good product quality and can present good photocatalytic activity in aqueous media, which could be directly applied for the degradation of some organic pollutants.

Reaction mechanism

A lot of experiments have indicated that the reactivity of benzyl alcohol with metal chlorides is much higher than common aliphatic alcohol. For the reactions without amines introduced, we have confirmed the generation of benzyl chloride by ESI-mass spectrometry. GC-mass spectrometry can confirm several main liquid products in benzyl alcohol solution, which include benzyl chloride, benzyl ether, and a small amount of benzaldehyde (ESI Fig. S7†). Benzyl chloride should result from the substitution of chloride ions for oxygen-containing group bonding with benzyl group. Benzyl ether might be derived from the dehydration of benzyl alcohol under the help of Lewis acids or other approaches, such as ether elimination proposed by Niederberger *et al.*,[38] but actually the easier dehydration of benzyl alcohol and easier ether elimination of alkoxides can both arise from the easier dissociation of carbon–oxygen bonds in benzyloxy group because the control experiments indicated that the reactions of common aliphatic alcohol with metal chlorides were much more difficult than benzyl alcohol, which means that dehydration or ether elimination of common aliphatic alcohol or their alkoxides were also more difficult than for benzyl alcohol or benzyloxides uneder same conditions, which can also be supported by the easier decomposition of tertiary alkoxides than primary alkoxides attributed to better stability of tertiary carbocations.[15,35] Based on these results and the unique properties of benzyl alcohol as well as a series of control experiments, we think that the key reaction that results in the formation of oxides can be classified as one category regardless of what happena in the reaction process because the formation of oxides is totally grounded on the same feature, the easier leaving of oxygen-containing group bonded with the benzyl group. The real reaction process may be complicated and distinct for different metal chlorides (ESI Fig. S8†), but should not impede their incorporation into S_N1 reaction due to the easier formation of benzyl carbocation in benzyloxy group and the final substitution of nucleophilic agents, such as chloride ions, amino group, benzyloxy groups, for hydroxyl group or –O–M–O– group (M represents metal). A proposed simplified S_N1 reaction mechanism is presented in Fig. 6 to show the formation process of metal oxides.

In this method, as-prepared oxide particles basically maintain small and uniform size and can present good dispersion in some polar solvents, such as DMF, NMP. However, some side reactions that may involve carbocation effect often occur to affect the quality of products, such as the easy formation of

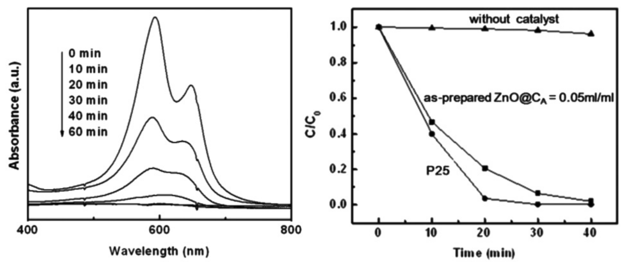

Fig. 5 (a) UV–Vis spectra of methylene blue (MB) solution with the photocatalyst ZnO before and after various durations of UV irradiation; (b) photocatalytic performances of the sample under UV irradiation under different catalysts: without catalyst, as-prepared ZnO particles, P25.

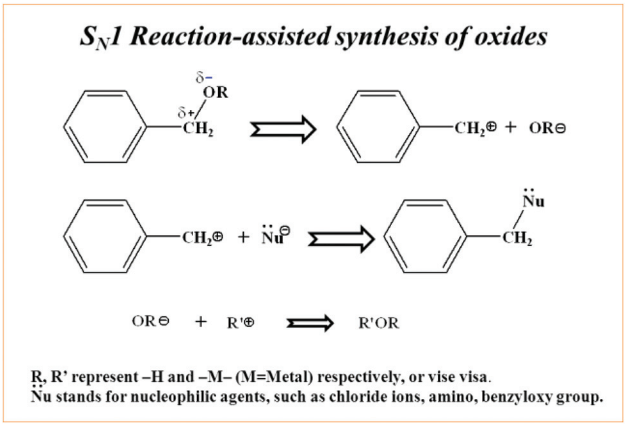

Fig. 6 Proposed S_N1 reaction mechanism in the reactions of benzyl alcohol and metal chlorides for the synthesis of metal oxide nanoparticles.

aggregates coated by a lot of organics (ESI Fig. S9†).[14,48] Even worse, in high precursor concentration, high-temperature or long-time reaction usually lead to the generation of polymer. Thus, in order to enhance the quality of the products, the aggregation and polymerization process should be avoided as much as possible. In the experiments, we found that the polymerization can be partly inhibited by decreasing the concentration of metal chlorides, reaction temperature and time. But obviously, it is not a good solution to this problem in consideration of low input–output efficiency in low precursor concentration so as to a realize high-yield low-cost synthesis. Thus, we propose a new approach to solve this problem while to broaden the application range of this reaction so as to make it suitable for the synthesis of more metal oxides. We introduced dodecylamine into benzyl alcohol solution. Dodecylamine has a higher boiling point and good compatibility with benzyl alcohol, and meanwhile its hydrochloric salt has a good solubility in many organic solvents due to long carbon chain which is beneficial for the subsequent removal, and thus the mixed solvent system can raise applicable reaction temperature while avoiding the aggregation of nanoproducts and the high-temperature polymerization of benzyl alcohol in the presence of metal chlorides due to the generation of benzyl chlorides to achieve better monodispersity of nanoproducts (Fig. 2d, 2i and 4). The reaction system has been proved to be feasible in the cases of ZnO, Co_3O_4, Mn_3O_4 and TiO_2, as other oxides were not investigated yet, and also the morphology of the products can be controlled by adjusting the concentration of amine, which have been described in the case of ZnO, and we believe that it should be a general method for the synthesis of metal oxides. In addition, sulfur powder can be also dissolved by dodecylamine and benzyl alcohol under mild temperature, and thus the synthesis of metal sulfide in this reaction system can also be expected in the future.

Conclusions

In conclusion, in this paper, we have successfully extended the reaction of benzyl alcohol with metal chlorides from high-valence metal chlorides (tetravalent or above) with the features of molecular compounds to low-valence metal chlorides (divalent and trivalent) with the features of ionic compounds and make the reaction suitable for the synthesis of more metal oxide nanoparticles. Metal chlorides are one of the most common low-cost precursors in the chemical lab, and the reactions between benzyl alcohol and metal chlorides can basically be carried out directly under atmosphere in a relatively low temperature, which will largely simplify the synthetic process, decrease the cost and favor large-scale production of different oxides and compound oxides. Furthermore, we think about the reaction kinetics from a novel perspective. These reactions can be explained from the perspective of an S_N1 reaction mechanism. The novel synthetic method will be beneficial for the acquirement of new materials with new phases, structures and properties. As-prepared metal oxides can present good application potential in many fields, such as lithium ion batteries, photovoltaics, photocatalysis, sensors, as well as functional fillers of polymer composites due to their good dispersion in polar solvents, such as DMF. In addition, the perspective of S_N1 mechanism involving carbocation intermediate can bring us new and further inspiration for the synthesis of more inorganic materials and is meaningful in science as well as in engineering.

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Notes and references

1 Y. Y. Liang, H. L. Wang, J. G. Zhou, Y. G. Li, J. Wang, T. Regier and H. J. Dai, *J. Am. Chem. Soc.*, 2012, **134**, 3517–3523.
2 Y. N. Xia, Y. J. Xiong, B. Lim and S. E. Skrabalak, *Angew. Chem., Int. Ed.*, 2009, **48**, 60–103.
3 X. C. Jiang, Y. L. Wang, T. Herricks and Y. N. Xia, *J. Mater. Chem.*, 2004, **14**, 695–703.
4 M. J. Hu, Y. Lu, S. Zhang, S. R. Guo, B. Lin, M. Zhang and S. H. Yu, *J. Am. Chem. Soc.*, 2008, **130**, 11606–11607.
5 M. J. Hu, B. Lin and S. H. Yu, *Nano Res.*, 2008, **1**, 303–313.
6 F. L. Jia, L. Z. Zhang, X. Y. Shang and Y. Yang, *Adv. Mater.*, 2008, **20**, 1050–1054.
7 W. Chen, L. L. Li, Q. Peng and Y. D. Li, *Nano Res.*, 2012, **5**, 320–326.
8 Z. F. Bian, J. Zhu, J. G. Wang, S. X. Xiao, C. Nuckolls and H. X. Li, *J. Am. Chem. Soc.*, 2012, **134**, 2325–2331.
9 N. Pinna and M. Niederberger, *Angew. Chem., Int. Ed.*, 2008, **47**, 5292–5304.
10 M. M. Toteva and J. P. Richard, *J. Am. Chem. Soc.*, 1996, **118**, 11434–11445.
11 J.-L. M. Abboud, I. Alkorta, J. Z. Davalos, P. Müller, E. Quintanilla and J.-C. Rossier, *J. Org. Chem.*, 2003, **68**, 3786–3796.
12 H. Grützmacher and C. M. Marchand, *Coord. Chem. Rev.*, 1997, **163**, 287–344.
13 L. G. Wade Jr., *Organic Chemistry*, Pearson/Prentice Hall, Upper Saddle River, New Jersey, USA, 6th edn, 2005.
14 J. M. Szeifert, J. M. Feckl, D. Fattakhova-Rohlfing, Y. J. Liu, V. Kalousek, J. Rathousky and T. Bein, *J. Am. Chem. Soc.*, 2010, **132**, 12605–12611.
15 H. Kominami, J.-I. Kato, Y. Takada, Y. Doushi, B. Ohtani, S.-I. Nishimotoa, M. Inoue, T. Inui and Y. Kera, *Catal. Lett.*, 1997, **46**, 235–240.
16 T. B. Phan, C. Nolte, S. Kobayashi, A. R. Ofial and H. Mayr, *J. Am. Chem. Soc.*, 2009, **131**, 11392–11401.
17 K. S. Peters, *Chem. Rev.*, 2007, **107**, 859–873.
18 B. L. Cushing, V. L. Kolesnichenko and C. J. O'Connor, *Chem. Rev.*, 2004, **104**, 3893–3946.

19 V. Polshettiwar, B. Baruwati and R. S. Varma, *ACS Nano*, 2009, **3**, 728–736.

20 J. Park, J. Joo, S. G. Kwon, Y. Jang and T. Hyeon, *Angew. Chem., Int. Ed.*, 2007, **46**, 4630–4660.

21 A. K. Ganguli, A. Ganguly and S. Vaidya, *Chem. Soc. Rev.*, 2010, **39**, 474–485.

22 A. Vioux, *Chem. Mater.*, 1997, **9**, 2292–2299.

23 R. J. P. Corriu, D. Leclercq, P. Lefevre, P. H. Mutin and A. Vioux, *J. Non-Cryst. Solids*, 1992, **146**, 301.

24 S. Acosta, R. J. P. Corriu, D. Leclercq, P. Lefevre, P. H. Mutin and A. Vioux, *J. Non-Cryst. Solids*, 1994, **170**, 234.

25 N. Pinna and M. Niederberger, *Angew. Chem., Int. Ed.*, 2008, **47**, 5292–5304.

26 N. Pinna, *J. Mater. Chem.*, 2007, **17**, 2769–2774.

27 M. Niederberger, M. H. Bartl and G. D. Stucky, *Chem. Mater.*, 2002, **14**, 4364–4370.

28 M. Niederberger, M. H. Bartl and G. D. Stucky, *J. Am. Chem. Soc.*, 2002, **124**, 13642–13643.

29 J. H. Ba, J. Polleux, M. Antonietti and M. Niederberger, *Adv. Mater.*, 2005, **17**, 2509–2512.

30 I. Djerdj, D. Sheptyakov, F. Gozzo, D. Arcon, R. Nesper and M. Niederberger, *J. Am. Chem. Soc.*, 2008, **130**, 11364–11375.

31 N. Pinna, G. Garnweitner, M. Antonietti and M. Niederberger, *Adv. Mater.*, 2004, **16**, 2196–2200.

32 N. Pinna, G. Neri, M. Antonietti and M. Niederberger, *Angew. Chem., Int. Ed.*, 2004, **43**, 4345–4349.

33 J. Polleux, A. Gurlo, N. Barsan, U. Weimar, M. Antonietti and M. Niederberger, *Angew. Chem., Int. Ed.*, 2006, **45**, 261–265.

34 I. Bilecka, P. Elser and M. Niederberger, *ACS Nano*, 2009, **3**, 467–477.

35 M. J. Hu, J. F. Gao, S. L. Yang, Y. C. Dong, J. J. Xu, J. S. P. Wong, G. C. Shan and R. K. Y. Li, *Nanoscale*, 2012, **4**, 6284.

36 T. J. Trentler, T. E. Denler, J. F. Bertone, A. Agrawal and V. L. Colvin, *J. Am. Chem. Soc.*, 1999, **121**, 1613–1614.

37 J. M. Szeifert, J. M. Feckl, D. Fattakhova-Rohlfing, Y. J. Liu, V. Kalousek, J. Rathousky and T. Bein, *J. Am. Chem. Soc.*, 2010, **132**, 12605–12611.

38 M. Niederberger and G. Garnweitner, *Chem.–Eur. J.*, 2006, **12**, 7282–7302.

39 G. Garnweitner and C. Grote, *Phys. Chem. Chem. Phys.*, 2009, **11**, 3767–3774.

40 J. S. Jennings, W. Wardlaw and W. J. R. Way, *J. Chem. Soc.*, 1936, 637–640.

41 G. V. Jensen, M. Bremholm, N. Lock, G. R. Deen, T. R. Jensen, B. B. Iversen, M. Niederberger, J. S. Pedersen and H. Birkedal, *Chem. Mater.*, 2010, **22**, 6044–6055.

42 G. S. Li, L. P. Li, J. Boerio-Goates and B. F. Woodfield, *J. Am. Chem. Soc.*, 2005, **127**, 8659–8666.

43 C. P. Tsonis, *J. Mol. Catal.*, 1990, **57**, 313–323.

44 J. Kuo and R. W. Lenz, *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14**, 2749–2761.

45 V. Müller, M. Rasp, G. Štefanic, J. H. Ba, S. Günther, J. Rathousky, M. Niederberger and D. Fattakhova-Rohlfing, *Chem. Mater.*, 2009, **21**, 5229–5236.

46 T. Lv, L.K. Pan, X. J. Liu and Z. Sun, *Catal. Sci. Technol.*, 2012, **2**, 2297.

47 R. Chauhan, A. Kumar and R. P. Chaudhary, *J. Sol-Gel Sci. Technol.*, 2012, **63**, 546.

48 M. Niederberger, G. Garnweitner, F. Krumeich, R. Nesper, H. Colfen and M. Antonietti, *Chem. Mater.*, 2004, **16**, 1202–1208.