

Preparation of nanosized cobalt hydroxides and oxyhydroxide assisted by sonication

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An α -cobalt hydroxide with an interlayer spacing of 12.65 Å has been synthesized in sheet shapes with dimensions of 100–120 nm with the aid of sonication. Acetate anions are intercalated into the interlayer region of the as-prepared α -cobalt hydroxide in the form of a free ion state. β -Cobalt hydroxide has also been prepared and formed as crystallized thin hexagonal platelets with a diameter of 100 nm. Pure cobalt oxyhydroxide with a particle size of 10–30 nm has also been obtained. Powder X-ray diffraction, thermogravimetric analysis, FT-IR spectroscopy, transmission electron microscopy, as well as elemental analysis, have been used in the characterization of the as-prepared samples.

Introduction

Lamellar materials have recently been widely researched, particularly those materials that have been designed to build a large variety of microporous materials.¹ Layered double hydroxides (LDHs) are an important group of lamellar materials. Layered hydroxide materials have attracted much interest in the production of catalysts, sorbents, ionic exchangers, ionic conductors and electrochemical materials.²

α -Cobalt hydroxide as an isomorph of LDHs, β -cobalt hydroxide, as well as oxyhydroxide, have recently received increasing attention due to their application as electric, magnetic and catalytic materials. Cobalt hydroxides and oxyhydroxides as additives can be used to improve the electrochemical activity of alkaline secondary batteries.³ Nanosized cobalt hydroxide as an oil additive can improve tribological properties.⁴ Cobalt hydroxide coatings are found to catalyze the oxygen evolution reaction in an alkaline medium.⁵ Sol-gel-deposited films of cobalt hydroxide show reversible electrochromic properties.⁶ In particular, there has been remarkable interest in the long-range magnetic ordering of cobalt hydroxides and organic groups have been incorporated into the interlayer region to form organic magnetic materials.⁷

The hydroxides of cobalt have a hexagonal layered structure in which a divalent metal cation is located in an octahedral site generated by six hydroxyl oxygen atoms. These two-dimensional metal-hydroxyl sheets are stacked *via* hydrogen bonding to form a three-dimensional structure. When no anion is incorporated into the interlayer space of the two-dimensional metal-hydroxyl sheet, cobalt hydroxide is in the brucite-like phase and is denoted as β -cobalt hydroxide.⁸ When anions are intercalated into the interlayer space, cobalt hydroxides will form two phase states. If the *d*-values corresponding to successive diffraction by the basal planes agree with each other, *i.e.*, $d_{003} \approx 2d_{006} \approx 3d_{009}$, and the diffraction assignment for hydroxide-like structure (unit cell with three slabs) is used, cobalt hydroxide is in the hydrotalcite-like phase denoted as α -cobalt hydroxide.^{8,9} If the *d*-values corresponding to successive diffraction by the basal planes do not agree with each other, *i.e.*, $d_{003} \approx 2d_{006}$ but $\neq 3d_{009}$, cobalt hydroxide is in

the pre-hydrotalcite-like phase.^{10,11} In some publications, these phases are also denoted α -cobalt hydroxide.^{12–14}

The α -hydroxide consists of a stacking of positively charged layers. Anions and water molecules are intercalated in the interlayer region to restore charge neutrality. The intercalation of anions and water molecules causes an expansion of the structure in the interlayer region. Thus, the α -hydroxides have a larger interlayer spacing compared with the β -hydroxides. Several models have been established to show the formation mechanism of the α -hydroxide phase and explain the process of the intercalation of anions.^{8,9,15–18} However, the viewpoints on the mechanism of intercalation of positive charge on the $M(OH)_2$ layers of the α -hydroxide phase is still disputed. In this work, a new α -cobalt hydroxide with a larger interlayer spacing has been synthesized, and some evidence is provided to confirm the formation mechanism of the α -hydroxide phase.

Cobalt hydroxides have been prepared mainly by chemical and electrochemical syntheses. The α -cobalt hydroxides are metastable and difficult to synthesize as they convert spontaneously into the more stable β -hydroxide in alkaline media. The α -hydroxide of cobalt was first electrochemically precipitated in the presence of organic additives in solution, but the stoichiometry of the α -phase product was not determined.¹⁹ α -Hydroxides of cobalt have also been obtained by cathodic reduction of an aqueous solution of $Co(II)$ ions at low pH and low current densities.¹² Homogeneous precipitation from solution by hydrolysis of urea yielded an ammonia-intercalated α -type of cobalt hydroxide.¹³ Cobalt oxyhydroxide can be obtained by the oxidation of cobalted precursors.²⁰ Although β -cobalt hydroxide and cobalt oxyhydroxide are important materials, the synthesis of their nanosized products has not received much attention. In this paper, the preparation of nanosized cobalt hydroxides and oxyhydroxide are presented.

Sonochemistry is an effective method that has been used to prepare new materials and materials with new structures. The effects of ultrasonic radiation on chemical reactions are to accelerate chemical reactions and initiate new reactions that are difficult to perform under normal conditions.²¹ These effects are due to the very high temperatures and pressures that develop in and around the collapsing bubble. The extreme conditions attained during the bubble collapse have been exploited to prepare amorphous metals, carbides, oxides, sulfides and composite nanoparticles.²² Sonication was used to prepare cobalt hydroxide with a pre-hydrotalcite-like structure

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in a previous work.¹⁴ The present work is an extension of our previous work, and we report here on the sonochemical synthesis of nanostructured cobalt hydroxides and oxyhydroxides. We have investigated the synthesis of an α -cobalt hydroxide from a solution comprised of water and ethanol as solvents, and using cobalt acetate as precursor. We obtained a new α -cobalt hydroxide with a hydrotalcite-like structure. Pure nanosized β -cobalt hydroxide platelets and cobalt oxyhydroxide particles have also been prepared. The details of the synthesis and characterization of these products are reported.

Experimental

1 Synthesis

In a typical synthesis, a solution was prepared by mixing 50 ml of deionized water with 50 ml of anhydrous ethanol, to which 0.885 g of cobalt acetate was added. The cobalt acetate was homogeneously dissolved in the solution at room temperature. The solution was sonicated with high intensity ultrasound radiation employing direct immersion of a titanium horn (Sonics Materials, VC-600, 1 cm Ceramic horn, 50 kHz, 100 W cm^{-2}) and a solution of 0.4 M NaOH was added dropwise to the reaction solution during the sonication process. The titanium horn was inserted to a depth of *ca.* 1 cm into the solution. The sonication cell was cooled and maintained at about 40 °C during irradiation. The precipitate was separated by centrifugation and washed with deionized water. The product was further dried under vacuum for 12 h. To prepare α -cobalt hydroxide, the reaction solution was purged with argon for 30 min and sonicated under argon atmosphere for 80 min. The pH of the reaction solution was controlled at 7.2. To prepare β -cobalt hydroxide, the reaction solution was purged with argon for 30 min and the sonication was performed under argon atmosphere for 70 min. The pH of the solution was controlled at 9.5. To prepare cobalt oxyhydroxide, the reaction solution was purged with oxygen for 10 min and the sonication was performed under oxygen atmosphere for 80 min. The pH of the solution was controlled at 9.5.

2 Product characterization

Powder X-ray diffraction patterns were recorded on a Rigaku X-ray diffractometer (Co-K α radiation, $\lambda = 1.7889 \text{ \AA}$). Transmission electron micrographs were obtained with a JEOL JEM100SX electron microscope. FTIR spectra were measured on a Nicolet Impact 410 infrared spectrophotometer from KBr pellets in the range 400–4000 cm^{-1} . Thermogravimetric analysis was carried out using a Mettler Toledo TGA/SDTA851 instrument in the temperature range 30–900 °C at a rate of 10 °C min^{-1} under an argon atmosphere. Elemental analysis was carried out using an Eager 200 CHN analyzer.

Results and discussion

1. α -Cobalt hydroxide

Fig. 1(a) and (b) show the powder X-ray diffraction (PXRD) patterns of the as-prepared sample obtained *via* sonochemical synthesis under argon atmosphere for 80 min and at a pH 7.5. Fig. 1(a) is obtained from the as-prepared fresh sample and Fig. 1(b) from the sample aged in an air atmosphere at room temperature for 5 months. Comparing Fig. 1(a) and (b), it can be seen that the two X-ray diffraction patterns show the same curve profile, which indicates that the as-prepared sample is air-stable.

The XRD pattern of Fig. 1(a) shows prominent reflections at 12.65, 6.32, 4.23 and 2.68 Å and indicate a hydrotalcite-like feature. The low angle peak at 12.65 Å can be assigned to the (003) diffraction of the hydrotalcite-like structure, and the

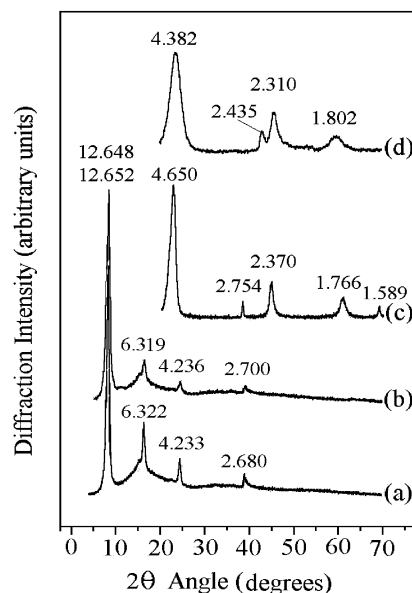


Fig. 1 Powder XRD patterns of cobalt hydroxides and oxyhydroxide obtained with the assistance of sonication: (a) fresh and (b) aged α -cobalt hydroxide, (c) β -cobalt hydroxides, (d) cobalt oxyhydroxide.

peaks at 6.32 and 4.23 Å can be assigned to the (006) and (009) diffraction peaks. It can be shown that the *d*-values of the as-prepared sample are related, *i.e.*, $d_{003} \approx 2d_{006} \approx 3d_{009}$, in accord with the hydrotalcite-like structure (unit cell with three slabs). Thus, the as-prepared cobalt hydroxide can be assigned to the α -phase. The product shows the typical blue coloration of α -cobalt hydroxide. The “saw-tooth” peak at 2.68 Å is due to the two-dimensional reflection of the turbostratically disordered α -cobalt hydroxide.²³ The morphology of the sample is shown in Fig. 2, which shows that the as-prepared sample has an irregular sheet-shape with dimensions of 100–120 nm.

The as-prepared sample is a novel α -cobalt hydroxide intercalated with CH_3COO^- groups and water molecules in the interlayer region. Evidence for the intercalation of acetate anions and water can be found in IR spectra which will be discussed later. The stoichiometry of the product is estimated to be $\text{Co}(\text{OH})_{1.7}(\text{CH}_3\text{COO}^-)_{0.3}(\text{H}_2\text{O})_{0.6}$ according to elemental analysis and the result of thermal gravimetric measurements.



Fig. 2 TEM image of the as-prepared α -cobalt hydroxide.

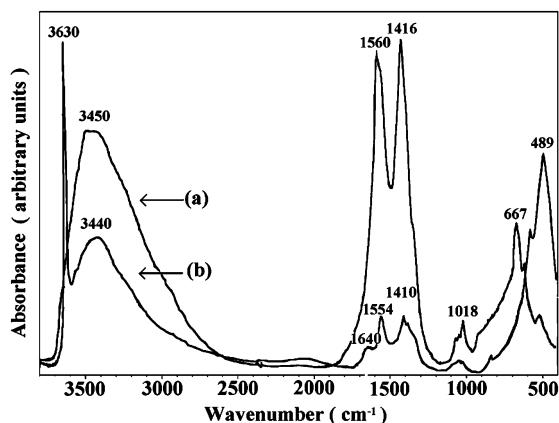


Fig. 3 Infrared spectra of sonochemically synthesized (a) α - and (b) β -cobalt hydroxide.

The cobalt content of the sample was determined gravimetrically using standard methods. The absence of trivalent cobalt cations in the α -hydroxides is confirmed by reaction with excess ferrous ammonium sulfate and back titrating the excess with standard potassium dichromate.

Fig. 3(a) shows the FTIR spectrum of the as-prepared α -type cobalt hydroxide. The large absorption band centered at *ca.* 3450 cm^{-1} can be assigned to the stretches of hydroxyl groups of gallery water molecules and hydrogen-bonded hydroxyl groups in cobalt hydroxide.²⁴ The peaks at 1560 and 1416 cm^{-1} with a frequency separation $\Delta\nu = 144\text{ cm}^{-1}$ can be attributed to the antisymmetric stretching $\nu_{\text{asym}}(\text{COO})$ and symmetric stretching $\nu_{\text{sym}}(\text{COO})$ vibrations of the free acetate ion, respectively.²⁵ The acetate anion may coordinate to metals in three modes, *i.e.*, monodentate, bidentate chelating and bidentate bridging, and their stretching vibration frequency differs according to their coordination modes.²⁵ In the as-prepared α -type cobalt hydroxide, however, they are evident as free acetate ion. The absorption band around 660 cm^{-1} can be ascribed to δ_{OH} and $\nu_{\text{Co-OH}}$ vibrations.¹⁴

Fig. 4(a) shows the thermogravimetric pattern of α -cobalt hydroxide in the temperature range $30\text{--}900\text{ }^{\circ}\text{C}$ with the final decomposition product being CoO. The α -cobalt hydroxide undergoes a three-step weight loss. The first step weight loss at $85\text{ }^{\circ}\text{C}$ is due to the dehydration of the inserted water in the interlayers. The second step weight loss at $201\text{ }^{\circ}\text{C}$ is due to the decomposition of the cobalt hydroxide, which is similar to the TG data shown previously.¹² The last step weight loss at $309\text{ }^{\circ}\text{C}$ is due to the decomposition of intercalated CH_3COO^- groups,²⁶ which was not found in the TG data of the α -cobalt hydroxide of ref. 12. The net weight loss observed (37.2%) is

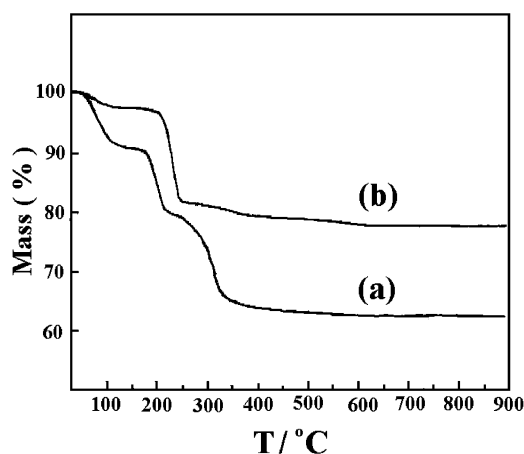


Fig. 4 Thermogravimetric data of sonochemically synthesized (a) α - and (b) β -cobalt hydroxide.

consistent with what is expected (36.9%) from the estimated formula.

The foregoing results show that the α -cobalt hydroxide is formed with intercalation of acetate anions and water molecules. The intercalation of anions into the interlayer space is the direct factor in the formation of α -hydroxide. The presence of mixed valent state (II,III) cations and hydroxyl vacancies can lead to the incorporation of anions in the interlayer space for charge neutralization.^{15,16} Anions can also be incorporated in the form of cation–anion pairs.⁹ Partial protonation of the hydroxyl ions is proposed to introduce a positive charge on the hydroxide layers and cause the incorporation of anions in the interlayer region.⁸ As for the formation mechanism of the as-prepared α -phase hydroxide, the possibility of a ‘‘mixed valent state (II,III)’’ model is excluded, as chemical analysis confirms the absence of trivalent ions in the α -hydroxide. The cation–anion pair model seems to be possible from the viewpoint of the large interlayer space of 12.65 \AA . However, the large interlayer space of the α -hydroxide is due to the long molecular chain of acetate ion and intercalation of organic groups into hydroxides can lead to large interlayer spaces.⁷ The ‘‘hydroxyl vacancy’’ model is the most likely for the formation of the α -hydroxide as reflected by the estimated formula $\text{Co}(\text{OH})_{1.7}(\text{CH}_3\text{COO}^-)_{0.3}(\text{H}_2\text{O})_{0.62}$.

Anions play an important role in the formation of α -hydroxides. The interlayer spacing of the α -hydroxides varies, depending on the inserted anion species. Inorganic anions and groups which have been incorporated into cobalt hydroxide layers are NH_3 , NO_3^- and CO_3^{2-} . The corresponding α -cobalt hydroxides intercalated with these anion species have been reported with different interlayer spacing ranging from 7.5 to 9.3 \AA .^{12–14} Organic groups inserted into the interlayer region of cobalt hydroxide include carboxylate, dicarboxylate, sulfate and cyanide and the basal spacings of the corresponding products are 22.8 , 16.2 , 25.0 and 11.5 \AA , respectively.⁷ The α -cobalt hydroxide obtained in this work is different from those listed above. The as-prepared α -cobalt hydroxide has a larger interlayer spacing than the intercalated inorganic anions. In the as-prepared α -cobalt hydroxide, the inserted acetate ions are in the free ion form, as confirmed by IR spectra, while the organic groups are directly coordinated to the metals in the hydroxides obtained in ref. 7.

2. β -Cobalt hydroxide

Fig. 1(c) shows the PXRD pattern of cobalt hydroxides obtained *via* sonochemical synthesis under argon atmosphere for 70 min and controlling the final pH of the solution to 9.5 . The sample shows reflections at 4.65 , 2.75 , 2.37 , 1.77 and 1.59 \AA , which matches with those assigned to brucite-like β -cobalt hydroxide (PDF: 30-0443). The product shows a pink–red color, typical for the brucite-like phase. The X-ray diffraction pattern shows that the product is pure β -cobalt hydroxide and no other phase can be found from the X-ray diffraction patterns. The formation of the brucite-like phase is also evidenced by FTIR spectra as shown in Fig. 3(b). The sharp peak at 3630 cm^{-1} , which is not observed in the α -cobalt hydroxide, can be assigned to the free hydroxyl groups in brucite-like structures. The peaks around 3440 and 1640 cm^{-1} can be assigned to surface absorbed water and hydrogen-bonded hydroxyl groups. The peaks at 1554 and 1410 cm^{-1} are due to the trace of the surface absorbed acetate groups. The absorption around 489 cm^{-1} can be assigned to metal–oxygen vibrations and metal–oxygen–hydrogen bending vibrations in the brucite-like octahedron sheet.^{15,27} Thermogravimetric analysis, Fig. 4(b), shows a small weight loss at $73\text{ }^{\circ}\text{C}$ due to the desorption of the surface absorbed groups. The second weight loss at $229\text{ }^{\circ}\text{C}$ is due to the decomposition of the β -cobalt hydroxide.

Fig. 5 shows the result of electron microscopic investigation

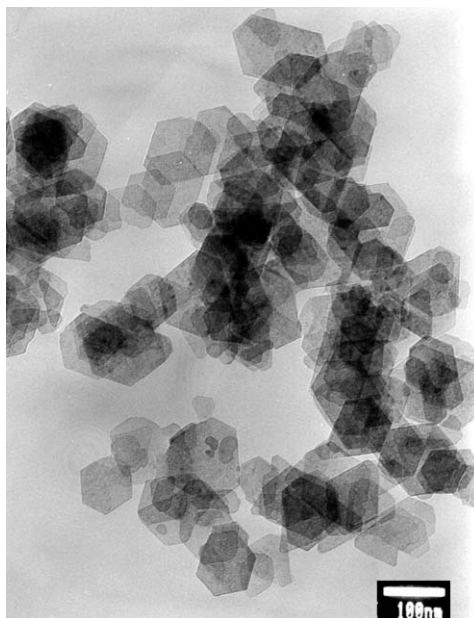


Fig. 5 TEM image of sonochemically synthesized β -cobalt hydroxide.

of β -cobalt hydroxide. Inspection of the micrographs of the as-prepared sample reveals hexagonal crystals of β -cobalt hydroxide. The products are well-crystallized thin platelets with a monodispersed dimension of *ca.* 100 nm.

3. Cobalt oxyhydroxide

Fig. 1(d) illustrates the PXRD pattern of the sample obtained *via* a sonochemical synthesis conducted under oxygen atmosphere for 80 min by controlling the pH of the solution to 9.5 at the end of the reaction. Prominent *d*-spacings are found at 4.38, 2.43, 2.31 and 1.80 Å. The XRD pattern of the product is identical to that of the cobalt oxyhydroxide (PDF: 7-169). A TEM picture of the as-prepared cobalt oxyhydroxide is shown in Fig. 6. Both hexagonal platelets and irregular particles are observed in the product, the major phase being irregular particles. The dimensions of the particles of the as-prepared sample lies in the range 10–30 nm.

The process of the formation of the cobalt oxyhydroxide can be explained as follows. The α -hydroxide is first formed when

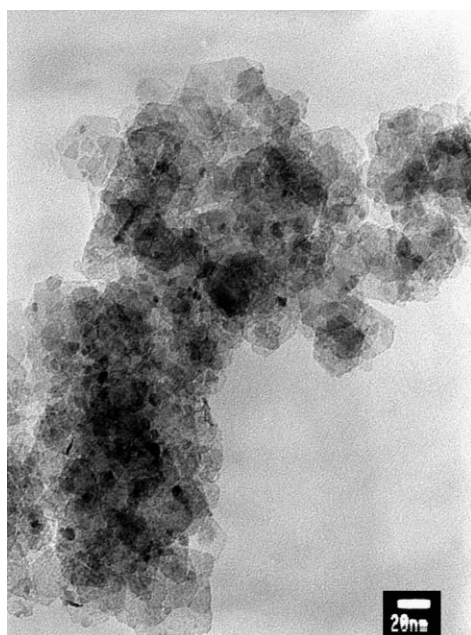


Fig. 6 TEM image of sonochemically synthesized cobalt oxyhydroxide.

the solution of 0.4 M NaOH is added dropwise into the cobalt acetate solution during the sonication process, as indicated by the color change of the solution from red to blue. Then, the α -phase changes rapidly into a β -phase with a color change from blue to pink. Finally, cobalt oxyhydroxide is formed following the color variation pink to brown to black. However, the mechanism of the formation of the cobalt oxyhydroxide is more complicated.^{20,28} The chemical oxidation of β -cobalt hydroxide to oxyhydroxide can follow two different pathways according to the oxidizing agent. Strong oxidizing agents cause solid state oxidation, while weak oxidizing agents, *e.g.* O_2 , lead to a two-step reaction, in which a dissolution/nucleation/growing process is involved.²⁰ In the current experiment, the main mechanism is a two-step reaction as indicated by the irregular granular products. The formation of some pseudo-hexagonal platelets is due to the use of a precursor Co^{2+} -based solution undergoing a germination/growth process.

The foregoing results show that nanosized pure α and β -phase cobalt hydroxides, as well as cobalt oxyhydroxide, have been synthesized sonochemically. The chemical effects of ultrasound arise from acoustic cavitation, *i.e.*, the formation, growth and implosive collapse of bubbles in the liquid.²⁹ In brief, during the process, the implosive collapse of the bubble generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. There are two regions of sonochemical reactivity, the inside of the collapsing bubble and the interface between the bubble and the liquid.³⁰ For volatile precursors, the sonochemical reaction takes place inside the collapsing bubbles, which results in an amorphous product. When the reaction occurs in the thin layer surrounding the collapsing cavity, crystalline nanoparticles are obtained.³¹ In the present study, an ionic solute is used as a precursor. This solute has a low vapor pressure, and crystallized products are obtained. We propose that the formation of cobalt hydroxides and oxyhydroxide take place at the interface between the bubble and liquid. For the preparation of nanosized cobalt hydroxides and oxyhydroxide, sonochemical synthesis is a more convenient method and takes a shorter time than other methods. For example, an oxidation process yielding cobalt oxyhydroxide takes more than 20 h.²⁰

Conclusion

In summary, a convenient and rapid approach has been carried out for the preparation of nanosized α , β -cobalt hydroxides and cobalt oxyhydroxide using sonochemical synthesis. All the three products are obtained in a pure phase state. The as-prepared α -cobalt hydroxide has an interlayer spacing of 12.65 Å and sheet-shaped dimensions of 100–120 nm. It is found that acetate anions are intercalated in the interlayers of the hydroxide in a free ionic state. The β -cobalt hydroxide has a thin hexagonal platelet structure, which is well crystallized with a diameter of 100 nm. The cobalt oxyhydroxide is obtained with a particle size of 10–30 nm. Based on the obtained results, attempts will be made to pillar lamellar materials to prepare a series of novel materials. In brief, sonochemistry proves to be a convenient method for the preparation and modification of nanosized materials.

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