Colloid Polym Sci (2004) 282: 1059–1062
DOI 10.1007/s00396-003-1032-9

SHORT COMMUNICATION

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Quantitative studies on the preparation of colloidal particles of cobalt hydroxide by the moving chemical reaction boundary method in agarose gel

Received: 6 January 2003
Accepted: 24 November 2003
Published online: 7 February 2004

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Abstract Quantitative investigations were performed for the synthesis of colloidal particles of cobalt hydroxide in agarose gel by the moving chemical reaction boundary method. The experimental results show that: (1) the sizes of the colloidal particles can be controlled by changing the concentration of agarose gel, (2) the concentration of the colloidal particles is also controlled by changing the concentrations of $CoCl_2$ and/or NaOH, and (3) most importantly, the concentration of colloidal particles can be predicted with the theory of moving chemical reaction boundary (MCRB). The colloidal particles prepared by the MCRB are amorphous and are more easily oxidized than particles prepared by other methods.

Keywords Cobalt hydroxide · Electrophoretic measurement · Moving chemical reaction boundary

Introduction

Colloidal particles are widely used in normal daily life [1, 2, 3] in such products as paints, inks, detergents, magnetic tapes, photographic films, television screens and cosmetics, and in the biomedicine and biochemistry industries [4, 5].

Numerous well-rounded methods, such as sol-gel [1, 6, 7], dispersion [1, 6], condensation [1], polymerization [8] and electro-chemical methods [9, 10], have been developed for the preparation of colloid particles. The sol-gel methods are old [7]. Colloidal milling, ultrasonic vibration and electric arc dispersion are used as dispersion methods.

Condensation is also widely used [7]. To obtain colloidal particles, one can convert a dissolved substance into a sol by lowering the temperature. Alternatively, one can prepare colloidal particles by reducing the solubility of a solute or by performing a precipitate reaction in an aqueous solution. Polymerization was used for the production of colloidal particles, e.g., surface-aminated poly-pyrrole-silica colloidal composites [8]. Electrochemical methods were used for the synthesis of colloidal nickel wires [9] and colloidal gold particles on silicon [10].

A more recent method is chemical vapor deposition, e.g., for the preparation of crystalline colloidal TiN [11]. The initially synthesized colloidal particles can be modified by further treatments such as solvent evaporation [12], molecular cross-linking [13], DNA [14] or bacterial [15] template-patterning, antigen-antibody recognition [16] and reverse micelles [17]. They can also be transferred into superlattices or superstructure materials, which possess some important size-dependent optical and opto-electronic properties.

The moving chemical reaction boundary (MCRB) —the counterpart of moving boundary system devel-

oped from the 1920s to the 1950s [18, 19, 20, 21, 22, 23] and going back to Tiselius' displacement electrophoresis for colloid and serum analysis [24], isotachophoresis [25], and the moving boundary method [18, 19, 20, 21, 22, 23, 26]—is a new physico-chemical model developed by the authors [27, 28, 29, 30, 31] on the basis of Deman-Rigole [32, 33] and Bocek et al. [34]. In order to investigate the validity of the MCRB theory, several MCRB methods [35, 36, 37, 38] were designed.

MCRB can greatly enhance the separation of amino acids in capillary zone electrophoresis [39], even in the presence of salt [40]. Recently, the method was used for the online preconcentration of phenols in wastewater [41].

The method was further used for the preparation of stable colloidal particles in [42]. Obviously, quantitative studies have not been carried out for preparation of colloidal particles of cobalt hydroxide [$Co(OH)_2$]. The purposes of this paper are quantitative studies on (1) the effect of gel concentration on the particle size, (2) the control of the concentration of colloidal particles in the gel by changing the electrolyte concentration, and (3) the the quantitative relationship between the concentration of the colloidal particles in the gel and the prediction by the theory of MCRB.

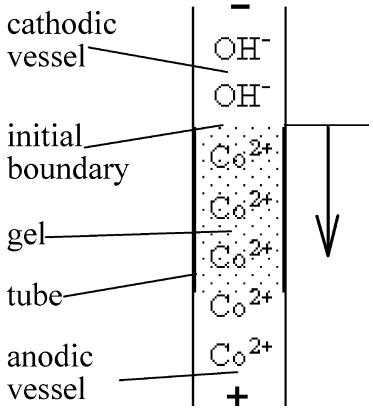

Fig. 1 Precipitation between $CoCl_2$ and NaOH by moving chemical reaction boundary method (MCRBM). +Anode, −cathode, *arrow* indicates the direction of boundary movement. Under the action of the electric field, the cobalt and hydroxyl ions migrate in opposite directions and form a blue precipitate of cobalt hydroxide [Co $(OH)_2$] when they collide. The boundary is designed to move toward the anode. In the experiment, a power supply (DYY III8A, Beijing Luyi, Beijing, China), with constant voltage 0–150 V or 0–600 V, constant current 0–25 mA or 0–100 mA, and timer equipment were used

Materials and methods

The reagents used were $CoCl_2{\cdot}6H_2O$, HNO_3, NaOH and KCl (AR, Shanghai Chemical Reagents Co., Shanghai, China), agarose (Shanghai Huang-Hua Pharmaceutical, Shanghai). The microporous membrane (0.2 μm pore-diameter, $\varphi = 50$ mm, Affiliated Membrane Factory, School of Beijing Chemical Industry, Beijing, China) was used as initial supporting medium for the preparation of the agarose gel membranes (Fig. 2).

The electromigration reaction between Co^{2+} and OH^-followed the procedure described in [35, 36] (Fig. 1). The morphology and size of colloidal $Co(OH)_2$ particles were determined using a scanning electron microscope (SEM) (H-800, Hitachi, Japan). Before the SEM examination, the gel was dialyzed with distilled water to remove the salts. The dialyzed gel was transferred onto a clean glass chip and dried by filter papers as shown in Fig. 2. The gel film was removed from the glass chip and observed under the SEM.

The concentration of colloidal particles in the gel was determined with an atomic absorption spectrophotometer (WFX-120, Beijing Ruili, Beijing, China). The samples were dissolved in acidic (HNO_3) boiling water for about 30 min. The X-ray diffraction pattern of the wet gel containing the blue precipitate was obtained on a X-ray diffractometer with graphite-monchromatized Cu $K\alpha$ radiation (Rigaku Dmax-γA, Japan).

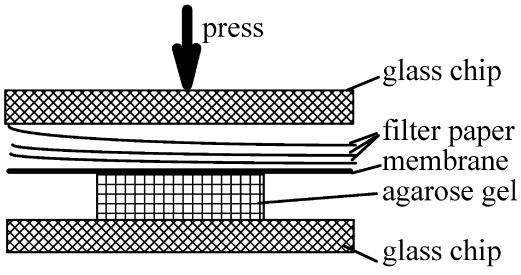

Fig. 2 The preparation of the agarose gel membrane containing colloidal particles of $Co(OH)_2$. A piece of the dialyzed gel containing the colloidal particles of $Co(OH)_2$ is transferred to a clean glass chip, covered with a clean microporous membrane and several filter papers. Another glass is put on the filter papers under slight pressure. The gel is dried overnight

Results and Discussions

As shown in Table 1, when the concentration of the agarose gel is 1.5% (w/v, 1.5 g dried gel dissolved in 100 ml solution containing $CoCl_2$ and 0.1 mol/l KCl), the distribution of particle size is from 0.6 to 4.0 μm and the average particle size is 1.5 μm. At 2.0% gel, the distribution ranges from 0.4 to 2.0 μm and the average value is 0.8 μm, and for 2.5% gel, from 0.2 to 1.4 μm with an average of 0.5 μm. These results imply that the concentration of agarose gel has some influence on the size of the colloidal particles. More highly concentrated gels yield smaller particles.

As revealed by X-ray diffraction, the colloidal $Co(OH)_2$ particles are amorphous. In contrast, the colloidal particles of Co $(OH)_2$ prepared by other methods, e.g., precipitation of Co^{2+} with OH^-, are crystalline [43]. The blue colloidal particles of Co $(OH)_2$ prepared by moving chemical reaction boundary method (MCRBM) became gradually brown from the end of the column within about 40 min. In contrast, the blue Co $(OH)_2$ produced by mixing $CoCl_2$ and NaOH solutions was

Table 1 Sizes of colloidal $Co(OH)_2$ particles prepared by the MCRBM in agarose gel with different concentrations. The experimental conditions are: 0.026 N $CoCl_2$, 0.026 N NaOH, 0.1 mol/l background electrolyte KCl, 5.2 mm in I.D. and 90 mm in length, current intensity of 0.6 mA/mm^2, flow rates of anolyte and catholyte of 0.6 ml/min, i.d. of tube 5.2–5.4 mm, 90 mm in length, and run time 10 min

Colloidal particles	Concentration of agarose gel[a]		
	1.5%	2.0%	2.5%
Distribution of particle size (μm)[b]	0.6–4.0	0.4–2.0	0.2–1.8
Number of particles	23	58	70
Average particle size (μm)	1.5	0.8	0.5

[a]The concentration of agarose gel means the dried weight (in grams) of agarose gel in 100 ml solution containing $CoCl_2$ and 0.1 mol/l KCl

[b]For the near-spherical particles, the sizes are their diameters; but for irregular particles, the sizes are the average values of their lengths and widths

quite stable, even when exposed to the air for a month (Fig. 1 in [42] and Figs. 4–6 in [44]. These phenomena imply that the colloidal particles of Co $(OH)_2$ by MCRBM are easily oxidized. It is therefore recommended to de-gas the gel and the solutions used for the preparation of the colloidal particles by the MCRBM. After the run of MCRBM, the ends of the tube must be closed immediately.

The concentration of the Co $(OH)_2$ particles in the gel is controlled by changing the concentration of $CoCl_2$ and/or NaOH. When the concentrations of $CoCl_2$ and NaOH were simultaneously increased from 0.01 to 0.026 N, the concentration of Co $(OH)_2$ in the gel raised linearly (correlation coefficient = 0.9983) (Fig. 3). These results demonstrate that the concentration of colloidal particles in the gel can be easily controlled by adjusting the concentration of $CoCl_2$ and/or NaOH.

$Co(OH)_2$ is considered as a uniform precipitation in the gel, so that the content of the colloid particles can be expressed as the concentration of $Co(OH)_2$ in gel. This concentration can be predicted by the MCRB theory. The equation

$$c_{pro} = c_+^{\alpha} c_-^{\beta} \frac{m_-^{\beta} - m_+^{\alpha}}{m_+^{\alpha} c_+^{\alpha} - m_-^{\beta} c_-^{\beta}} \tag{1}$$

is derived from the equations of MCRB [28, 29, 30], where c is the equivalent concentration (in equivalents/meter cubed). The subscripts + and − indicate the charge of ions, the subscript "pro" the concentration of the electromigration reaction product, the superscripts α and β phases α and β. The equivalent concentration c is taken as positive for cations and negative for anions [18, 19, 20, 21, 22, 23, 28, 29, 30, 31, 32, 33]. The m is mobility in meters squared per second per volt.

As shown in Fig. 4, the detected concentration of Co $(OH)_2$ in the agarose gel agrees with the theoretical prediction by Eq. 1. Linear regression analyses give $Y = -7.48E\text{-}4 + 1.07X$ [Y = experimental concentration of $Co(OH)_2$, X = theoretical concentration of $Co(OH)_2$].

In conclusion, colloidal particles of $Co(OH)_2$ can be prepared by the MCRBM (Fig. 1). The size of the colloidal particles is controlled by adjusting the concentration of agarose gel. The concentration of colloidal $Co(OH)_2$ particles in the gel can also be controlled by the concentration of $CoCl_2$ and NaOH, and can be predicted by Eq. 1 developed from the MCRB theory. The colloidal particles of Co $(OH)_2$ made by MCRBM are different from particles prepared by other methods, since the colloidal particles made by the MCRBM are amorphous and easily oxidized.

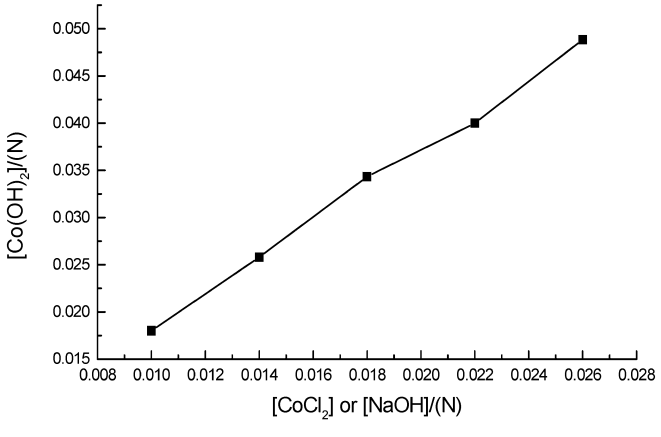

Fig. 3 Concentration of colloidal particles of Co $(OH)_2$ in agarose gel as a function of $CoCl_2$ or NaOH concentration. Conditions: $[CoCl_2] = [NaOH]$, 0.1 mol/l KCl, 2.0% agarose, 0.6 mA/mm^2, 0.6 ml/min flow rates, inner diameter of tube 5.2–5.4 mm, length 90 mm, run time 10 min

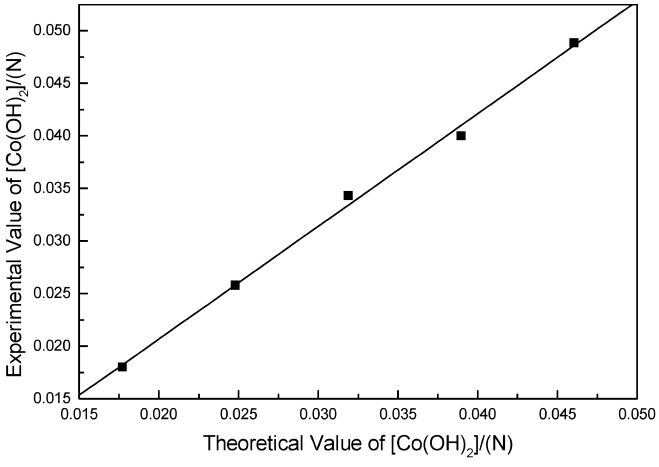

Fig. 4 Comparison between experimental and theoretical concentrations of colloidal particles of Co $(OH)_2$ obtained by the MCRBM in agarose gel. The conditions are the same as in Fig. 3

Acknowledgements Financially, this project is supported by the National Scientific Foundation of China (Apr. No. 29775014 and No. 20245004), and the Natural Scientific Foundation of the Scientific and Technological Committee of Anhui Province (Apr. No. 01043905).

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