



Aggregation behavior in the early stage of sol solutions formation

Dengteng Ge^{a,*}, Lili Yang^b, Yao Li^a

^a Centre for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, PR China

^b School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin 150090, PR China

ARTICLE INFO

Article history:

Received 22 April 2010

In final form 23 June 2010

Available online 1 July 2010

ABSTRACT

Formation of sol solutions is intrinsically a non-equilibrium phenomenon governed by a competition between kinetics and thermodynamics. This Letter investigates the aggregation behavior of sols in early formation process through monitoring microstructures of sols experimentally. Two kinds of aggregation structures and a dynamic feedback disaggregation structure evolution were found determined by reflux time through the particles' sticking probability. It can be deduced that the clusters/aggregations were formed through a process of nucleation, ramous growth and disaggregation. Moreover, it was shown that the initial concentration had no effects on the structure or size of clusters.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The sol–gel process provides a means to prepare homogeneous, high purity materials with tailored chemical and physical properties [1]. The strategies for control of sols exist in both formation in the first stage and aging in the late stage. The features characterizing the microstructure of sols are the structure of clusters and the aggregation kinetics. The particle/cluster structures of colloids and aggregation process are usually studied through experimental investigations and computer simulations, which have yielded a significant insight into the processes involved. It has been pointed out that, different morphological patterns are formed by different models, and originate in physics from the interaction energy between individual particles [2–5]. The structures of aggregates in the late stage have been observed experimentally and studied numerically. For example, Terao and Weitz studied experimentally the aggregation structures through adjustments of temperature of system or the aging time [6,7]. It is found that the fractal dimension of clusters of silica particles restructured from 1.75 to 2.1 with increasing aging time [8,9]. However, the evolution of formation and growth of sol solutions in the early stage has not yet been studied experimentally. The effects of experimental parameters of sol solutions on the colloidal aggregation have not been conclusive. In this Letter sol solutions for indium tin-doped oxide (ITO) were explored and simply controlled by the changes of concentration of starting sols and thermal reaction time. As excellent semiconductors, ITO materials have large variety applications such as optoelectronic devices, sensors and heat reflecting mirrors due to the excellent optical and electric properties [10,11]. For sol–gel derived ITO films, it has been proved that the microstructure and properties of thin films have a great dependence not only on the

preparation or heat treatment condition but also on the physico-chemical nature and microstructure of starting sols [12,13]. In this research, the aggregation behavior of ITO sol solutions were discussed by transmission electron microscope (TEM), Fourier transform infrared (FTIR) and small angle X-ray scattering (SAXS) techniques, including the morphological structures, the mechanisms of cluster/particle formation and growth.

2. Experiment

2.1. Preparation of sols

The preparation process was widely described [14]. Aqueous indium nitrate ($\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$, 99.99%) was dissolved in acetylacetone (AcAc) in a beaker with the molar ratio of 1:4, then the solution was refluxed at 83 °C for 1 h. Hydrated tin chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 99.99%) was dissolved in absolute isopropanol. The two solutions were refluxed at 60 °C for different time and the molar ratio between tin and indium is kept at 1:10 and the total concentration is kept 0.6 M. The color of sol solution changes from light yellow to dark reddish-brown with the increase of reflux time. Four concentrations of sols were obtained by a variety of isopropanol's volume while the thermal reflux time of 4 h. Then obtained sols were aged for 24 h at room temperature before tested.

2.2. Characterization

FTIR spectrometer (Perkin–Elmer Spectrum One, America) was used to characterize the molecular structure of sol solution. TEM measurements were performed by using a TECNAI-G2 (Netherlands, Philips) transmission electron microscope operating at 200 kV. SAXS experiments were carried out using an X'Pert diffractometer (Philips, Holland) with a position sensitive detector (Graz,

* Corresponding author. Fax: +86 451 86402345.

E-mail address: dentenge@gmail.com (D.T. Ge).

Australia) and a Kratky compact small angle system, which was equipped with a stationary-anode copper-target X-ray tube with a one-coordinate position sensitive detector.

3. Results and discussion

The chemical structures of sols with different thermal reflux time are shown in Fig. 1. The strong absorption peak near

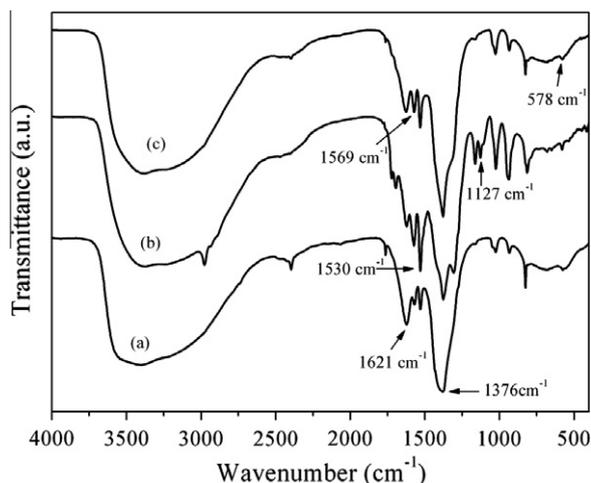


Fig. 1. FTIR spectra of ITO sol solutions with different reflux time: (a) 0 h, (b) 2 h and (c) 4 h. The curves are shifted vertically for clarity.

1623 cm^{-1} represents the carbonyl group in enol AcAc, which decreases to near 1569 cm^{-1} and 1530 cm^{-1} when enol AcAc complex with indium ion stably [15]. The absorption peak of 1127 cm^{-1} and 578 cm^{-1} represent In–OH and In–O–In. It is summarized that in the sol system stable metal complexing ligands and thermo hydrolytic polymer coexist, including indium complexing ligands, hydrolysate of indium, oligomers, polymer clusters, primary nucleus particles, and aggregates. However, it was shown that the ratios for each part are just different between three samples.

Fig. 2 shows typical TEM micrographs of cluster aggregates of three samples. Colloids in Fig. 2a and Fig. 2c both reveal a compact and non-branched morphology. However, Fig. 2b shows a different structure with dense, spherical clusters at short length scale, but ramified, open-pore and branched clusters/aggregations at large length scale. To get statistic microstructure information, SAXS method was used here, which is the most valid way in understanding of kinetic growth of sol–gel process. The small angle scattering intensity by a system of identical particles can be approximated by Guinier's law [16]:

$$I(q) \propto \exp\left(-\frac{1}{3}R_G^2q^2\right) \quad (1)$$

where R_G represents the electronic radius of gyration and it is defined as the average mean square distance from the center of gravity of scatter. If the particles are spherical, it has relationship with the average radius of particles shown that,

$$R = \sqrt{\frac{5}{3}}R_G \quad (2)$$

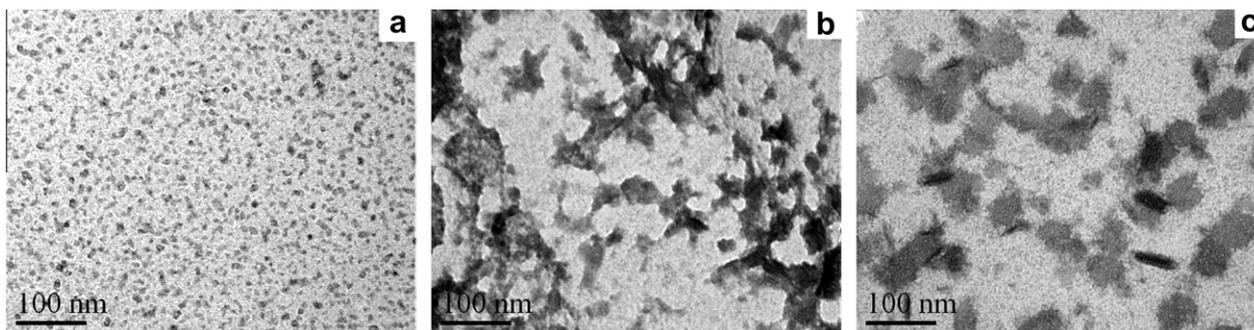


Fig. 2. TEM graphs of sol solutions with the concentration of 0.6 M and different reflux time: (a) 0 h; (b) 2 h; and (c) 4 h.

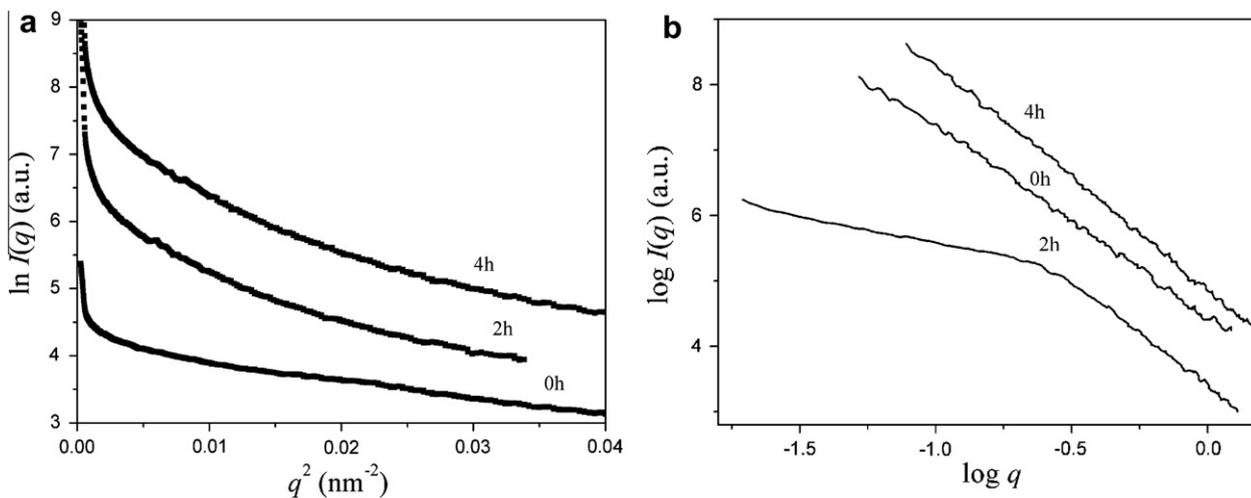


Fig. 3. In $I(q)$ versus q^2 plots (a) and $\log I(q)$ versus $\log q$ (b) of three samples with different reflux time.

Fig. 3a shows the $\ln I(q)$ versus q^2 plots at low angles from SAXS tests of these three samples. According to Eqs. (1) and (2), the average radius of particle/cluster is obtained 15.2 nm, 19.4 nm, and 20.1 nm, respectively. It means the growth of particle/cluster is fast at the beginning but very slow then. Moreover, the scattering intensity at higher angles can be analyzed in terms of a power law with the fractal dimension D , which is called the Porod's law. For mass fractal structures, the Porod's law is described under collimation test system as [17]:

$$I(q) \propto q^{-D_m} \quad (0 < D_m \leq 3) \quad (3)$$

where D_m represents the mass fractal dimension. Fig. 2b shows the $\log I(q)$ versus $\log q$ plots at higher angles. According to the Porod's law, particles/clusters shown in Fig. 2a and c have mass fractal structures and the mass fractal dimension $D_m = 2.8$ and $D_m = 2.9$ respectively, which are all very close to the dimension value of dense materials. The particles/clusters seen in Fig. 3b have hierarchical mass fractal structure and the mass fractal dimension are

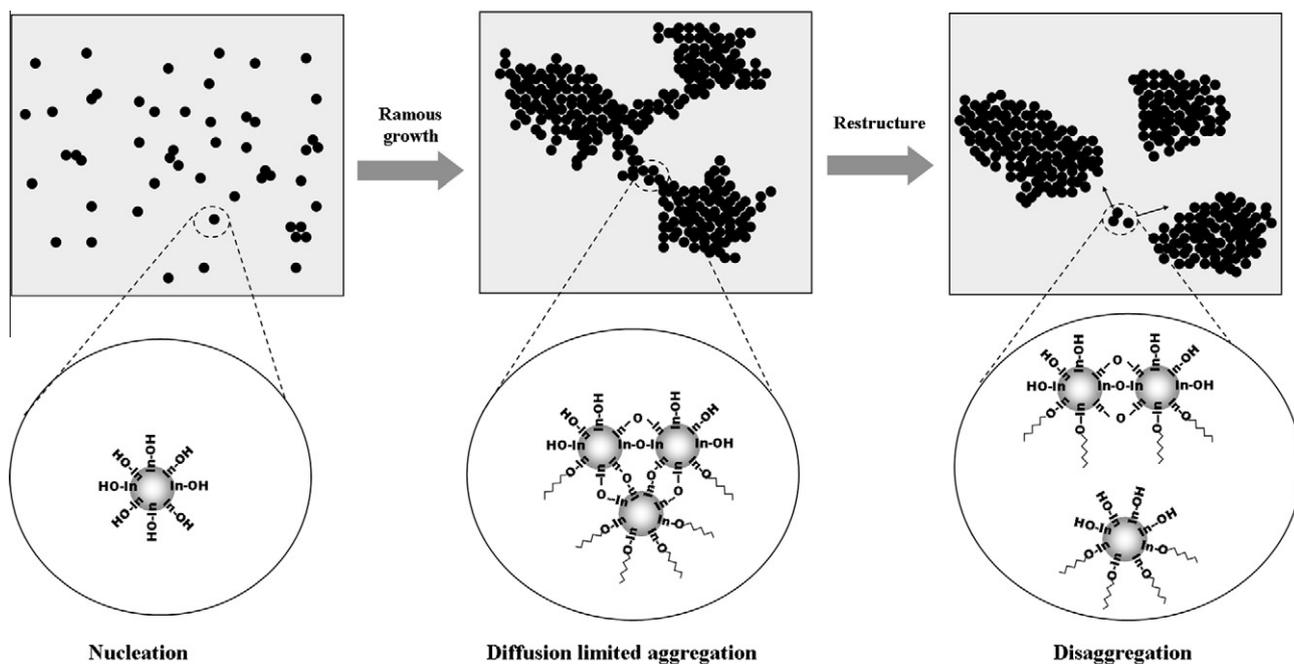


Fig. 4. A schematic plot of the aggregation behavior during the reflux process.

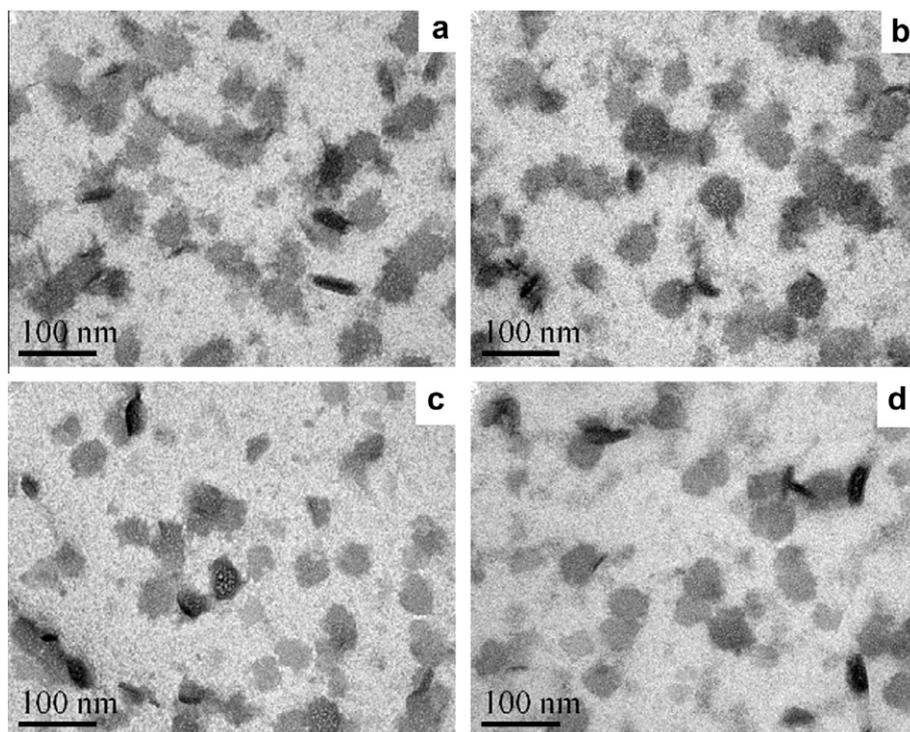


Fig. 5. Typical TEM graphs of sol solutions with different concentrations: (a) 0.6 M; (b) 0.45 M; (c) 0.36 M; and (d) 0.3 M.

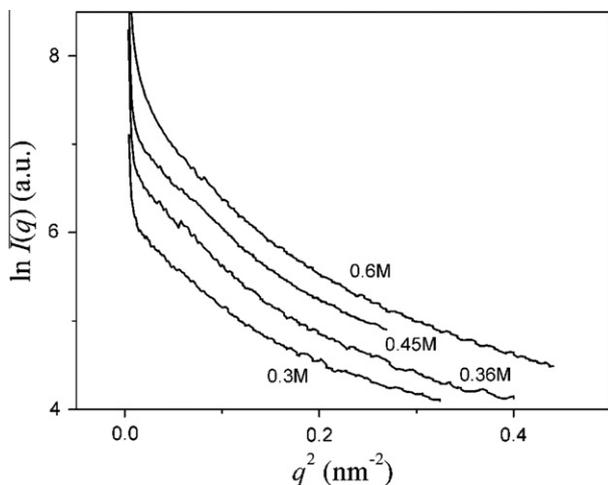


Fig. 6. $\ln I(q)$ versus q^2 plots of samples with different concentrations.

$D_m = 1.4$ and $D_m = 2.9$, which means the particles/clusters are dense at small characteristic length and sparser at large characteristic length. These results correspond well with the TEM results. This is a good proof that there is a disaggregation evolution during the thermal reflux process. A schematic plot of the whole procedure is shown in Fig. 4. The primary dense particles (i.e. nucleation) are formed at the start through complexation, hydrolysis and polymerization, however the growth of particles are then controlled by the forced thermal process. With the increase of heating-up time and the enhancement of reactions, the aggregation force changes mainly from diffusion of particles to reaction between particles. At the beginning of thermal reflux process, interactions between clusters mainly include relative weak attraction, such as short-range van der Waals attraction and the electrostatic repulsion. Then the difference of interaction energy ΔE increases, which results in a total non-equilibrium system. As well known, the aggregation rate is equal to the collision frequency multiply aggregation probability. The aggregation probability P_b of such moves depends on the difference of the total interaction energy ΔE of the system due to this process, which is given as [3]:

$$P_b = \begin{cases} 1 & \Delta E < 0 \\ \exp(-\Delta E/k_B T) & \Delta E \geq 0 \end{cases} \quad (4)$$

where k_B is the Boltzmann constant and T is the temperature of the system. Therefore, it can be obtained from Eq. (4) that as the heating-up time increases, the sticking probability of particles/clusters is decreased. Moreover higher energy is provided for further intra-cluster polymerization reactions, which results in dense clusters. The probability of particles or clusters sticking to other particles or clusters decreases, which result in the disaggregation of particles or clusters with weak bonding force, and rearrangement of clusters, i.e., the particles have more chances into the inside of clusters to have polymerization within clusters. It is in accordance with the fact that there are seldom In–OH but more In–O–In in

the sample seen in Fig. 1. The formation mechanism for clusters could be deduced through collapse of ramified polymeric network based on this work. Therefore, the aggregations in sol solutions are not stable especially at high temperature.

We adjusted the concentration of sols and structures of obtained sols are shown in Fig. 5. Similar dense and spherical cluster aggregations were observed and there were also a small amount of rod-like clusters present. However, the concentration of clusters decreases with metal ion concentration. Fig. 6 shows the $\ln I(q)$ versus q^2 plots of the above samples. Obviously, the curves are almost parallel. It means the radii of clusters are so close in these four sols. Therefore, the aggregation regime does not depend on the initial concentration of sols, which just has effects on the final concentration of clusters/aggregates.

4. Conclusion

In this Letter, sol solutions for ITO materials were obtained by changing initial concentrations and thermal reflux time. On the combination of microstructures, chemical structures obtained by TEM, SAXS, FTIR methods, the aggregation behavior in the early formation stage of sols was studied. The formation starts from the nucleation and growth to compact spherical or spheroidal clusters. Then branched-dense structure is formed under diffusion limited aggregation regime due to the non-equilibrium state, which increases the energy of system. To get a relative thermal equilibrium state, a structural transition from ramified to dense through restructuring within particles/clusters happens. It indicates that the solution-to-sol transition process follows from growth of clusters, collapse of polymer and finally restructure to stable sol. However, the structure and size of clusters would hardly be affected by the initial concentration. Our work will shed light on the solution-to-sol process through experimental results and strengthen the understanding of sols formation over a wide range of conditions.

References

- [1] R.A. Assink, B.D. Kay, *Annu. Rev. Mater. Sci.* 21 (1991) 491.
- [2] P. Dimon, S.K. Sinha, D.A. Weitz, C.R. Safinya, G.S. Smith, W.A. Varady, H.M. Lindsay, *Phys. Rev. Lett.* 57 (1986) 595.
- [3] T. Terao, T. Nakayama, *Phys. Rev. E* 58 (3) (1998) 3490.
- [4] D.A. Weitz, J.S. Huang, M.Y. Lin, J. Sung, *Phys. Rev. Lett.* 54 (13) (1985) 1416.
- [5] A.M. Puertas, A. Fernandez-Barbero, F.J. de las Nieves, *J. Chem. Phys.* 115 (12) (2001) 5662.
- [6] C. Aubert, D.S. Cannell, *Phys. Rev. Lett.* 56 (7) (1986) 738.
- [7] D.A. Weitz, J.S. Huang, M.Y. Lin, J. Sung, *Phys. Rev. Lett.* 53 (17) (1984) 1658.
- [8] B. Urbanc, L. Cruz, S.V. Buldyrev, S. Havlin, B.T. Hyman, H.E. Stanley, *Phys. Rev. E* 60 (1999) 2.
- [9] Y.V. Ivanenko, N.I. Lebovka, N.V. Vygornitskii, *Eur. Phys. J. B* 11 (1999) 469.
- [10] M.J. Alam, D.C. Cameron, *Thin Solid Films* 377–378 (2000) 455.
- [11] T.F. Stoica, V.S. Teodorescu, M.G. Blanchin, T.A. Stoica, M. Gartner, M. Losurdo, M. Zaharescu, *Mat. Sci. Eng. B* 101 (2003) 222.
- [12] R.B. Hadj Tahar, T. Ban, Y. Ohya, Y. Takahashi, *J. Appl. Phys.* 82 (2) (1997) 15.
- [13] M.R. Ayers, A.J. Hunt, *J. Non-Cryst. Solids* 290 (2001) 122.
- [14] S.S. Kim, S.Y. Choi, C.G. Park, H.W. Jin, *Thin Solid Films* 347 (1999) 155.
- [15] M. Toyoda, J. Watanabe, T. Matsumiya, *J. Sol-gel Sci. Technol.* 16 (1–2) (1999) 93.
- [16] R. Xie, B.X. Yang, B.Z. Jiang, *Phys. Rev. B* 50 (1994) 3636.
- [17] P. Wong, *Phys. Rev. B* 32 (1985) 7417.