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A quick and simple method to test silica colloids' ability to resist aggregation

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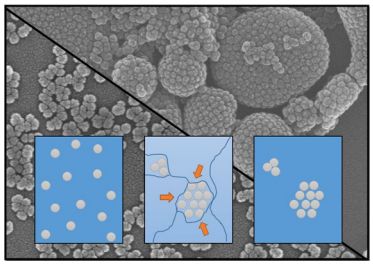
HIGHLIGHTS

- Freeze/thaw test for silica stability against aggregation.
- Both effects of solution pH and quantity of PVP addition are investigated.
- In alkaline condition, small amount of PVP is needed to stabilize silica colloids.
- In acid condition (pH = 4), PVP addition promotes aggregation instead.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple freeze/thaw method to quickly test the ability of silica colloids against aggregation under different conditions is presented here. A solution of silica colloids, with size of about 50 nm, was immersed in liquid nitrogen for 1 min to force the aggregation of these colloids and then thawed at 60 °C for 10 min to room temperature. The dynamic light scattering (DLS) technique was used to measure the particle size both before and after the freeze/thaw (F/T) procedure to assess the silica's ability to resist aggregation via size changes. Both the effects of pH and addition of polyvinyl pyrrolidone (PVP) were investigated here. Under alkaline condition (pH = 10), the silica colloid was more negatively charged and less PVP was needed to stabilize these silica colloids against this F/T test. However, when the pH was changed to 7.0, more PVP was needed to stabilize these silica colloids. When the pH was further lowered to acidic conditions (pH = 4), PVP lost its ability as a protective agent for the silica colloids, which aggregated immediately after the addition of PVP.

1. Introduction

Stable dispersion is often required for various colloids in many operations [1–5] of which chemical mechanical polishing (CMP) in IC processing is one example [6–8]. Here, scratching after polishing is often a result of the appearance of large particles [9–11]. Therefore it is necessary to understand the behavior of particle aggregation and take proper actions to stabilize these colloids. However, stability of colloids is dependent upon the magnitude of applied stress. In other words, a colloid may appear stable during storage, yet it becomes agglomerated when vigorously stirred.

Silica colloids are often used in CMP processes to polish the surface of deposited silica layers [6,12]. The silica slurry is generally stable during storage at room temperature for up to several months. However, when it is used for a CMP process, the shear stress from this process may induce agglomeration of these silica colloids [9–11]. In order to simulate the shear stress acting on these silica colloids in a typical CMP process, it is necessary to use expensive equipment to produce high shear stress for the test. On the other hand, a silica colloid can be very stable due to electric

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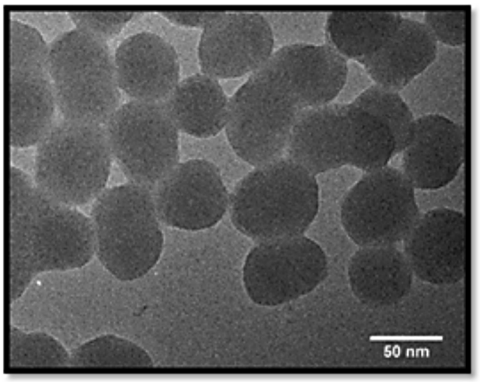

Fig. 1. TEM picture of silica colloids used in this work.

repulsive forces from the negative charge on its surface. In addition, it can adsorb dispersing agents, such as PVP [6,13,14] to resist agglomeration due to steric hindrance. Therefore, the pH and the quantity of dispersing agent are parameters that can be manipulated to maintain colloid stability.

This work demonstrates a novel, quick and relatively cheap method of freeze/thaw to test the stability of silica colloids against very strong forces toward aggregation. The concept of freeze/thaw has been discussed in the literature [15–20] for different purposes, and the specific methods and temperatures of freezing were different in various reports. In this work we use liquid nitrogen for freezing to quickly generate ice in the solution which exerts a strong force toward particle aggregation in order to test silica colloids' ability to resist aggregation under various conditions. It can provide researchers a convenient method to assess the performance of different efforts to stabilize a colloidal system.

2. Experimental

The commercial silica colloids used in this work were prepared from hydrolysis of tetraethyl orthosilicate (TEOS) (supplied by TSMC), and the particles were spherical with an average size of about 50–60 nm. A TEM picture (ARM 200F, JEOL, Japan) is shown in Fig. 1. The silica colloid was diluted with DI water to 1% solid content and the solution pH was adjusted by either KOH or HNO_3 (Union Chemical, Taiwan). After 24 h, different amounts of PVP (molecular weight 40,000; PVP-4K, SIGMA) were added and the solution was stored for another 24 h before further experiments.

The colloid size was measured by dynamic light scattering (DLS) technique (NICOMP 370ZLS, PSS, USA) after diluting by 100 times with DI water, and the solution was put into a vortex mixer (VTX-3000L, LMS, Tokyo, Japan) for 10 s to ensure uniform dispersion before measurement. Though it is possible that some of the soft agglomerates will disperse (i.e. become deagglomerated) during this stage, hard agglomerates will remain agglomerated after this short mixing procedure. For DLS measurement, the Gaussian volume mean diameter is used for comparison. The data obtained here also match observations from TEM pictures.

The freeze/thaw method was used here to assess the ability of silica colloids to resist aggregation under various conditions (different pH and different additions of PVP). The colloidal solution in 50 ml PP test tube was first immersed in liquid nitrogen for 1 min, so the freezing of water into ice would force these colloids together, providing opportunity to agglomerate. Next, the frozen silica solution was thawed at 60 °C for 30 min to return to room temperature. DLS was used to obtain size data for comparison both before and after this quick and simple freeze/thaw test. At 1 wt%, a well-dispersed silica solution was transparent to the naked eye, but it would appear cloudy if aggregation had occurred between these colloids. Therefore it would immediately be clear if whether the solution had returned to its original state of good dispersion or became coagulated after the test. Our DLS data were consistent with this visual observation.

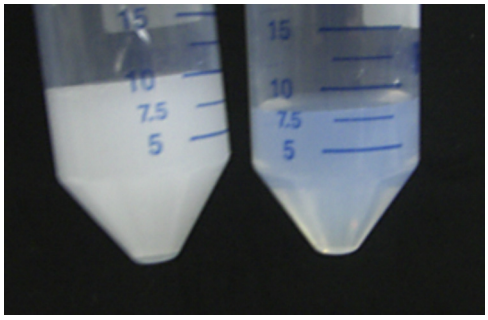

Fig. 2. Pictures of slurry solution before (right) and after (left) the freeze/thaw test.

3. Results and discussion

3.1. Observations on the slurry going through the test

Here the slurry pH was kept at 7.0 and no PVP was added. Fig. 2 shows two pictures of the slurry solution, before and after the freeze/thaw test. The difference is quite obvious: the solution has turned cloudy after the test, while the original solution is a transparent blue. Presumably, the freezing ice provides sufficient force to the silica colloids so they form aggregates during the freezing step, and these colloids remain aggregated after thawing. A representative SEM picture is shown in Fig. 3, where large particles formed by aggregating smaller colloids during the freezing step can be clearly seen. But due to the random nature of ice formation, the aggregated particles may have various shapes, as seen in Fig. 3.

3.2. Effects of PVP and pH

To assess the ability of silica colloids against aggregation, we changed the solution pH and quantities of PVP addition before the test. DLS was used to provide quantitative data on particle size and representative results are shown in Fig. 4. Here a log scale is used to show particle size since the difference is quite large. The DLS measurement for the original colloid is about 58 ± 17 nm. Therefore if the DLS data of different samples after the freeze/thaw test are within this range, then the silica colloids are considered to have

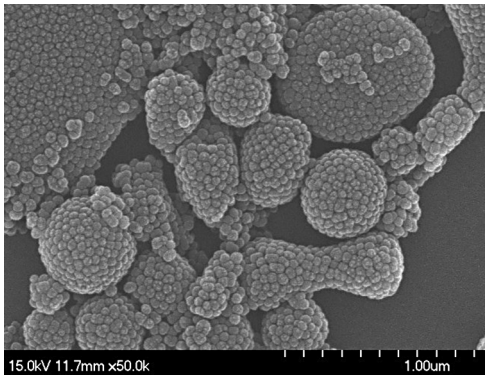

Fig. 3. SEM of aggregated particles after F/T test.