



## Charged micelle halo mechanism for agglomeration reduction in metal oxide particle based polishing slurries



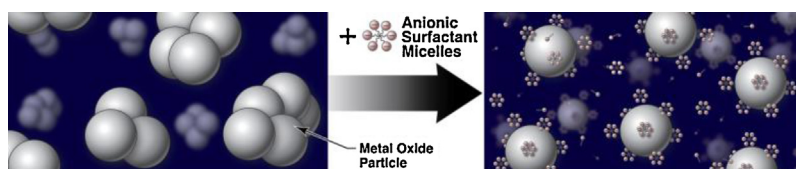
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### HIGHLIGHTS

- Agglomeration reduction is demonstrated in metal oxide polishing slurries.
- Stabilization substantially maintains material removal rate during polishing.
- Stabilization improves filterability and reduces roughness of the polished surfaces.
- Formation of charged micelles is shown to be critical to agglomeration reduction.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A method for chemically stabilizing metal oxide polishing slurries to prevent their agglomeration *while maintaining their surface activity* is demonstrated experimentally. Negatively charged ceria, zirconia, and alumina particles are reversibly size-stabilized under low ionic strength conditions at and above their isoelectric points using anionic surfactants.

Stability is imparted only at surfactant concentrations above the critical micelle concentration and when the particle and the micelle have like-signed charges. Zeta potential measurements demonstrate that little adsorption of anionic surfactant occurs under conditions where the particles are negatively charged. Changes to pH, hydrophobicity, and ionic strength disrupt the surfactant's ability to size-stabilize the slurries. These results suggest that the charged micelles electrosterically hinder the agglomeration of oxide particles.

Because the stabilization method does not rely on adsorption, the particle surface remains accessible for chemical reactions, such as those involved in polishing. Metal oxide slurries stabilized by this method remove material at a rate comparable to that of unstabilized slurry. In addition, stabilized slurry is easier to filter, which improves the quality of the polished surface. Stabilizing colloids by this method may prove valuable for systems where particle surface functionality is important, such as those used in ceramics processing, optical polishing, and chemical-mechanical planarization.

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## 1. Introduction

Optimizing the size uniformity of polishing slurries is important for the optical polishing and chemical-mechanical planarization

(CMP) industries from the perspective of both reducing raw material consumption and improving polishing outcomes. Agglomeration of colloidal slurry particles leads to settling, increased slurry consumption, and reduced filter lifetimes. In addition, polishing in the presence of large or agglomerated particles at the upper end of the size distribution has been shown to degrade the quality of the finished surface, producing microscratches and increasing surface roughness [1–7].

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Ceria and zirconia slurries are commonly used for optical polishing, as they are two of the most effective polishing compounds for silica based glasses in terms of material removal [8,9]. Commercial optical polishing slurries are typically comprised of particles with average diameters of 0.1–0.5  $\mu\text{m}$  and are used at working concentrations of 2–10 wt%. Unfortunately, particle agglomeration is a common problem for colloidal slurries, as stability is extremely sensitive to solution conditions [4,10–13].

Agglomeration of colloids is typically prevented using electrostatic or steric stabilization, either separately or in combination. In electrostatic stabilization, the surface charge of the colloids is adjusted to increase the electrostatic repulsion between particles. Ceria and zirconia have neutral charge at their isoelectric points (IEP) of pH 6.6 and 6.2, respectively. Therefore, working particles are negatively charged at typical optical polishing conditions of pH 7–10 [14]. However, metal oxide slurries have been shown to exhibit shear thinning behavior at pH > IEP, suggesting that agglomeration is likely even under conditions where the electrostatic repulsion between particles is high, as inter-particle attractive forces continue to dominate [15]. Thus, electrostatic stabilization alone is not sufficient to prevent particle agglomeration in metal oxide slurries.

Efforts have been made to improve dispersion of metal oxide slurries for CMP and ceramics applications using adsorbed polymers, which provide steric stabilization. For example, anionic polyelectrolytes, such as polyacrylic acid, induce steric repulsive forces while increasing the surface charge and have been shown to enhance the dispersion of ceria and zirconia [13,16,17]. Care must be taken to properly adjust surface coverage, as low levels of polyelectrolyte adsorption can also lead to bridging interactions, which instead de-stabilize the slurry and cause flocculation [17,18].

Chemical dispersants and slurry additives that tightly bind to the surface or require high fractional coverage have the potential to decrease polishing activity [19,20]. Material removal in polishing is facilitated by a chemical reaction between the metal oxide and hydroxyl groups on the silica surface [8]. Therefore, the degree of coverage or size of species needed to stabilize the particles may block chemically active sites on the surface of the polishing particles and reduce the material removal rate.

Smaller molecules, such as surfactants, can also prevent agglomeration through either steric or electrosteric stabilization. Surfactant adsorption on metal oxide surfaces has received considerable attention given its applications in froth flotation, detergency, and separations. Studies of surfactant adsorption have typically focused on conditions where there is a clear electrostatic driving force for adsorption; *i.e.*, where surfactants have *opposite* charge from the metal oxide surface [21–23]. In this regime, researchers have provided rheological and electrokinetic evidence that charged surfactants adsorb to the surface and reduce inter-particle attraction in metal oxide dispersions. For example, Wei and coworkers have recently demonstrated that the anionic surfactants sodium hexametaphosphate and sodium dodecyl benzene sulfonate reduce the viscosity of nanoceria suspensions [11]. In addition, reduction in maximum shear yield stress has been achieved by adding charged surfactants to concentrated ceria and zirconia suspensions [24,25]. Although these experiments have focused over a range of pH, the most substantial rheological effects were observed at a pH where the particles are either charge neutral or are of opposite charge to the surfactant. These results all suggest that the charged surfactants increase inter-particle repulsive forces, but the studies referenced above provide no direct evidence of a reduction in agglomeration. Palla and Shah used settling experiments to suggest a reduction in particle agglomeration in alumina suspensions with the addition of charged surfactants; however, their study did not address the practical implications of using such surfactant stabilized suspensions [12].

In the present work, we directly demonstrate reduction of agglomeration in metal oxide particle based polishing slurries imparted by the use of anionic surfactants under low ionic strength conditions and where the bare particles are negatively charged (*i.e.*, pH > IEP). We discuss conditions under which colloidal stability is achieved and conditions that reverse this stability. We address practical processing concerns associated with addition of a chemical stabilizer, such as maintaining material removal and filterability, and discuss the benefits of using these stabilized slurries for optical finishing. Finally, we postulate a mechanism which is consistent with our observations of metal oxide particle stability in the presence of charged anionic surfactants. Although demonstrated here for optical polishing slurries, the method is expected to be broadly applicable.

## 2. Materials and methods

### 2.1. Slurry sample preparation

All experiments were conducted using commercial polishing slurries, which were used without further purification or pre-treatment (*e.g.* polishing or ultrasonics). Ceria slurries (Universal Photonics) were prepared using the optical polishing compounds Hastilite PO (supplied as concentrated slurry) or Cerox 1663 (supplied as powder). These were diluted with deionized (DI) water, in accordance with common manufacturing practice, to 4.4 wt% and 7.7 wt% solids, respectively. As-manufactured mean particle sizes were reported by the vendors as 0.2  $\mu\text{m}$  for Hastilite PO and 1–2  $\mu\text{m}$  for Cerox 1663. Concentrated zirconia slurry ZOX-PG (Universal Photonics), which has a reported median particle size of 1.0–1.4  $\mu\text{m}$ , was diluted with DI water to 4.6 wt% solids. Alumina slurries were prepared using Linde 0.3- $\mu\text{m}$  alumina polishing powder (Union Carbide) and DI water to 10 wt% solids. A stir rod and stir plate were used to mechanically mix all dry polishing compounds for a minimum of 2 h. Details of the slurries, including their measured conductivities and IEPs, are summarized in Table 1.

Indicated concentrations of nonionic, anionic or cationic surfactants, and other species tested were added to the aqueous slurries, prepared as described above, to test their effects on particle agglomeration. A full list of these species, known critical micelle concentrations (CMC), as well as the pH conditions and surfactant concentrations under which they were tested, is provided in Table 2. For experiments performed at or near pH 10 or pH 4, pH adjustment was made using KOH or HCl, respectively. Measurements of pH were made using an Accumet AR60 pH meter with pH/ATC Double Junction electrode. A few of the surfactant-stabilized ceria samples were titrated with a 5 M NaCl stock solution to determine the point when stability was lost. NaCl concentrations for these samples are indicated in Table 2 in the column labeled “Additional NaCl”.

### 2.2. Slurry characterization

The degree of particle agglomeration was quantified by directly measuring the particle size distributions of the slurry samples. Particle size distributions were measured using two different techniques: (1) laser light scattering on the ensemble of particles (Saturn Digsizer, Micromeritics) and (2) single particle light obscuration (Accusizer 780A, Particle Sizing Systems). Test samples were pre-diluted 100–500x from their working concentrations with DI water just prior to PSD analysis and mixed continuously with a magnetic stir bar before each sample was injected into the test chamber.

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