Optical properties of silica colloids suspensions in electric field postprint

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Abstract

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Full Text

Preamble

Optical Properties of Silica Colloid Suspensions in Electric Fields

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Abstract. We investigated the optical properties of silica colloid suspensions composed of nanospheres with average diameters of 50, 90, 120, and 300 nm under applied electric fields. Our results demonstrate that colloidal suspensions with 120 nm particles exhibit a dramatic shift in reflection peak position in response to applied potential. With increasing particle concentration, the peak maximum undergoes a slight blue shift while the reflection intensity increases moderately. We also examined the influence of solvents on the optical properties of silica colloid suspensions, revealing that significant peak position changes occur only in propylene carbonate, with no marked changes observed

in ethylene glycol or water. The reflection peak intensity was strongest in water. We analyze the underlying mechanism and attribute this phenomenon to the hydrogen-bonding ability of the solvents.

1. Introduction

The self-organization of colloidal building blocks has attracted considerable attention in materials chemistry and soft condensed-matter physics [1]. Responsive photonic crystals can be fabricated from these colloidal building blocks and hold promise for diverse applications including color displays [3, 4], bio- and chemical sensors [5], photonic printing, decorative coatings [6], and anti-counterfeit labels [7]. In principle, these applications can be realized by modulating the periodicity and dielectric constants of the crystals in response to external stimuli such as electric or magnetic fields, temperature [8], light, molecules and ions, or applied mechanical forces. Among these, electric and magnetic fields are considered optimal for tuning the lattice constants of colloidal crystals and inverse opals in display applications. Candidate materials for such systems include Fe_2O_3 [9], Fe_3O_4@SiO$_{2}$ [10], ZnS@SiO_2 [11], highly charged polystyrene (PS) [12], SiO_2 [13], TiO_2 [14], and others. Among these various inorganic materials, silica has long been regarded as an ideal candidate for photonic crystals due to the ease of processing monodisperse spherical colloids in large quantities [13].

However, most studies have focused on solid samples composed of silica spheres [4, 15]. For example, Hernán Míguez [5, 16] developed a method to create mesostructured Bragg reflectors using SiO_2 and TiO_2 nanoparticles as building blocks, while Arsenault et al. [3] fabricated photonic crystals from silica-metallopolymer composites to demonstrate electric field-assisted swelling of colloidal crystal lattices. Additionally, particle arrays formed by mixing two different-sized particles have shown angle-independent color [17]. These examples all involve solid silica sphere samples. Another reason for the limited attention to suspensions is the low refractive index contrast between silica and the solvent. Consequently, only a few studies have explored the optical properties of silica colloid suspensions in electric fields.

In this work, we employ silica colloid suspensions containing monodisperse spherical silica particles of various diameters to investigate their optical properties under electric fields. We find that the reflection peak positions in these suspensions shift with varying electric field strength, and we analyze the underlying mechanism governing this photonic response.

2. Experimental Methods

2.1 Materials

Tetraethoxysilane ($C_8H_{20}O_4Si$, A.R.), ethanol (C_2H_6O, A.R.), and $NH_3 \cdot H_2O$ (25%, A.R.) were purchased from Sinopharm Chemical Reagent Company

(Shanghai, China). Propylene carbonate (99%) and ethylene glycol were obtained from Aladdin Chemicals. Indium tin oxide (ITO) coated glass with a resistivity of 7 Ω · cm was purchased from Corning Corp. All chemicals were used as received without further purification. Deionized (DI) water with a resistivity of 18.2 MΩ · cm from a Millipore-Q purification system (Millipore, USA) was used throughout this work.

2.2 Synthesis Procedures

SiO_2 particles were prepared using the ammonia-catalyzed Stöber method [13], which yields highly uniform spheres. This synthesis route involves the hydrolysis of tetraethoxysilane in an alcohol-ammonia solution. By adjusting the proportions of ethanol, $NH_3 \cdot H_2O$, and H_2O, we obtained monodisperse spherical silica particles with diameters of 50 nm, 90 nm, 120 nm, and 300 nm.

2.3 Device Preparation

The photonic display cell consisted of transparent top and bottom electrodes separated by 200 µm thick epoxy spacers. SiO_2 suspensions (5.4-20 v% in propylene carbonate) were injected between the electrodes using a conventional syringe, after which an electric field was applied to the cell.

2.4 Characterization

The morphology and particle size of the samples were examined using a Hitachi S4800 field emission scanning electron microscope (FESEM) and an FEI Tecnai G2 F20 transmission electron microscope (TEM). The reflection spectra of the silica colloid suspensions under electric field were measured with an Ocean Optics HR 2000CG-UV-NIR spectrometer coupled to a six-around-one reflection/backscattering probe. Electric fields were applied to the silica colloid suspensions using a function generator (Agilent, 33220A) for DC power supply.

3. Results and Discussion

Fig. 1 shows TEM images of monodisperse spherical silica particles with average diameters of (a) 50 nm, (b) 90 nm, (c) 120 nm, and (d) 300 nm, confirming their uniform size distribution.

The reflection spectra reveal that the photonic properties change with applied electric field. As shown in Fig. 2a, 2b, and 2d, the peak maximum positions remain essentially unchanged for 50 nm, 90 nm, and 300 nm particles, while the reflection intensity decreases slightly with increasing electric field. In contrast, Fig. 2c demonstrates a dramatic shift in peak position for the 120 nm particle suspension. In the absence of an electric field, a reflection peak appears at 710 nm due to Bragg diffraction from polycrystalline structures [18]. When an electric field of 0.5 V is applied, the reflection peak maximum decreases slightly in intensity. At 1.0 V, the peak maximum blue-shifts to 600 nm and a second peak emerges around 750 nm. Further increasing the field to 1.5 V shifts the 600 nm peak to a shorter wavelength of 525 nm with slightly increased intensity, while the 750 nm peak remains but with reduced intensity.

These results indicate that for 50 nm, 90 nm, and 300 nm particles, the reflection peak intensity changes gradually without significant peak position shifts under external electric fields, whereas 120 nm particles exhibit dramatic peak position changes. This difference arises from the colloidal structures formed. Among the four particle sizes, only the 120 nm SiO_2 particles assemble into structures with average interparticle distances comparable to visible wavelengths, enabling the observed dramatic peak position changes attributed to visible light Bragg diffraction.

The variation in reflection peak intensity can be explained by the Fresnel equation:

$$R_s = \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2$$

where R_s is the reflection coefficient, n_1 is the refractive index of air, n_2 (calculated as $\phi \cdot n_{\text{spheres}} + (1-\phi) \cdot n_{\text{media}}$, where ϕ is the solid fraction) is the effective refractive index, and θ_i is the incident angle relative to the interface normal. Since the spherical SiO_2 particles are negatively charged, they migrate toward the positive electrode under electrostatic force, altering the solid fraction (ϕ) in the region near the positive electrode. This change in solid fraction consequently modifies the reflection coefficient.

The shift in reflection peak position depends on both particle diameter and concentration. We prepared SiO_2 suspensions (120 nm) at various concentrations (5.4 v%, 10.0 v%, 15.0 v%, 20.0 v%) in propylene carbonate. In the absence of an external electric field, these suspensions display different colors that vary from pink to blue as concentration increases, corresponding to changes in their reflection spectra (Fig. 3).

As shown in Fig. 4a, the reflection peak blue-shifts to 600 nm with higher intensity compared to Fig. 2c due to the increased concentration. With increasing electric field, the reflection wavelength further blue-shifts from 600 nm to 410 nm. Figs. 4b and 4c show the reflectance spectra for 120 nm SiO_2 colloid suspensions at 15.0 v% and 20.0 v% concentrations under electric field. Compared to Fig. 4a, the peak maximum shows only a slight blue shift and the reflection intensity decreases sharply. When the electric field reaches 1.5 V, the peak position remains essentially unchanged. This behavior at high concentrations likely occurs because the interparticle distance has reached its minimum limit.

It is well established that multilayered colloidal crystals form under DC fields due to electrophoretic movement [20]. The number of periodic colloidal layers stacked on the electrode surface varies proportionally with the electric field gradient, and this thickness change directly affects reflection intensity [21]. This theory is confirmed by the results shown in Fig. 5, where 120 nm SiO_2 nanospheres at 5.4 v% concentration assemble into a stratified structure on the positive electrode, while only a monolayer remains on the negative electrode after applying voltage.

To examine the reversibility of the bandgap shift, we removed the electric field after applying DC voltages from 0 to 2.5 V to a 10.0 v% 120 nm SiO_2 suspension in propylene carbonate. As shown in Fig. 6, the reflectance peak returned to its original position but with lower intensity due to particle aggregation on the electrodes after 390 s.

Notably, for 120 nm SiO_2 suspensions in ethylene glycol and water, the reflection peak intensity changes gradually without peak position shifts under external electric fields. We attribute this phenomenon to the hydrogen-bonding ability of the solvents, which is a key factor determining interparticle interactions and the resulting reflection spectra [22]. Propylene carbonate is a weakly hydrogen-bonding liquid that interacts weakly with the silica surface, enabling adjacent particles to adhere through hydrogen bonds between surface silanol groups. These particle-particle bonds are weak, allowing dramatic peak position changes in response to applied electric fields. In contrast, ethylene glycol and water are strongly hydrogen-bonding liquids that form solvation layers around each particle through hydrogen bonding with surface silanols. This creates repulsive solvation forces that stabilize the silica particles, preventing peak position shifts under external electric fields. For ethylene glycol suspensions, the reflection peak intensity remains unchanged until the electric field reaches 2.5 V, possibly due to the high viscosity restricting SiO_2 nanosphere movement. For aqueous suspensions, the very high reflection peak intensity likely results from water’ s high dielectric constant (Fig. 7).

4. Conclusions

In summary, we have systematically investigated the spectroscopic properties of SiO_2 nanoparticle suspensions with various particle diameters under external electric fields. The 120 nm SiO_2 suspensions exhibit dramatic shifts in reflection peak position with applied potential. With increasing concentration, the peak maximum shows a slight blue shift, though the position stabilizes at electric fields above 1.5 V. Solvent-dependent reflection behavior under external electric fields was examined using propylene carbonate, ethylene glycol, and water. Significant peak position changes occur only in propylene carbonate. We anticipate that these results provide valuable insights into the photonic properties of silica colloid suspensions in electric fields and establish an important platform for studying aggregation and assembly at the single-particle level.

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