

Light-Regulated Electrostatic Interactions in Colloidal Suspensions

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Colloidal suspensions enjoy widespread use in applications ranging from advanced materials to drug delivery. By tailoring the interactions between particles, one can design colloidal fluids, gels, or crystals needed for ceramic,¹ coating,² ink,³ photonic,^{4,5} and pharmaceutical materials.⁶ One common strategy is to alter their electrostatic interactions by varying either the pH or ionic strength of the solution in which they are suspended.⁷ However, problems such as nonuniform mixing and disruption of suspension microstructure arise when acid, base, or electrolyte species are added. The ability to tailor electrostatic interactions between colloids with spatial and temporal control in the absence of chemical additions would not only alleviate these problems but also open new possibilities in colloidal assembly. Here we demonstrate an approach to modulate the surface charge of colloidal particles and, hence, their electrostatic interactions by irradiation with UV light.

To generate light-sensitive colloidal particles, we designed a new self-assembled monolayer (SAM) that undergoes charge inversion upon photocleavage (Figure 1). Each molecule of the SAM is initially terminated with a positively charged ammonium ($-\text{NH}_3^+$) group. Photocleavage of the ortho-nitrobenzyl linker⁸ then exposes an underlying negatively charged carboxylate ($-\text{COO}^-$) group. Accordingly, silica particles functionalized with this SAM are expected to possess an effective charge (or zeta potential) that can be tuned through a broad range of positive, neutral, and negative values at fixed pH simply by exposure to UV light for varying times. Because their zeta potential (ζ) can be regulated by irradiation alone, it should be possible to induce phase changes within colloidal suspensions without externally altering their solution composition.

As described in detail in the Supporting Information, chlorosilane **1** is synthesized in three steps from the known 4-(hydroxymethyl)-3-nitrobenzoic acid.⁹ Immobilization of **1** on dried silica microspheres ($\sim 1 \mu\text{m}$ diameter) is accomplished in toluene with triethylamine as an acid scavenger (Figure 1). Brief exposure to trifluoroacetic acid (TFA) in methylene chloride converts the BOC group to an ammonium cation. This stable colloidal suspension undergoes rapid flocculation upon exposure to TFA. After washing with methylene chloride, the ammonium-terminated microspheres (silica-SAM- NH_3^+) are washed with benzene and lyophilized.

To confirm the expected photochemical transformation, the particles' surface composition was examined via X-ray photoelectron spectroscopy (XPS) before and after irradiation. As shown in Figure 2, the nitrogen 1s photoelectron peak decreases substantially upon exposure of colloidal suspensions to UV light. This observation is consistent with photoinduced cleavage of the bifunctional SAM, which results in a loss of amino and nitro groups from the microsphere surface. From the XPS integrated intensities, it is estimated that 85–95% of the nitrogen has been removed from the silica-SAM after 40 min of UV exposure.¹⁰

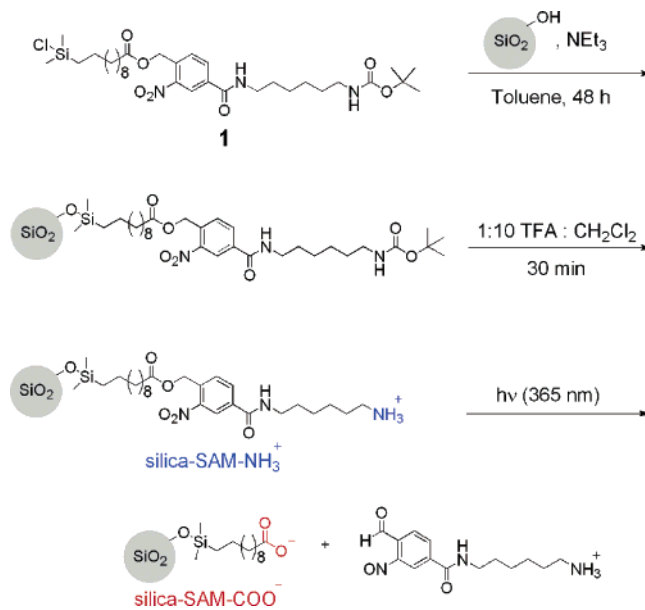


Figure 1. Immobilization of a bifunctional, photocleavable SAM on the silica particle surface.

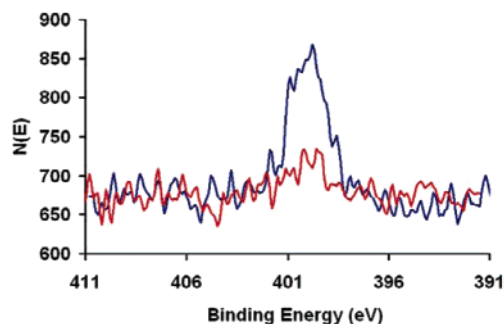


Figure 2. XPS spectra of the nitrogen 1s photoelectron. Silica-SAM- NH_3^+ microspheres irradiated by UV light for 40 min (red) contained 85–95% less nitrogen than their as-synthesized counterparts (blue).

To quantify the photosensitivity of particle charge, colloidal suspensions of silica-SAM- NH_3^+ microspheres were systematically exposed to UV light for varying times. Particles collected from the various UV exposure times were then resuspended in an aqueous solution (ca. pH 7)¹¹ and subsequently analyzed by microelectrophoresis. Figure 3 shows that ζ varied from an initial positive value of +26 mV and reached an asymptotic limit in the negative range (–60 mV) after ca. 40 min. It is worthwhile to note that these changes are accomplished at constant pH.

To demonstrate a photoinduced phase transition in silica-SAM- NH_3^+ microsphere suspensions, a binary colloidal suspension was prepared by slowly adding a suspension of the photosensitive silica-SAM- NH_3^+ microspheres to a suspension of negatively charged, rhodamine-labeled silica microspheres (this mixture will be referred

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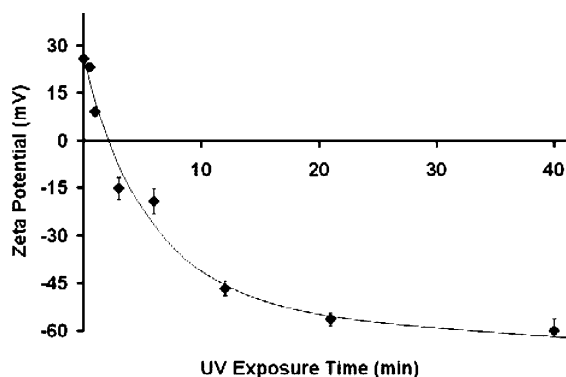


Figure 3. Zeta potential of silica-SAM-NH₃⁺ microspheres as a function of UV irradiation time. Solid line was added to show the trend.

to as the control suspension). Confocal microscopy of this mixture reveals the presence of clusters of oppositely charged particles that form immediately upon adding the suspensions together (Figure 4). More specifically, chainlike aggregates comprised of alternating silica-SAM-NH₃⁺ and rhodamine-labeled microspheres can be seen in the control suspension, as expected due to the heteroflocculation.^{12–15} A second colloidal suspension was prepared in the same way as the control, except that it was irradiated with UV light for 40 min after mixing. A dramatic change in the colloidal packing efficiency accompanies UV irradiation, which is visually apparent by comparing the light-exposed suspension to the control. The sediment height for the control suspension is substantially higher than that of the UV exposed sample, consistent with a gel-to-fluid phase transition in response to light-based stimuli (Supporting Information). Confocal images of the sediment assembled from the light-exposed suspension reveals the dense structure formed under gravity-driven microsphere settling. Time-resolved microscopy carried out on this sample after gentle shaking confirmed the particles to be fully dispersed, undergoing uncorrelated Brownian displacements (data not shown) that suggest all of the silica microspheres now possess a net negative charge.

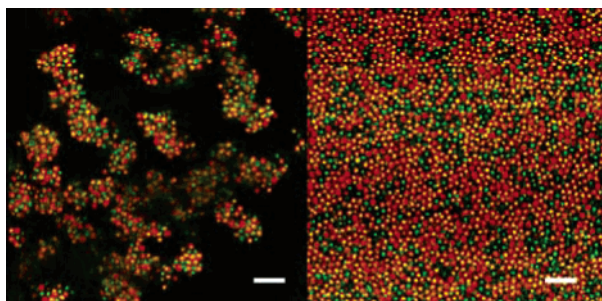


Figure 4. Confocal images (*x-y* scans) of a binary colloidal suspension of rhodamine-labeled silica microspheres (red, imaged in fluorescent mode) and silica-SAM-NH₃⁺ (green, imaged in reflection mode) before (left) and after (right) irradiation by UV light for 40 min. Scale bar = 4 μm.

In conclusion, a novel silica-based photocleavable SAM has been developed that provides exquisite control over interparticle interac-

tions via irradiation with UV light. The approach opens up new avenues for investigating the phase transitions and dynamic structure evolution of both unary and binary colloidal suspensions. As one example, we demonstrated the gel-to-fluid transition in binary mixtures that were initially oppositely charged and, ultimately, like-charged after exposure to UV light for an appropriate time. However, a myriad of phase changes are possible using this approach, including fluid-to-gel, gel-to-fluid, or gel-to-crystal transitions for pure silica-SAM-NH₃⁺ suspensions of increasing colloid volume fraction as well as a fluid-to-gel transition in binary mixtures, depending on whether the colloids begin as like-charged or neutral species that are converted into neutral-, like-, or oppositely charged species, respectively, upon irradiation. These light-responsive systems will further enable novel assembly routes for creating colloidal structures via photoinduced patterning without the use of photopolymerizable resins.

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Supporting Information Available: Experimental protocols, image of colloidal assembly in sedimentation tube. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) The C, N, and O content of these samples before and after cleavage is quantified as: 52.6% C, 2.8% N, and 44.6% O for silica-SAM-NH₃⁺ before UV exposure and 45.7% C, 0.2% N, and 54.1% O after 40 min exposure. Because the signal-to-noise is low, an exact quantification of the cleavage yield was not obtainable.
- (11) Not surprisingly, added salt attenuates the effects described here. Thus, all of the experiments were performed in deionized water, whose pH was adjusted to a value of ca. 7 by the addition of 1.0 mM NaOH.
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