

## Light-Regulated Electrostatic Interactions in Colloidal Suspensions

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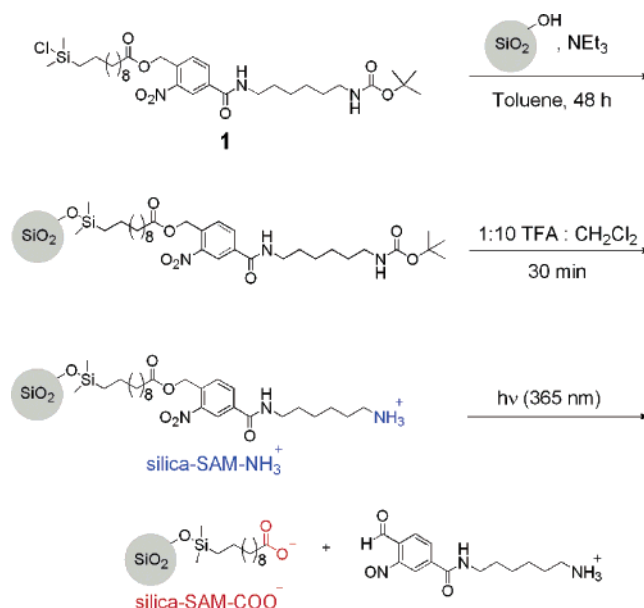
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Colloidal suspensions enjoy widespread use in applications ranging from advanced materials to drug delivery. By tailoring the interactions between particles, one can design colloidal fluids, gels, or crystals needed for ceramic,<sup>1</sup> coating,<sup>2</sup> ink,<sup>3</sup> photonic,<sup>4,5</sup> and pharmaceutical materials.<sup>6</sup> 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.<sup>7</sup> 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.

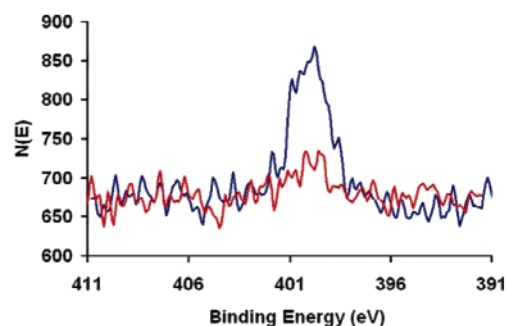
To generate light-sensitive colloidal particles, we designed a new self-assembled monolayer (SAM) that undergoes charge inversion upon photocleavage (Figure 1). Each molecule of the SAM is initially terminated with a positively charged ammonium ( $-\text{NH}_3^+$ ) group. Photocleavage of the ortho-nitrobenzyl linker<sup>8</sup> 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 ( $\zeta$ ) 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.<sup>9</sup> 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- $\text{NH}_3^+$ ) 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.<sup>10</sup>



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



**Figure 2.** XPS spectra of the nitrogen 1s photoelectron. Silica-SAM- $\text{NH}_3^+$  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- $\text{NH}_3^+$  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)<sup>11</sup> and subsequently analyzed by microelectrophoresis. Figure 3 shows that  $\zeta$  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.

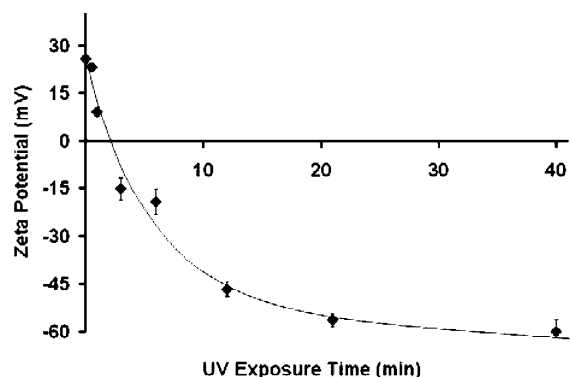
To demonstrate a photoinduced phase transition in silica-SAM- $\text{NH}_3^+$  microsphere suspensions, a binary colloidal suspension was prepared by slowly adding a suspension of the photosensitive silica-SAM- $\text{NH}_3^+$  microspheres to a suspension of negatively charged, rhodamine-labeled silica microspheres (this mixture will be referred

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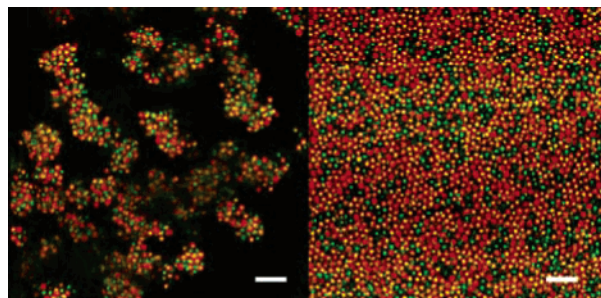
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## COMMUNICATIONS



**Figure 3.** Zeta potential of silica-SAM-NH<sub>3</sub><sup>+</sup> microspheres as a function of UV irradiation time. Solid line was added to show the trend.

68 to as the control suspension). Confocal microscopy of this mixture  
 69 reveals the presence of clusters of oppositely charged particles that  
 70 form immediately upon adding the suspensions together (Figure  
 71 4). More specifically, chainlike aggregates comprised of alternating  
 72 silica-SAM-NH<sub>3</sub><sup>+</sup> and rhodamine-labeled microspheres can be seen  
 73 in the control suspension, as expected due to the heteroflocculation.<sup>12–15</sup> A second colloidal suspension was prepared in the same  
 74 way as the control, except that it was irradiated with UV light for  
 75 40 min after mixing. A dramatic change in the colloidal packing  
 76 efficiency accompanies UV irradiation, which is visually apparent  
 77 by comparing the light-exposed suspension to the control. The  
 78 sediment height for the control suspension is substantially higher  
 79 than that of the UV exposed sample, consistent with a gel-to-fluid  
 80 phase transition in response to light-based stimuli (Supporting  
 81 Information). Confocal images of the sediment assembled from the  
 82 light-exposed suspension reveals the dense structure formed under  
 83 gravity-driven microsphere settling. Time-resolved microscopy  
 84 carried out on this sample after gentle shaking confirmed the  
 85 particles to be fully dispersed, undergoing uncorrelated Brownian  
 86 displacements (data not shown) that suggest all of the silica  
 87 microspheres now possess a net negative charge.  
 88



**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-NH<sub>3</sub><sup>+</sup> (green, imaged in reflection mode) before (left) and after (right) irradiation by UV light for 40 min. Scale bar = 4 μm.

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

tions via irradiation with UV light. The approach opens up new  
 91 avenues for investigating the phase transitions and dynamic structure  
 92 evolution of both unary and binary colloidal suspensions. As one  
 93 example, we demonstrated the gel-to-fluid transition in binary  
 94 mixtures that were initially oppositely charged and, ultimately, like-  
 95 charged after exposure to UV light for an appropriate time.  
 96 However, a myriad of phase changes are possible using this  
 97 approach, including fluid-to-gel, gel-to-fluid, or gel-to-crystal  
 98 transitions for pure silica-SAM-NH<sub>3</sub><sup>+</sup> suspensions of increasing  
 99 colloid volume fraction as well as a fluid-to-gel transition in binary  
 100 mixtures, depending on whether the colloids begin as like-charged  
 101 or neutral species that are converted into neutral-, like-, or oppositely  
 102 charged species, respectively, upon irradiation. These light-  
 103 responsive systems will further enable novel assembly routes for  
 104 creating colloidal structures via photoinduced patterning without  
 105 the use of photopolymerizable resins.  
 106

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

- (1) Lewis, J. A. *J. Am. Ceram. Soc.* **2000**, *83*, 2341–2359. 122
- (2) Martinez, C. J.; Lewis, J. A. *Langmuir* **2002**, *18*, 4689–4698. 123
- (3) Smay, J. E.; Gratson, G. M.; Shepherd, R. F.; Cesarano, J. I.; Lewis, J. A. *Adv. Mater.* **2002**, *14*, 1279–1283. 124
- (4) Joannopoulos, J. D.; Villeneuve, P. R.; Fans, S. *Nature* **1997**, *386*, 143–149. 125
- (5) Braun, P. V.; Wiltzius, P. *Nature* **1999**, *402*, 603–604. 126
- (6) Muller, R. H. *Colloidal Carriers for Controlled Drug Delivery and Targeting, Modification, Characterization, and In Vivo Distribution*; CRC Press: Boca Raton, FL, 1991. 127
- (7) Hunter, R. J. *Foundations of Colloid Science*; Clarendon Press: Oxford, 1986; Vols. I and II. 128
- (8) Rich, D. H.; Gurwara, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 1575–1579. 129
- (9) Eisenfuhr, A.; Arora, P. S.; Sengle, G.; Takaoka, L. R.; Nowick, J. S.; Famulok, M. *Bioorg. Med. Chem.* **2003**, *11*, 235–249. 130
- (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-NH<sub>3</sub><sup>+</sup> 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. 131
- (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. 132
- (12) Kim, A. Y.; Berg, J. C. *J. Colloid Interface Sci.* **2000**, *229*, 607–614. 133
- (13) Kim, A. Y.; Hauch, K. D.; Berg, J. C.; Martin, J. E.; Anderson, R. A. *J. Colloid Interface Sci.* **2003**, *260*, 149–159. 134
- (14) Luckham, P.; Vincent, B.; Hart, C. A.; Tadros, T. F. *Colloid Surf.* **1980**, *1*, 281–293. 135
- (15) Rasa, M.; Philipse, A. P.; Meeldijk, J. D. *J. Colloid Interface Sci.* **2004**, *278*, 115–125. 136

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