DOI: 10.1002/ange.200901119

Self-Erasing Paper

Writing Self-Erasing Images using Metastable Nanoparticle “Inks”**

*Rafal Klajn, Paul J. Wesson, Kyle J. M. Bishop, and Bartosz A. Grzybowski**

Fans of the “Mission Impossible” movies might recall the self-destructing messages used to brief the secret agent on the details of his new mission. Even beyond the realm of fictitious espionage, materials that store textual or graphical information for a prescribed period of time are desirable for applications in secure communications.[1,2] Furthermore, if such materials are rewritable, they can help to limit the use of traditional paper, thereby reducing the costs, both industrial and environmental,[3] associated with paper production and recycling. To date, most research on self-erasing media has relied on the use of photochromic molecules[4–7]—that is, molecules that isomerize and change color when exposed to light of appropriate wavelength—embedded in or attached to a polymeric or gel matrix. In one widely publicized example, Xerox Corporation recently announced[8] the development of photochromic paper that self-erases in 16 to 24 h. While writing with light can be both rapid[9] and accurate,[5,7] photochromic “inks” are not necessarily optimal for transforming light-intensity patterns into color variations, because they have relatively low extinction coefficients,[10] are prone to photobleaching,[11] and usually offer only two colors corresponding to the two states of photoisomerizing molecules.[10]

Herein, we describe a conceptually different self-erasing material in which both the “writing” and self-erasure of color images are controlled by the dynamic non-equilibrium aggregation[12] of photoresponsive metal (here, gold and silver) nanoparticles (Au and AgNPs “inks”) embedded in thin, flexible organogel films. When exposed to UV light, the *trans*-azobenzene groups coating the NPs isomerize to *cis*-azobenzene with a large dipole moment.[13] As a result, the NPs aggregate into supraspherical (SS) assemblies,[13–16] whose apparent color depends on the duration of UV irradiation (Figures 1 and 2). Since the SS are metastable and fall apart spontaneously in the absence of UV irradiation, the two-color and multicolor images written into the films gradually self-erase (Figures 2 and 3). The erasure times can be controlled by the number of dipoles induced on the nanoparticles and can also be accelerated by exposure to visible light or by heating the material. Multiple images can be written into the same film either concurrently or after erasure.

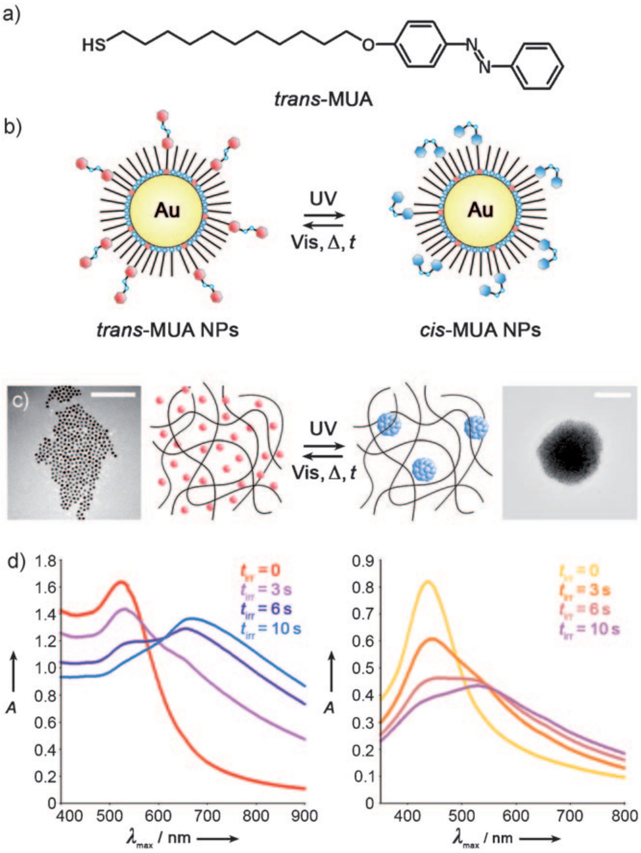

Figure 1. Reversible aggregation of photoactive nanoparticles. a) Structural formula of *trans*-4-(11-mercaptoundecanoxy)azobenzene (*trans*-MUA). b) UV irradiation of nanoparticles (here, gold) covered with a mixed monolayer of MUA and dodecylamine (DDA) causes photoisomerization of *trans*-MUA to *cis*-MUA. The *cis* isomer reverts to the *trans* form either spontaneously (slowly), upon irradiation with visible light, or by heating (both rapidly). c) Upon UV irradiation, photoactive NPs form metastable aggregates. The colors shown here correspond to gold particles: free AuNPs are red, aggregated NPs are blue. Scale bars on the corresponding TEM images are 100 nm. d) UV/Vis spectra of AuNP (left) and AgNP (right) films exposed to 365 nm UV light (10 mW cm^{-2}) for times t_{irr} varying from 0 to 10 s. In both cases, the red shift of the surface plasmon resonance (SPR) band is due to the aggregation of particles into aggregates of mean diameter $d = 150$ nm. Colors of the curves correspond to those observed in experiments.

In a wider context, the present system demonstrates the flexibility and promise of non-equilibrium nanostructures to create “smart” materials capable of changing their properties or function on demand in response to external stimuli.

Our experiments were based on AuNP (5.6 ± 0.6 nm diameter) or AgNP (5.3 ± 0.3 nm diameter) inks coated with mixed self-assembled monolayers (mSAMs) of dodecylamine (DDA) and photoswitchable azobenzene-terminated thiol (4-

---

[*] R. Klajn, P. J. Wesson, K. J. M. Bishop, Prof. Dr. B. A. Grzybowski
Department of Chemical and Biological Engineering
Department of Chemistry, Northwestern University
2145 Sheridan Rd., Evanston, IL 60208 (USA)
E-mail: grzybor@northwestern.edu
Homepage: http://dysa.northwestern.edu

[**] This work was supported by the Alfred P. Sloan Fellowship and the Dreyfus Teacher–Scholar Award (both to B.A.G.). R.K. was supported by the NSF Northwestern MRSEC. K.J.M.B. was supported by the NSF Graduate Fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200901119.

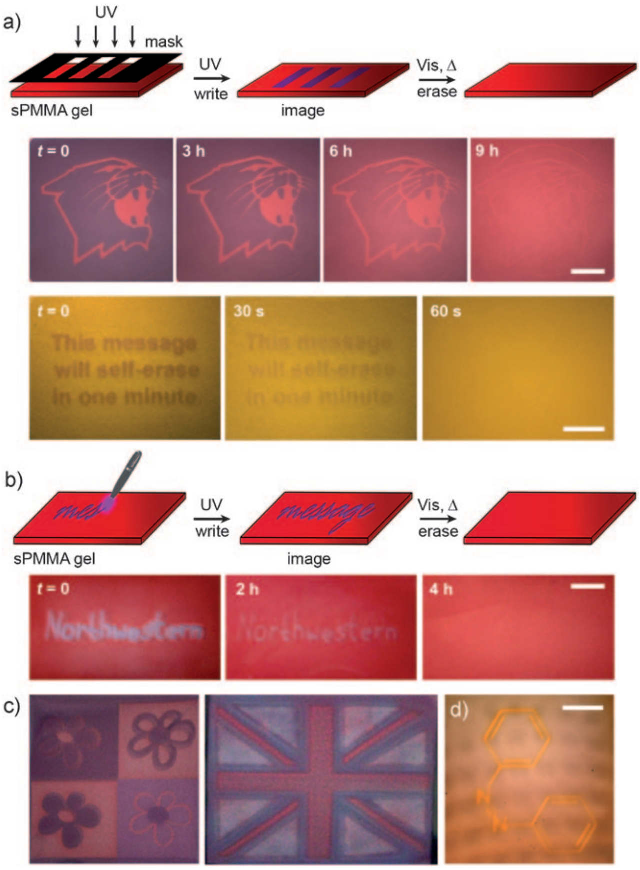

Figure 2. Writing into self-erasable NP films. a) Images created in AuNP (fractional surface coverage of MUA $\chi = 0.3$, upper row) and AgNP films ($\chi = 0.3$, lower row) by $t_{irr} \approx 0.8$ s exposure through a transparency photomask. The image in the AuNP film self-erases in daylight within 9 h. The image in the AgNP film is erased within 60 s by exposure to intense (0.3 mW cm^{-2}) visible light. b) Writing into AuNP film ($\chi = 0.27$) using a light pen ($I_{UV} = 10$ mW cm^{-2}) moved over the film at 3 mm s^{-1}. Owing to a lower surface concentration of azobenzene thiols, the self-erasure of this film in daylight takes less time (4 h) than for the one shown in (a). c) Multicolor images written into AuNP films. In the "flowers" picture, the purple regions were irradiated for shorter times than the purple-bluish ones. In the Union Jack, the whitish-blue regions were irradiated longest so that all NPs in these regions aggregated (see Figure 1 d). d) Multicolor images written into AgNPs. The entire film was first exposed to UV light, causing a color change from yellow to pale red. The film was then bent and the pattern of squares was "written in" (transition from pale red to purple). Finally, the film was flattened and an image of azobenzene was created by exposure to visible light, which caused disassembly of the supraspheres in the irradiated region and return to the original light-orange hue. All scale bars are 1 cm.

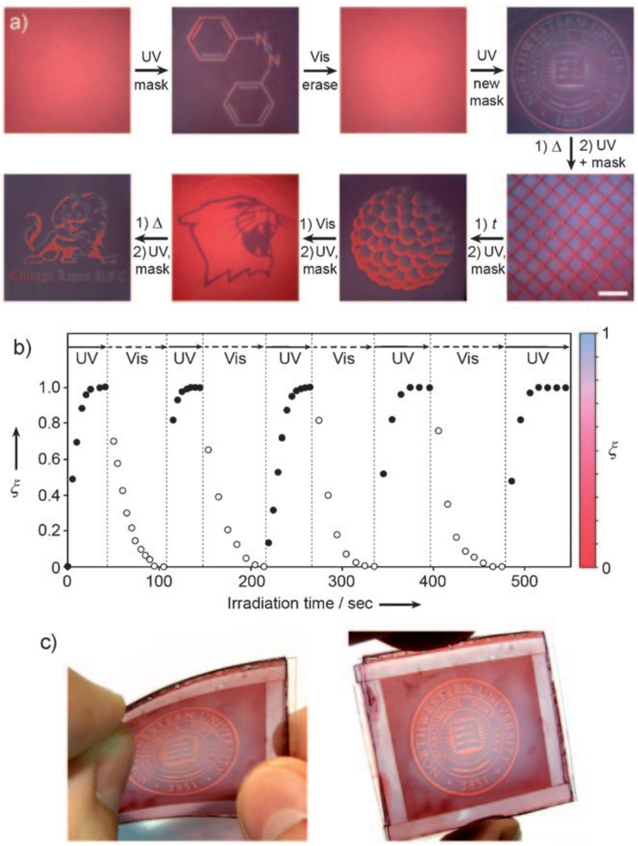

Figure 3. Rewritable and flexible films. a) Sequential writing into and erasing from the same AuNP film. In all images, the writing times were $t_{irr} \approx 2$ s using 10 mW cm^{-2} UV light, except for the array of squares ($t_{irr} \approx 5$ s). Images were erased either by long-time (hours) exposure to daylight (indicated by *t* over the arrows), by short (seconds) exposure to intense visible light (Vis), or by heating the film to approximately 50 °C for 20 s (Δ). The images from top left clockwise are: structural formula of *cis*-azobenzene, Northwestern University seal, array of squares, scheme of a suprasphere, Northwestern Wildcats logo, and the Chicago Lions rugby team logo. Scale bar is 5 mm. b) Reversible spectral changes of a AuNP ($\chi = 0.3$) film upon alternating exposures to UV (0.7 mW cm^{-2}) and visible light. Here, ξ is a "progress variable" calculated from the experimental extinction spectra using the CIE 1931 standard observer functions. This variable characterizes the apparent color of the film and ranges from zero (unaggregated; red for AuNPs) to one (fully aggregated; light blue for AuNPs); see the Supporting Information for more details on the derivation of this coordinate. The film's optical response does not change for at least 300 cycles. c) Patterned films can be mechanically distorted without disrupting the imprinted image (here, Northwestern University seal).

(11-mercaptoundecanoxy)azobenzene, MUA, Figure 1 a,b; see also the Supporting Information for experimental details).

This system offers three important advantages over the previously studied photoactive NPs coated with azobenzene dithiols (ADT) and stabilized in solution by a large excess of didodecyldimethylammonium bromide (DDAB) surfactant.[13] First, the absence of the second terminal thiol group enables full reversibility of aggregation (i.e., no covalent cross-linking takes place) for at least several hundred cycles (vs. fewer than 20 in the ADT/DDAB system). Second, although in the absence of dithiol cross-linking the NPs cannot self-assemble into well-ordered crystals, they aggregate and disaggregate (into similarly sized but orderless structures) much more rapidly (ca. 1 s vs. ca. 10 min). Third, the surfactant-free NPs are stable in gel matrices. This stability extends to high NP concentrations (greater than 30 mM vs. less than 1 mM previously in solution) and gives deep colors even to thin gel films. Together, these properties enable dispersion of the NP inks in the gel photopaper and allow for rapid, high-contrast writing using light.

In a typical procedure, the nanoparticles were dispersed in thin, approximately 150 μm films of syndiotactic poly(methyl methacrylate) (sPMMA) organogel[17] laminated between two flexible poly(vinyl chloride)-coated poly(ethylene terephthalate) sheets (up to 5×5 cm). Despite relatively low concentrations of these NPs, but owing to their high extinction cross-sections ($4.2\times10^{-18}\,\mathrm{m}^2$ for gold and $1.2\times10^{-17}\,\mathrm{m}^2$ for silver[18]), the films were colored brightly: red for AuNPs and yellow for AgNPs. Importantly, in the absence of UV irradiation, the NPs in the gel had UV/Vis spectra nearly identical to those of free NPs in toluene ($\lambda_{\mathrm{max,Au}} \approx 525$ nm, $\lambda_{\mathrm{max,Ag}} \approx 420$ nm[18]), thus indicating that the particles were not aggregated. When, however, the films were exposed to UV light, they changed color in the irradiated regions, and the degree of this change depended on the duration of UV irradiation (Figure 1c,d and Figure 2). In the absence of irradiation, the images written into the films gradually self-erased (Figures 2 and 3), with the erasure times controlled by the composition of the mSAMs coating the NP inks.

The changes observed upon UV irradiation (365 nm, $I_{\mathrm{UV}}=0.7$–$10\,\mathrm{mW\,cm^{-2}}$) were due to the rapid *trans*-to-*cis* isomerization of the azobenzene groups of MUA. This isomerization caused a significant increase of the dipole moment ($\mu\approx5$ debye for the *cis* form vs. $\mu\approx1$ debye for the *trans* isomer[19]), which mediated attractive interactions between the NPs. The strength of these interactions[13] depended on the surface concentrations of the MUA tethered to the NPs. For low coverage of MUA ($\chi<0.23$) the dipole–dipole forces between NPs were too weak to cause aggregation; for $\chi>0.34$, irreversible aggregation occurred even in the absence of irradiation. For $0.23<\chi<0.34$, the NPs aggregated reversibly into disordered, metastable aggregates (ca. 150 nm in diameter by TEM), which disintegrated in the absence of UV light (Figure 1c). This reversible NP aggregation was the basis of rewritable and self-erasing materials.

Formation of the metastable aggregates in the UV-exposed regions manifested itself by the broadening and red-shifting of the NPs' SPR band and by concomitant color changes. The degree of these changes reflected the proportion of aggregated NPs (see the Supporting Information) and depended on the nature of the NPs in the film and on the irradiation dose: AuNP inks evolved gradually from red to pale blue (Figure 1d, left) and AgNP inks from yellow to violet (Figure 1d, right). Figure 2a shows examples of two-color images created in AuNP and AgNP films by photomask exposure to $I_{\mathrm{UV}}=10\,\mathrm{mW\,cm^{-2}}$ for approximately 0.8 s. In Figure 2b, the violet text was written into the film using a UV pen ($I_{\mathrm{UV}}=10\,\mathrm{mW\,cm^{-2}}$) scanned above the surface at about $3\,\mathrm{mm\,s^{-1}}$. Remarkably, multicolor images could be created with one nanoparticle ink by varying the irradiation dose over different regions of the film. For example, the flowers and the Union Jack shown in Figure 2c were created in AuNP films by irradiating ($I_{\mathrm{UV}}=10\,\mathrm{mW\,cm^{-2}}$) the purple regions for 0.8 s, purple-bluish regions for 4 s, and pale-blue regions for 10 s. Figure 2d shows a multicolor AgNP film into which two images were written consecutively, one of them onto a bent film giving the overall illusion of curvature.

Owing to the reversibility of the nanoparticle aggregation, all types of photopatterned images gradually self-erased as the aggregates reverted to free NPs. When the films were left on the benchtop and exposed to ambient laboratory light, the erasure times were hours to several days depending on χ; in the dark, the images remained stable for over a week. When, however, the films were heated or exposed to intense visible light, erasure took only a few to tens of seconds. Once erased, the films could be rewritten multiple times. Figure 3a shows a series of images written into and erased from AuNP films. We have verified that the quality of these images did not deteriorate with the number of write/erase cycles for at least several hundred cycles (Figure 3a,b). Finally, all photopatterned films were flexible, and the images remained intact upon mechanical bending or twisting (Figure 3c).

The times required to write (t_{w}) and erase (t_{e}) high-contrast images depended on and could be controlled by the intensity of light (UV for writing, Vis for erasure) and by the fractional surface coverage χ of the MUA ligands. Specifically, t_{w} decreased with increasing I_{UV} and varied between approximately 20 s for $I_{\mathrm{UV}}=0.7\,\mathrm{mW\,cm^{-2}}$ and 0.8 s for $I_{\mathrm{UV}}=10\,\mathrm{mW\,cm^{-2}}$. For a given value of I_{UV}, t_{w} decreased with increasing χ (Figure 4a). On the other hand, the times required to erase the images decreased with increasing intensity of the visible light (e.g., $t_{\mathrm{e}}\approx24$ h in $I_{\mathrm{Vis}}=10\,\mathrm{nW\,cm^{-2}}$ lighting vs. $t_{\mathrm{e}}\approx20$ s for $I_{\mathrm{Vis}}=0.8\,\mathrm{mW\,cm^{-2}}$ halogen lamp) and with decreasing χ (Figure 4b).

To explain these effects, we first observe that the equilibrium solubility of NPs depends on the fractional surface coverage of the *cis*-MUA isomer, χ_{cis} ($0<\chi_{\mathrm{cis}}<\chi$, see the Supporting Information). When χ_{cis} exceeds a critical value ($\chi_{\mathrm{cis}}{}^*\approx0.23$) the NP dispersion becomes unstable, and NPs aggregate until equilibrium is reestablished between the dispersed and the aggregated phases. The characteristic duration of this process is controlled primarily by the *trans*-to-*cis* isomerization of the MUA ligands on the NP surfaces. Upon UV irradiation, χ_{cis} evolves in time as $\chi_{\mathrm{cis}}=\chi_{\mathrm{cis}}{}^{\infty}[1-\exp(-k_{\mathrm{tc}}t)]$, where k_{tc} is the first-order rate constant for *cis*–*trans* isomerization[19] (this rate increases approximately linearly with the intensity of the incident UV light[20]), and $\chi_{\mathrm{cis}}{}^{\infty}$ is the *cis*-MUA coverage at the photostationary state (here, $\chi_{\mathrm{cis}}{}^{\infty}\approx\chi$) corresponding to all MUA being in the *cis* form. Therefore, the characteristic writing time t_{w} is given by $\chi_{\mathrm{cis}}(t_{\mathrm{w}})\approx\chi_{\mathrm{cis}}{}^*$ or $t_{\mathrm{w}}\approx k_{\mathrm{tc}}{}^{-1}\ln[\chi/(\chi-\chi_{\mathrm{cis}}{}^*)]$. For example, for intensity $I_{\mathrm{UV}}=0.7\,\mathrm{mW\,cm^{-2}}$ corresponding to $k_{\mathrm{tc}}\approx0.1\,\mathrm{s}^{-1}$,[19,20] the writing time in a gel containing NPs with $\chi=0.33$ is estimated to be $t_{\mathrm{w}}\approx15$ s; for more intense irradiation ($I_{\mathrm{UV}}=10\,\mathrm{mW\,cm^{-2}}$ and $k_{\mathrm{tc}}\approx1\,\mathrm{s}^{-1}$) the estimated writing time in the same gel decreases to $t_{\mathrm{w}}\approx1$ s, in agreement with experiment. Note than since $k_{\mathrm{tc}}\propto I_{\mathrm{UV}}$, even faster writing should be possible with more intense irradiation.

We emphasize that the erasure is not due to the diffusion of the aggregates, which would "smear" the images, but only to their disassembly, which changes the color by weakening the electrodynamic coupling between proximal NPs. The diffusivities of single NPs and of the suprasphere in the homogeneous sPMMA organogel may be estimated as $D=D_0\exp(-\alpha R\phi^{0.75})$,[21] where $D_0=kT/6\pi\mu R$ is the Stokes–Einstein diffusivity, kT is the thermal energy, μ is the solvent

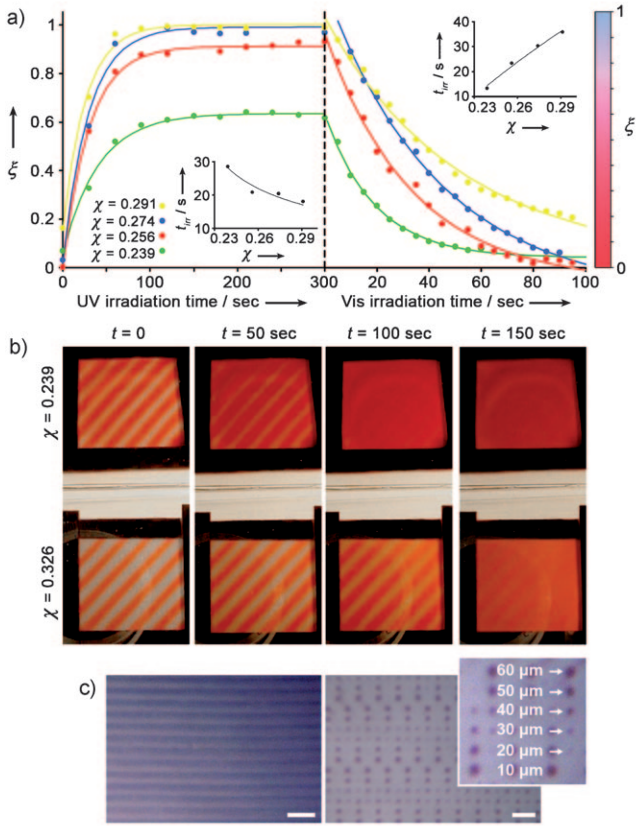

Figure 4. Quantification of the writing and erasure times. a) Quantification of spectral changes upon irradiation with UV light ($I_{UV} = 0.7$ mW cm^{-2}, left) and erasure with visible light ($I_{Vis} = 0.8$ mW cm^{-2}, right) for films differing in the surface concentrations χ of azobenzene thiols coating AuNPs. The values of χ are given in the legend. As in Figure 3 b, the progress variable ξ was calculated from the experimental extinction spectra and corresponds to the colormap on the right (see the Supporting Information for details). The curves represent best exponential fits to the experimental data and were used to estimate the half times for writing and erasure (insets left and right, respectively). Films characterized by low values of χ and weak dipole–dipole forces between the NPs take longer to write into, but they can be erased more rapidly. High-χ films in which dipole–dipole forces are stronger are more easily and rapidly patterned but are harder to erase. b) Erasure of two AuNP films differing in χ. The film characterized by higher χ erases more slowly. c) Microscope images of the smallest features resolved in AuNP-containing gels: array of 10 µm parallel lines (left) and array of circular dots (right). The smallest dot resolved in this film is approximately 20 µm. Scale bars are 200 µm (left) and 50 µm (right).

viscosity, R is the particle or aggregate radius, $\phi \approx 0.03$ is the gel volume fraction, and $\alpha \approx 0.5$ Å^{-1} is a constant specific to a given solute–gel pair. Thus, for a single NP, $D_{NP} \approx 10^{-6}$ cm^{2}s^{-1}; for an aggregate with a radius of approximately 50 nm, however, the diffusion coefficient drops dramatically to $D_{SS} \approx 10^{-15}$ cm^{2}s^{-1}. Therefore, the characteristic times required for the aggregates to diffuse $L \approx 100$ µm (typical size of the written features) are very long, on the order $L^2/D_{SS} \approx 10^{10}$ s. Instead, erasure of the images is due entirely to NP disassembly, which is limited by the *cis*-to-*trans* isomerization rate and not by diffusion.

Although negligible for larger features, NP diffusion plays a critical role in the spatial resolution at microscopic scales. The smallest features that can be resolved in the films we used are on the order of ten micrometers (Figure 4 c). Within such small features (or near the edges of larger features), NPs diffuse into and out of the UV-irradiated regions on time scales commensurate with typical irradiation times ($t_w \approx 1$–100 s). The diffusive mixing of irradiated and non-irradiated NPs results in an effective decrease of χ_{cis} on the particles located within the irradiated regions. Mathematically, this process can be described by considering the average *cis*-MUA coverage of the NPs, $\chi_{cis}{}^0$. This quantity evolves according to the following reaction-diffusion (RD) equation: $\partial\chi_{cis}{}^0/\partial t = D_{NP}\nabla^2\chi_{cis}{}^0 + k_{tc}(\chi - \chi_{cis}{}^0)$, where $k_{tc} \approx 1$ s^{-1} within the irradiated regions (assuming 10 mW cm^{-2} irradiation at 365 nm), and $k_{tc} = 0$ otherwise (see the Supporting Information). Appreciable color change occurs only when the condition $\chi_{cis}{}^0 \approx \chi_{cis}{}^*$ is satisfied and the interparticle interactions are sufficiently strong to induce NP aggregation. Importantly, the above equation is characterized by an intrinsic length scale $(D_{NP}/k_{tc})^{1/2} \approx 10$ µm, over which the processes of reaction and diffusion (RD) are of similar importance. For large irradiated features, $L \gg (D_{NP}/k_{tc})^{1/2}$, diffusion is negligible (except near the edges of the pattern), and the time required to resolve the image is controlled only by the isomerization rate (cf. discussion of writing times above). For small features, $L \leq (D_{NP}/k_{tc})^{1/2}$, diffusion opposes the increase of $\chi_{cis}{}^0$ within the feature and increases the time required to resolve the image. For example, if the irradiated feature is an isolated, circular dot of radius L, the solution to the RD equation predicts that only circular features larger than about 16 µm can be resolved even with very long irradiation times, in agreement with experiment (cf. Figure 4 c). The RD model (see the Supporting Information) also suggests that higher resolution and/or faster writing could best be achieved by increasing the initial concentration of NPs or by increasing the power of UV irradiation.

In summary, we described a class of self-erasable and rewritable materials in which information is written into metastable nanoparticle “inks”. We believe that these materials can be useful for storing sensitive or temporary information (our favorite is self-expiring bus tickets). Although the inks themselves are nontoxic (in fact, AgNPs have antibacterial properties[22]), the need to use organogels as the supporting medium is environmentally undesired, and alternative water-based materials using hydrophilic photoswitchable NPs should be considered in future research.

Received: February 27, 2009

Keywords: gold · nanoparticles · photochromism · self-assembly · silver

---

[1] F. Jedema, *Nat. Mater.* **2007**, *6*, 90–91.
[2] H. J. Borg, R. van Woudenberg, *J. Magn. Magn. Mater.* **1999**, *193*, 519–525.
[3] A. Villaneuva, H. Wenzel, *Waste Manage.* **2007**, *27*, S29–S46.

[4] Special Issue "Photochromism: Memories and Switches", *Chem. Rev.* **2000**, *100*, 1683–1890.

[5] M. Häckel, L. Kador, D. Kropp, H. W. Schmidt, *Adv. Mater.* **2007**, *19*, 227–231.

[6] F. Li, J. P. Zhuang, G. Y. Jiang, H. H. Tang, A. D. Xia, L. Jiang, Y. L. Song, Y. L. Li, D. B. Zhu, *Chem. Mater.* **2008**, *20*, 1194–1196.

[7] S. J. Lim, B. K. An, S. D. Jung, M. A. Chung, S. Y. Park, *Angew. Chem.* **2004**, *116*, 6506–6510; *Angew. Chem. Int. Ed.* **2004**, *43*, 6346–6350.

[8] http://www.xerox.com/innovation/exp_paper.shtml.

[9] S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778–781.

[10] *Photochromism* (Ed.: G. H. Brown), Wiley, New York, **1971**.

[11] R. Del Vecchio, N. V. Blough, *Mar. Chem.* **2002**, *78*, 231–253.

[12] M. Fialkowski, K. J. M. Bishop, R. Klajn, S. K. Smoukov, C. J. Campbell, B. A. Grzybowski, *J. Phys. Chem. B* **2006**, *110*, 2482–2496.

[13] R. Klajn, K. J. M. Bishop, B. A. Grzybowski, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 10305–10309.

[14] R. Klajn, K. J. M. Bishop, M. Fialkowski, M. Paszewski, C. J. Campbell, T. P. Gray, B. A. Grzybowski, *Science* **2007**, *316*, 261–264.

[15] R. Klajn, A. O. Pinchuk, G. C. Schatz, B. A. Grzybowski, *Angew. Chem.* **2007**, *119*, 8515–8519; *Angew. Chem. Int. Ed.* **2007**, *46*, 8363–8367.

[16] R. Klajn, T. P. Gray, P. J. Wesson, S. K. Smoukov, B. A. Grzybowski, *Adv. Funct. Mater.* **2008**, *18*, 2763–2769.

[17] H. Abe, K. Imai, M. Matsumoto, *J. Pol. Sci. Part B* **1966**, *4*, 589–594.

[18] U. Kriebing, M. Vollmer, *Optical Properties of Metal Clusters*, Springer, Berlin, **1995**.

[19] H. Akiyama, K. Tamada, J. Nagasawa, K. Abe, T. Tamaki, *J. Phys. Chem. B* **2003**, *107*, 130–135.

[20] I. Mita, K. Horie, K. Hirao, *Macromolecules* **1989**, *22*, 558–563.

[21] B. Amsden, *Macromolecules* **1998**, *31*, 8382–8395.

[22] S. K. Smoukov, K. J. M. Bishop, B. Kowalczyk, A. M. Kalsin, B. A. Grzybowski, *J. Am. Chem. Soc.* **2007**, *129*, 15623–15630.