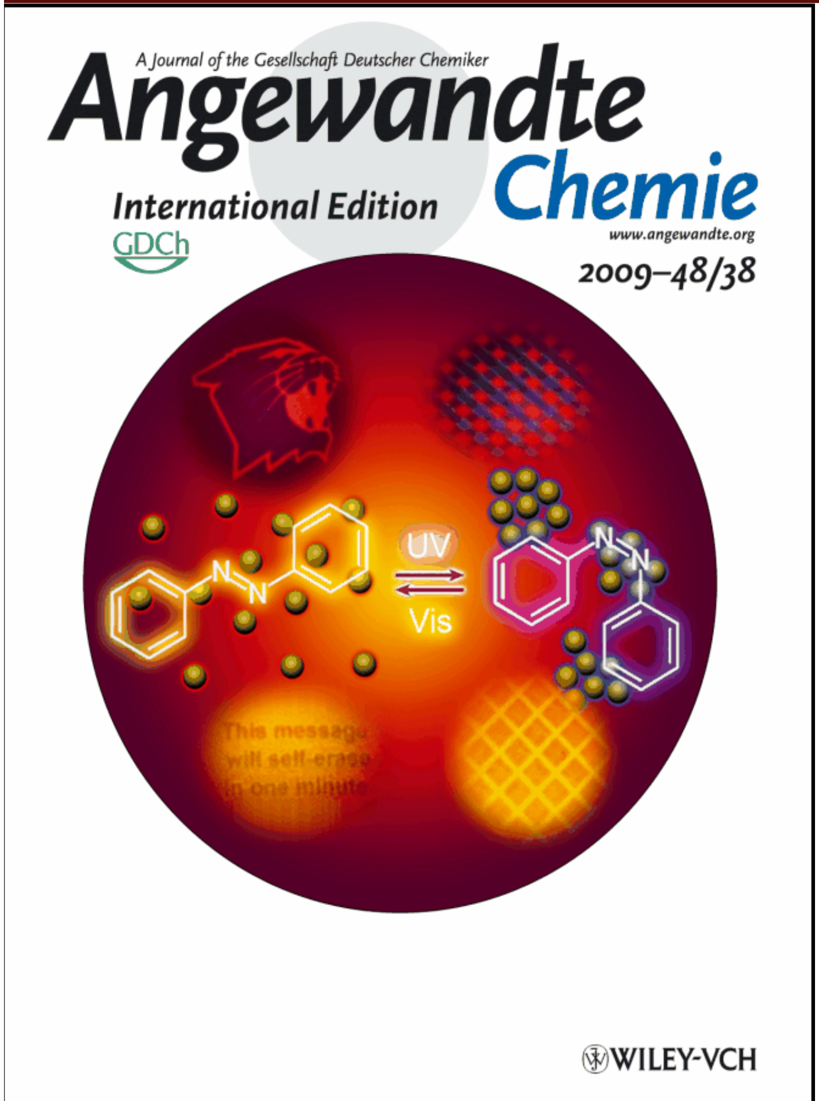
Writing Self-Erasing Images using Metastable Nanoparticle "Inks"



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

Department of Chemical and Biological Engineering, Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208 (USA)

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Introduction

Self -erasable paper → Materials that store textual or graphical information for a prescribed period of time are desirable for applications in secure communications.

→ They can help to limit the use of traditional paper, thereby reducing the costs, both industrial and environmental

→ Temporary images can be created by developing compounds that change color when they absorb a certain wavelength of light.

→ Photochromic "inks" are not necessarily optimal for transforming light-intensity patterns into color variations, because they have relatively low extinction coefficients.

❖ They are prone to photobleaching.

❖ They can provide only two colors corresponding to the two states of photoisomerizing molecules.

About the paper

- 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 of photoresponsive metal (here, gold and silver) nanoparticles (Au and AgNPs “inks”) embedded in thin, flexible organogel films.

- In contrast to previous techniques, present method allows for multi-colored pictures.

- Concept is based on an 'ink' made of nanoscopic metal particles that clump together-in a reversible process-under the influence of light.

Experimental

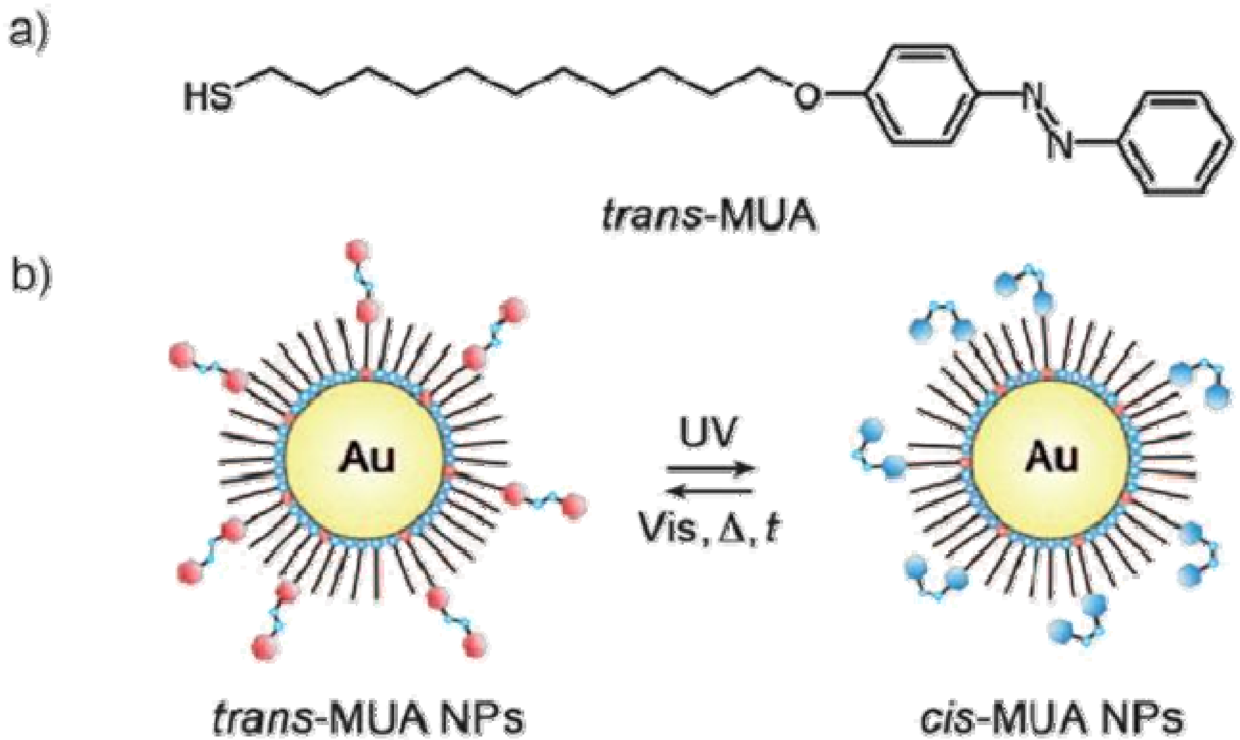
1. Dodecylamine (DDA) capped Au or Ag NPs were synthesized by a seeded growth method [(AuNP (5.6±6 nm diameter) or AgNP (5.3±3 nm diameter)].

2. Functionalization of gold and silver nanoparticles: *To as prepared surfactant-free solution of Au and Ag NPs, appropriate amount of a toluene solution of 4-(11 mercaptoundecanoxy)azobenzene (MUA) was injected*.

3. Syndiotactic poly(methylmethacrylate) (sPMMA) was prepared via stereo-controlled Ziegler-Natta cationic polymerization of methyl methacrylate (MMA).

4. Preparation of the self-erasing paper: *Toluene with syndiotactic PMMA was heated at T = 80 ^{o}C until the polymer dissolved to form a clear solution. At the same temperature, photoswitchable gold or silver NPs in toluene were added and stirring was continued until a homogeneous solution was obtained. This solution was then injected between two preheated sheets of a flexible polymer (poly(vinyl chloride) coated poly(ethylene terephthalate (150 µm thick) separated by four thin stripes made the same material and allowed to cool down to room temperature.*

Reversible aggregation of photoactive nanoparticles



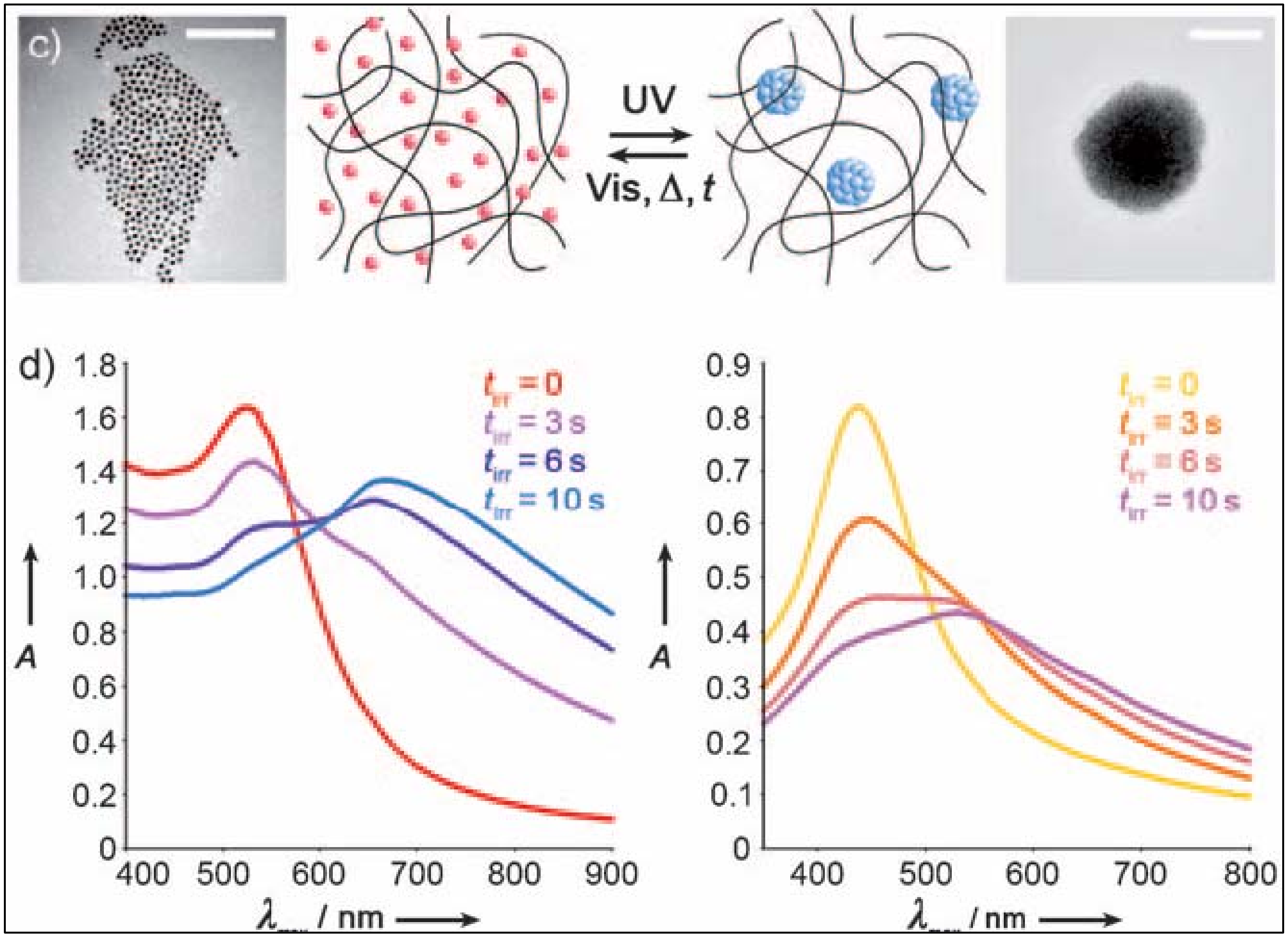
Cis-trans isomerization with a large dipole moment

Advantages

✓ The absence of the second terminal thiol group enables full reversibility of aggregation.

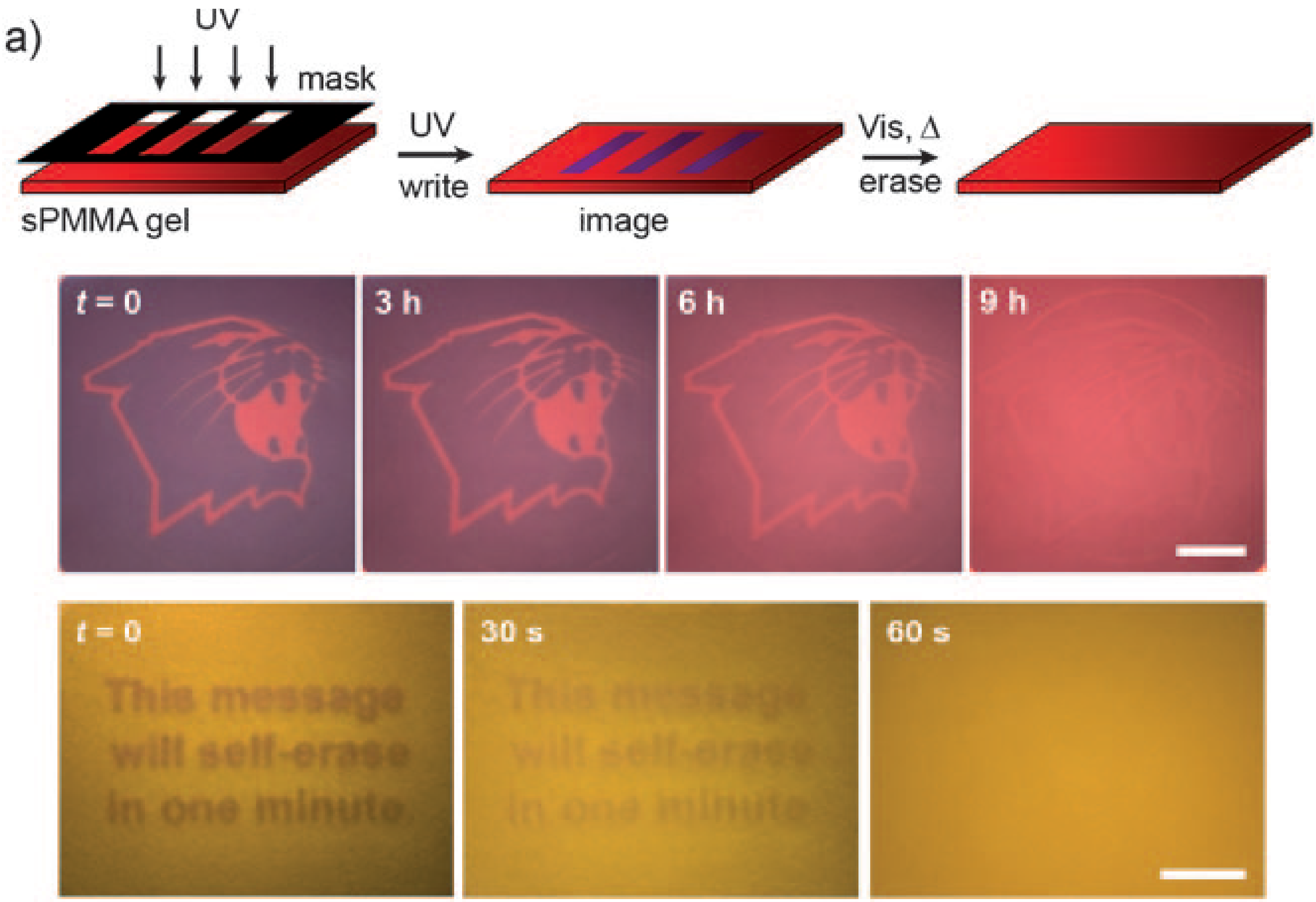
✓In the absence of dithiol cross-linking, the NPs cannot self-assemble into well-ordered crystals, they aggregate and disaggregate much more rapidly.

✓Third, the surfactant-free NPs are stable in gel matrices. This stability extends to high NP concentrations and gives deep colors even to thin gel films.



c) Upon UV irradiation, photoactive NPs form metastable aggregates. d) UV/Vis spectra of AuNP (left) and AgNP (right) films exposed to 365 nm UV light (10 $mWcm^{-2}$) 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.

How to write into the self-erasable NP film?



Images created in AuNP and AgNP films by t_{irr}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 $mWcm^{-2}$) visible light.

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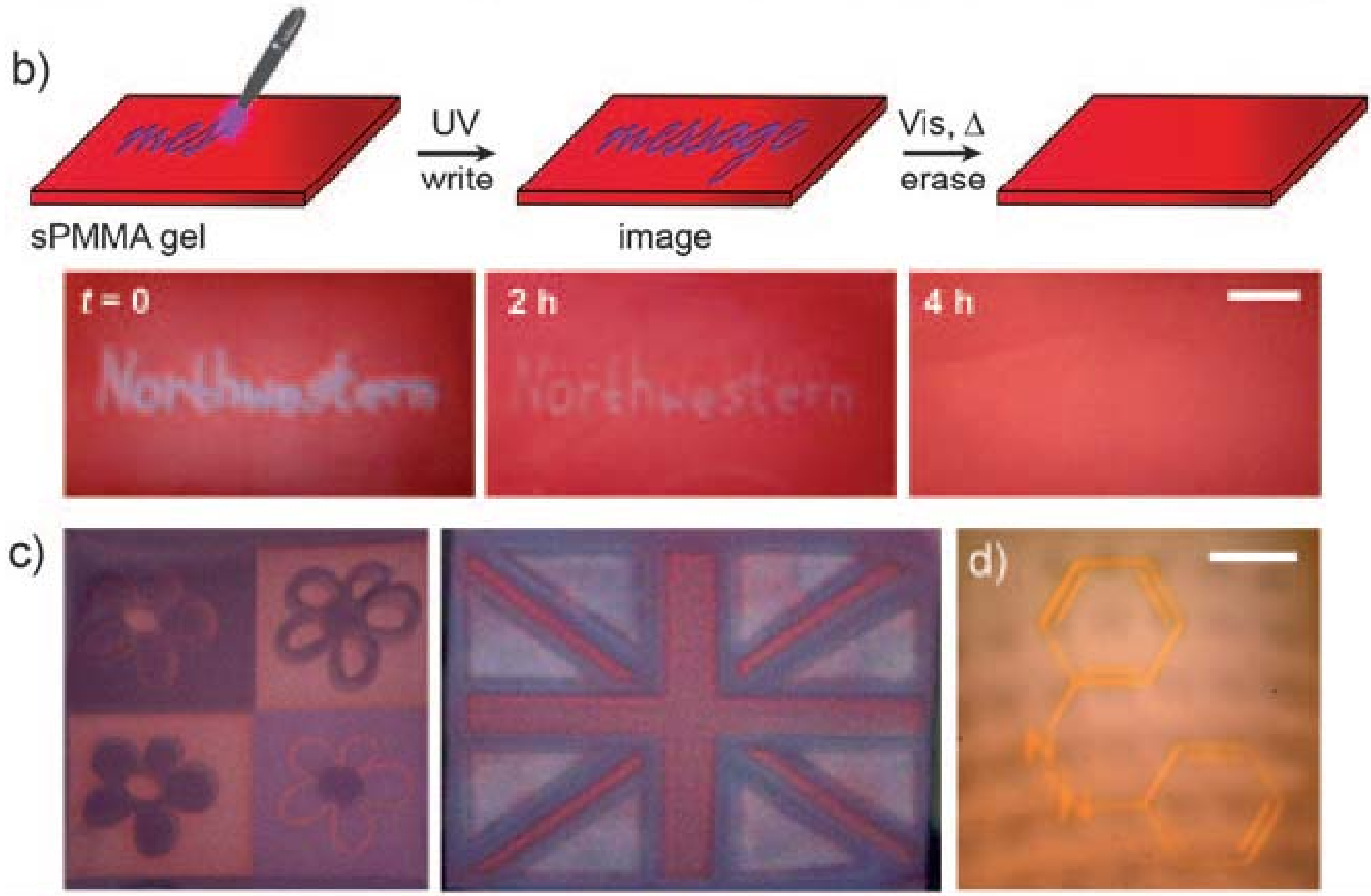
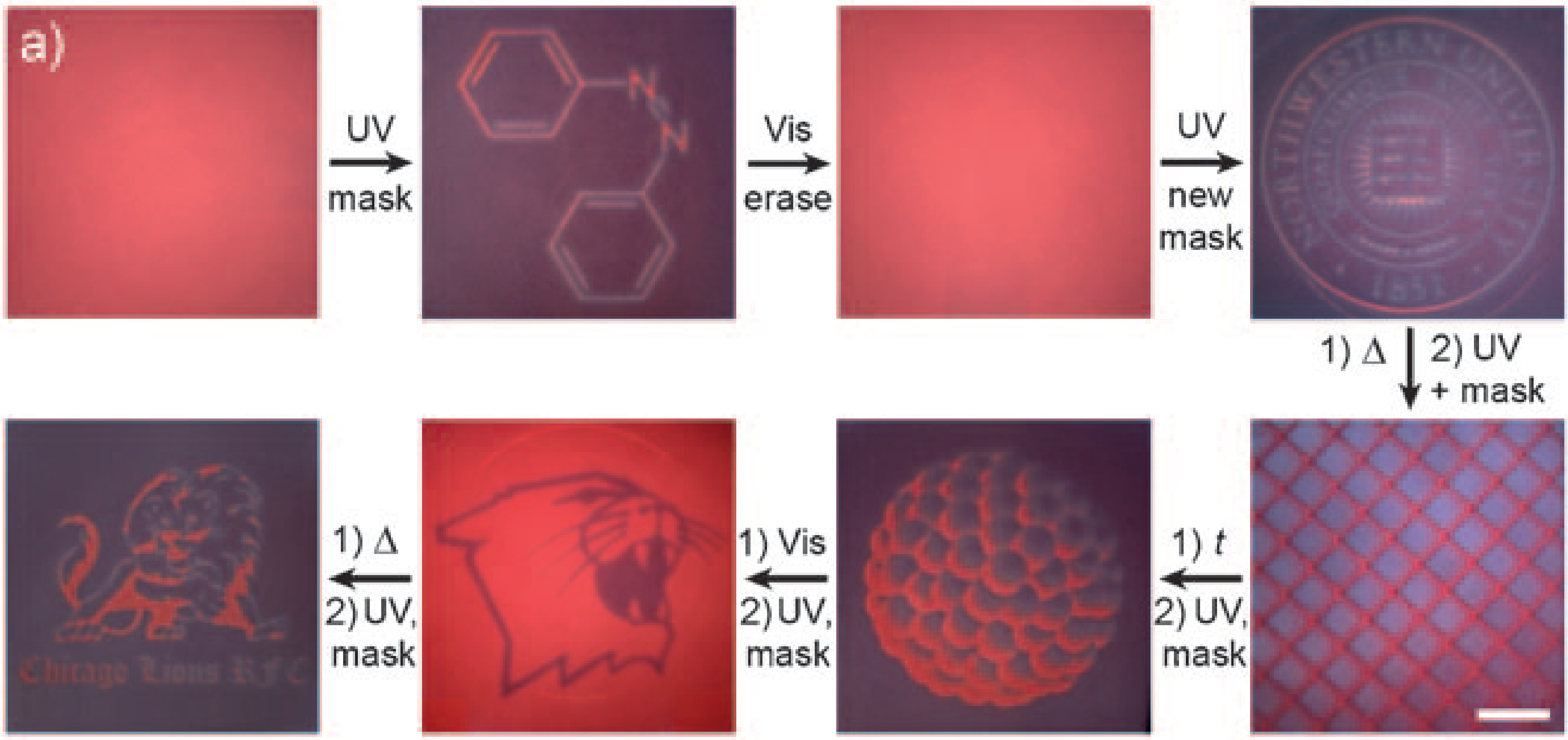
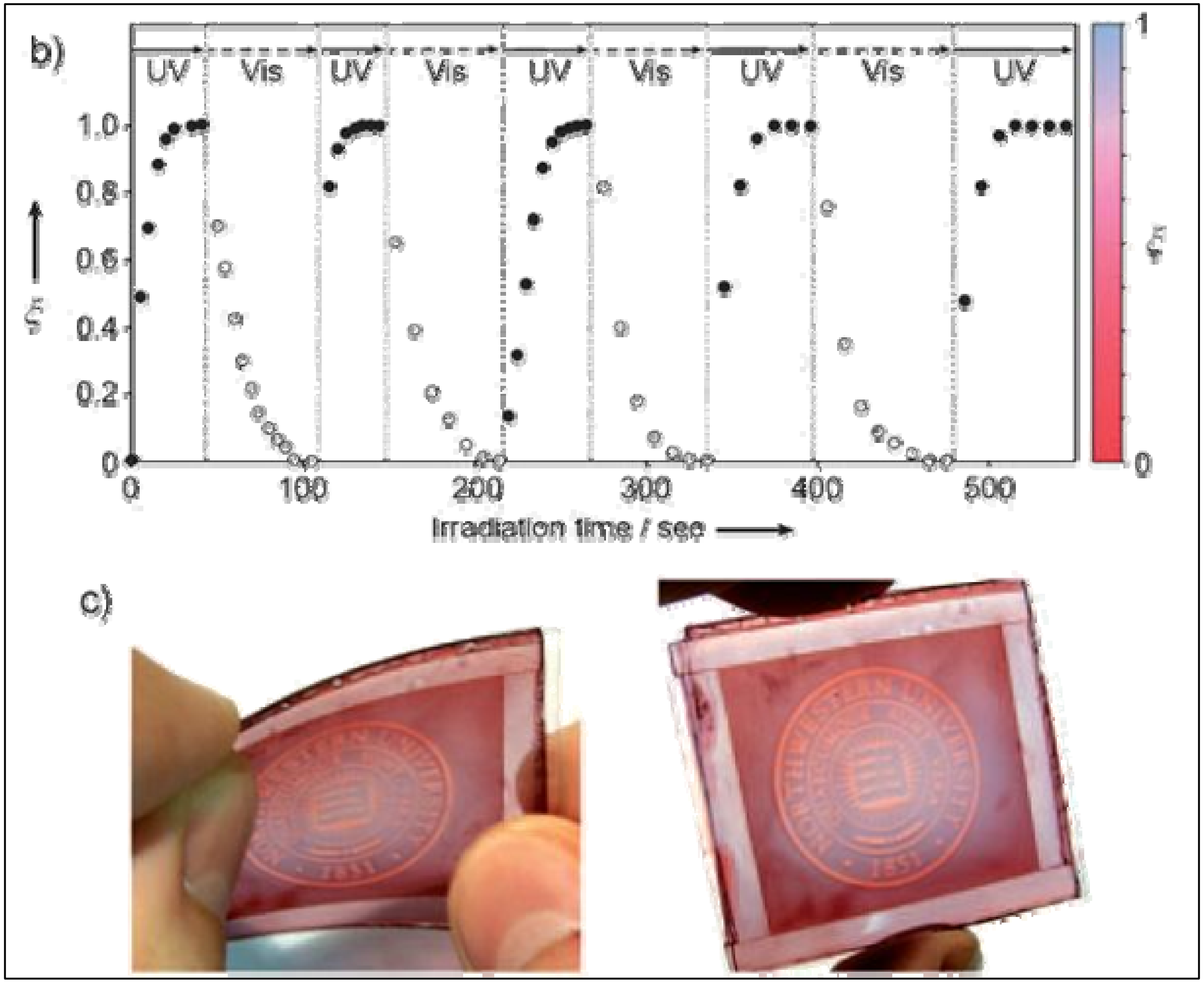


Writing into AuNP film using a light pen (I_{UV}=10 mWcm^{-2}) moved over the film at 3 mms^{-1}. c) Multicolor images written into AuNP films. In the “flowers” picture, the purple regions were irradiated for shorter times than the purple-bluish ones. In the Union Jack, the whitish-blue regions were irradiated longest so that all NPs in these regions aggregated (see Figure c). d) Multicolor images written into AgNPs. All scale bars are 1 cm.

Various images written into and erased from AuNP films

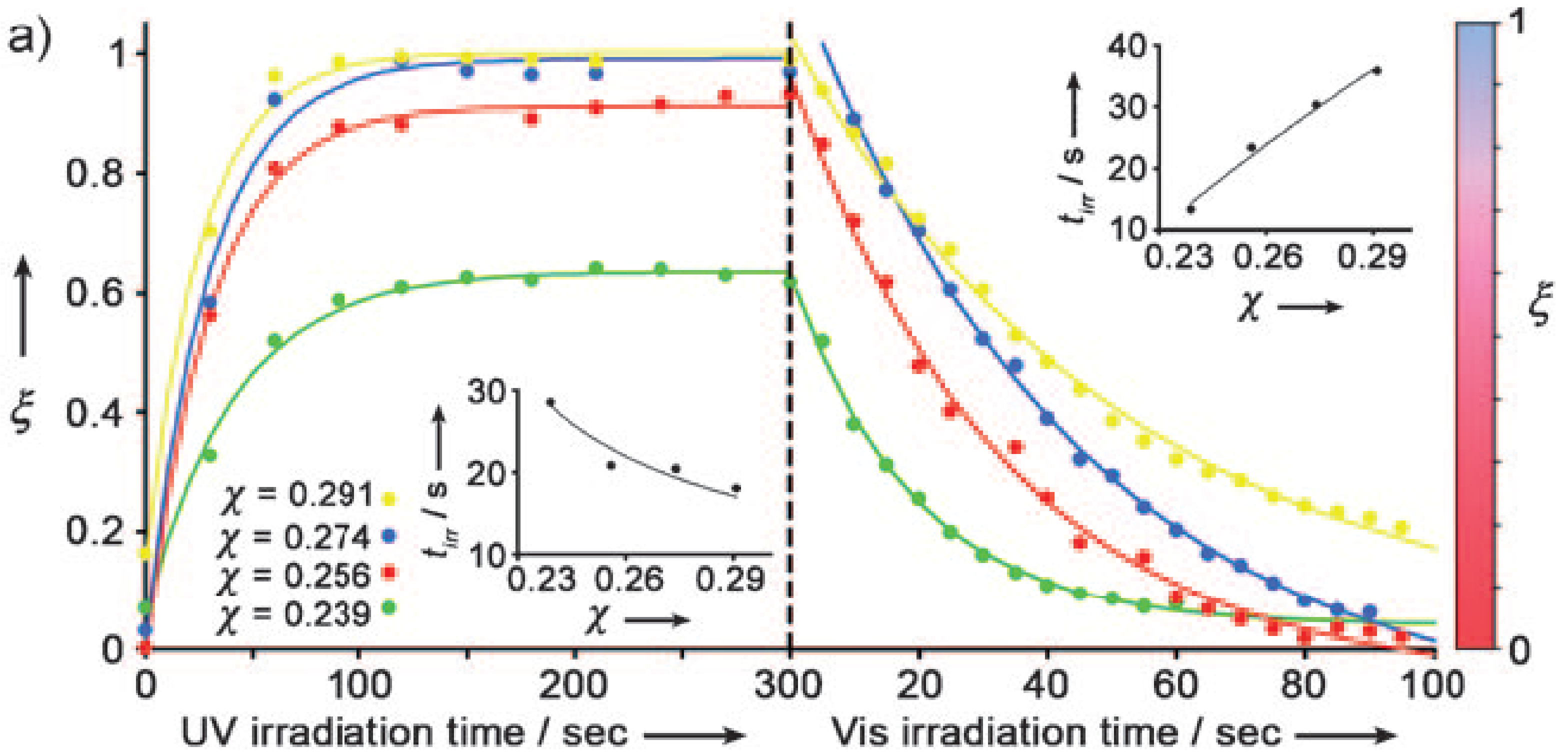


In all images, the writing times were t_{irr}2 s using 10 $mWcm^{-2}$ UV light, except for the array of squares (t_{irr}5 s). Images were erased either by long-time (hours) exposure to daylight (t), by short (seconds) exposure to intense visible light (Vis), or by heating the film to approximately 50 ^{0}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.

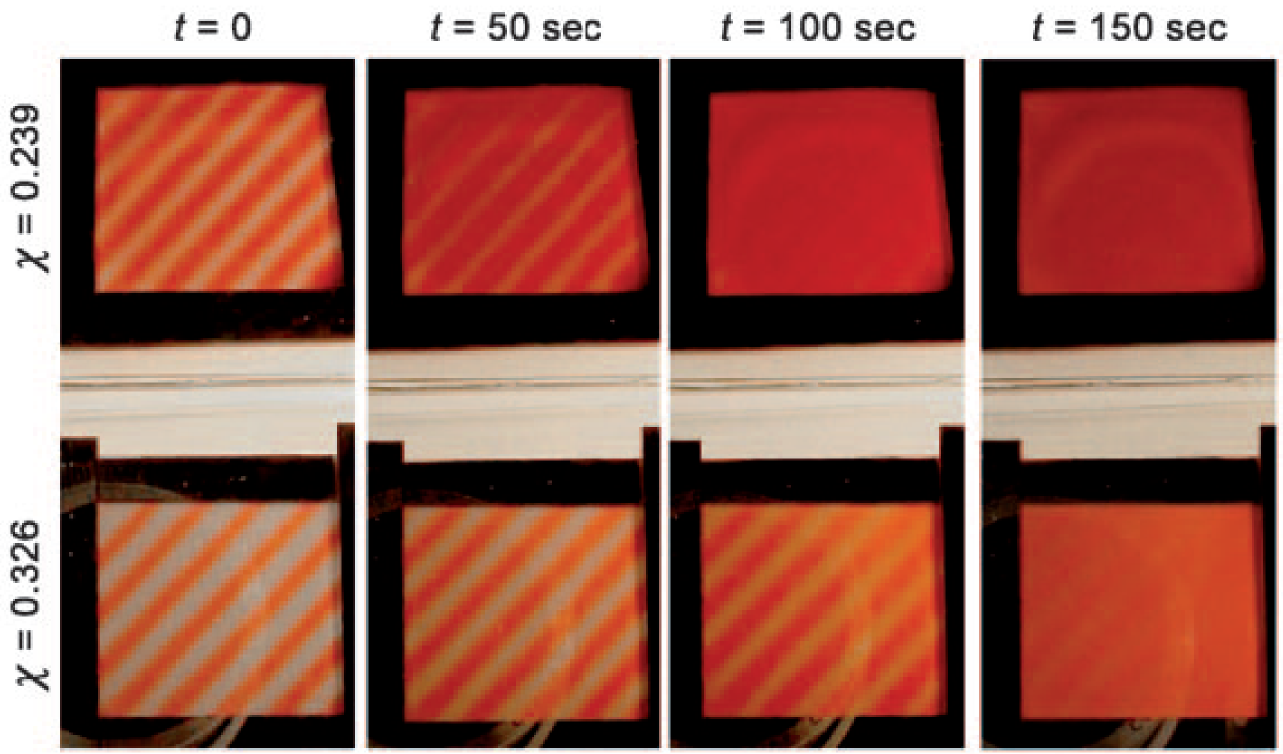


Reversible spectral changes of a AuNP film upon alternating exposures to UV (0.7 $mWcm^{-2}$) and visible light. Here, ξ is a “progress variable” calculated from the experimental extinction spectra. This variable characterizes the apparent color of the film and ranges from zero (unaggregated; red for AuNPs) to one (fully aggregated; light blue for AuNPs); 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.

Quantification of the writing and erasure times.

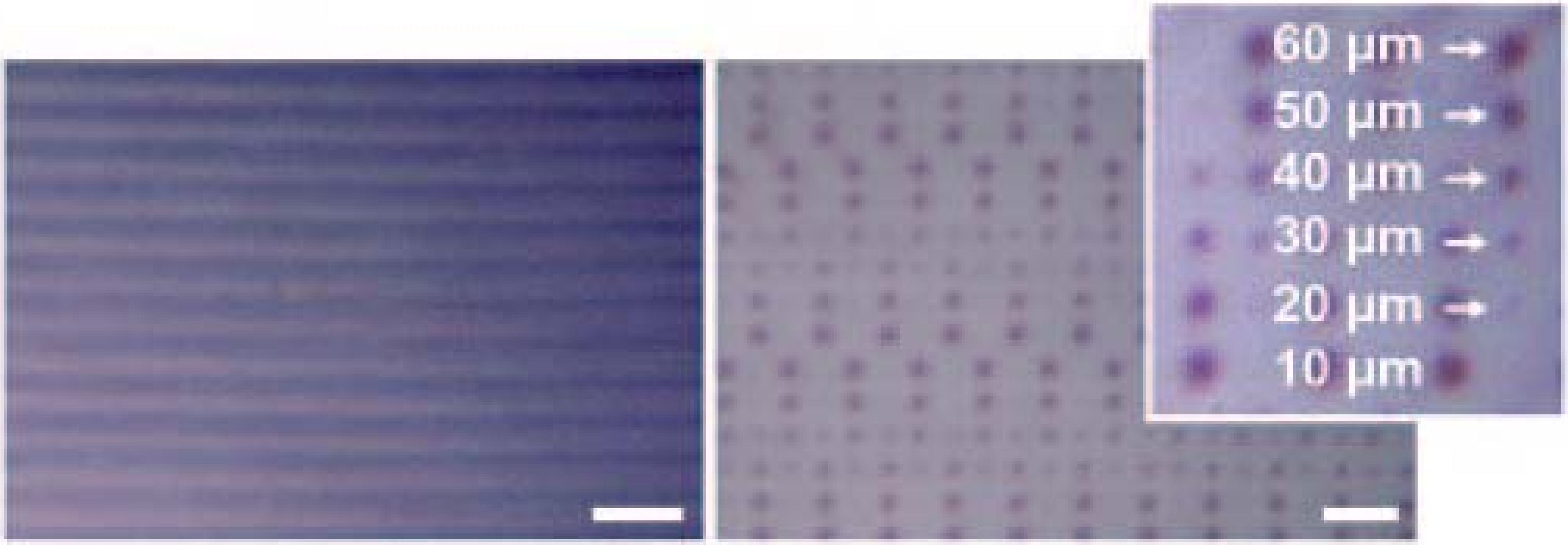


Spectral changes upon irradiation with UV light (I_{UV}=0.7 mWcm^{-2}, left) and erasure with visible light (I_{Vis}=0.8 mWcm^{-2}, right) for films with different coverage of AuNPs. The progress variable ξ was calculated from the experimental extinction spectra. The curves represent best exponential 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.



Erasure of two AuNP films differing in χ. The film characterized by higher χ erases more slowly.

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.



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).

Although negligible for larger features, NP diffusion plays a critical role in the spatial resolution at microscopic scales. 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 ~1– 100 s).

Summary

❖ Demonstrated a class of self-erasable and rewritable materials in which information is written into metastable nanoparticle “inks”.

❖These materials can be useful for storing sensitive or temporary information.

❖ Although the inks themselves are nontoxic (in fact, AgNPs have antibacterial properties), 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.

THANKS