

# Rewritable and pH-Sensitive Micropatterns Based on Nanoparticle “Inks”

Dawei Wang, István Lagzi, Paul J. Wesson, and Bartosz A. Grzybowski\*

Materials and patterns incorporating functionalized nanoparticles (NPs) are of considerable interest for their potential applications in photonic materials,<sup>[1–3]</sup> electronic devices,<sup>[4,5]</sup> biosensors,<sup>[6,7]</sup> or template fabrication,<sup>[8,9]</sup> to name just a few. To date, various techniques have been developed that produce NP patterns on different length-scales<sup>[10,11]</sup> and comprising NPs of different shapes,<sup>[12]</sup> sizes,<sup>[13]</sup> and material compositions;<sup>[14]</sup> several of these methods are rapid<sup>[11,12]</sup> and inexpensive.<sup>[10,14]</sup> Recently, we have proposed<sup>[15]</sup> that metal NPs exhibiting surface plasmon resonance (SPR) can provide working elements of “dynamic” NP patterns whose imprinting/writing and erasure are due to the particles’ local assembly and disassembly. When the particles assemble, the degree of electrodynamic coupling between them increases, resulting in the SPR shift and color change (much like in the colorimetric NP assays<sup>[16,17]</sup>) – in effect, the particles play a role of a rewritable “ink”. This idea was demonstrated<sup>[15]</sup> in a system, where NPs functionalized with photoswitchable ligands aggregated under UV irradiation and dispersed when the sample was exposed to visible light. Here, we extend and apply the concept of rewritable nanoparticle inks to patterns responsive to pH. Our inks comprise water-soluble, charged metal particles suspended in thin hydrogel films in which patterns are created and erased – over multiple cycles – by Wet Stamping<sup>[18]</sup> of acids, bases, or salts. The color changes in the patterned regions reflect the degree of NP aggregation therein which, in turn, is determined by the balance of electrostatic and van der Waals forces between the NPs. When the color changes are calibrated, our patterned films act as multiple-use pH sensors. The patterning method can be extended to other types of NPs whose aggregation/dispersion is controlled by different chemical “stimuli” (for examples, see<sup>[19–22]</sup>).

Most experiments were based on AgMUA NPs (with the diameter of the metal cores  $6.0 \pm 0.7$  nm) prepared according to a previously described procedure.<sup>[23]</sup> These NPs were functionalized with 11-mercaptopundecanoic acid

( $\text{HS}(\text{CH}_2)_{10}\text{COOH}$ , MUA;  $\text{p}K_{\text{a}} \sim 6$  for a self-assembled monolayer of MUA on a curved surface<sup>[24]</sup>) and their  $\sim 8$  nm solution was mixed with 1.5 w/w% aqueous solution of agarose (OmniPur, EM Science, Darmstadt, Germany) with pH adjusted to  $\sim 11$  using tetramethylammonium hydroxide (TMAOH) to fully deprotonate MUA on AgNPs. This mixture was heated in a microwave oven for  $\sim 30$  s and was then cast between two glass slides separated by spacers to yield a  $\sim 250$   $\mu\text{m}$  thick layer of agarose gel. An agarose stamp ( $\sim 7$  w/w% agarose) patterned in bas relief (feature depth 200–500  $\mu\text{m}$ , typical feature size 50  $\mu\text{m}$  – 1 mm) was fabricated as described in.<sup>[25]</sup> The stamp was soaked in a solution of HCl or NaCl (typically, 3–100 mM) for  $\sim 1$  h, and immediately prior to use its surface was blotted dry under the stream of nitrogen. The stamp was then placed onto the gel film containing the NPs (**Figure 1a**).

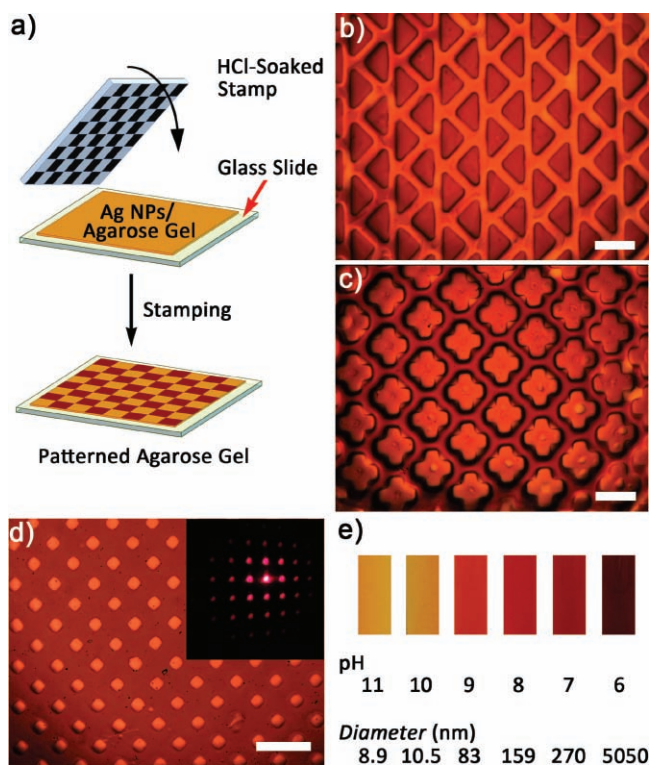
When the features of the stamp came into contact with the film, the acid diffused<sup>[26,27]</sup> from the former into the latter causing aggregation of the NPs. **Figure 1b–d** show examples of patterns produced by Wet Stamping of HCl solutions (3–5 mM). As seen, stamping resolves features down to tens of micrometers in size; these patterns remain intact when the stamped gels are subsequently dried. Also, the color of the patterns depends on the effective pH in the stamped regions and changes from yellow at pH = 11, through orange at pH = 9, to dark red at pH = 6 (**Figure 1e**, also see UV-Vis spectra in **Figure S1** in the Supporting Information, SI). Dynamic light scattering (DLS) measurements show that these changes reflect the degree of NP aggregation – at pH = 11, the NPs are not aggregated but at pH = 9, they form  $\sim 80$  nm aggregates that grow to  $\sim 5$   $\mu\text{m}$  at pH = 6. Below pH = 6, the aggregates are even larger and precipitate from solution (hence the stamped regions appear lighter than at higher pH’s). We note that NP precipitation at pH =  $\sim 5$ –6 coincides with the  $\text{p}K_{\text{a}}$  of the MUA ligands<sup>[24]</sup> – as expected on the basis of simple DLVO theory,<sup>[28]</sup> the electrostatic repulsions between the NPs are greatly weakened when  $\text{pH} \sim \text{p}K_{\text{a}}$ , and the behavior of the NPs is then dictated by van der Waals (vdW) attractions.

Patterns written by acid stamping can be erased by exposing the film to a solution of base. **Figure 2** illustrates three write/erase cycles in which various images are Wet Stamped ( $\sim 3$  min) using 10 mM HCl and are then erased by placing  $\sim 20$   $\mu\text{L}$  of a 10 mM solution of TMAOH onto the gel (for 2 min and then blotting the gel’s surface dry with a stream of nitrogen). Pattern erasure is due to the deprotonation of the MUA ligands such that the electrostatic repulsions between the NPs become stronger than vdW attractions allowing the particles to disperse.<sup>[29]</sup> We verified that up to

D. Wang, Dr. I. Lagzi, P. J. Wesson, Prof. B. A. Grzybowski  
Department of Chemical and Biological Engineering  
Department of Chemistry  
Northwestern University  
2145 Sheridan Road, Evanston, IL 60208, USA  
E-mail: grzybor@northwestern.edu

D. Wang  
School of Materials Science and Engineering  
Northwestern Polytechnical University  
Xi’an 710072, P. R. China

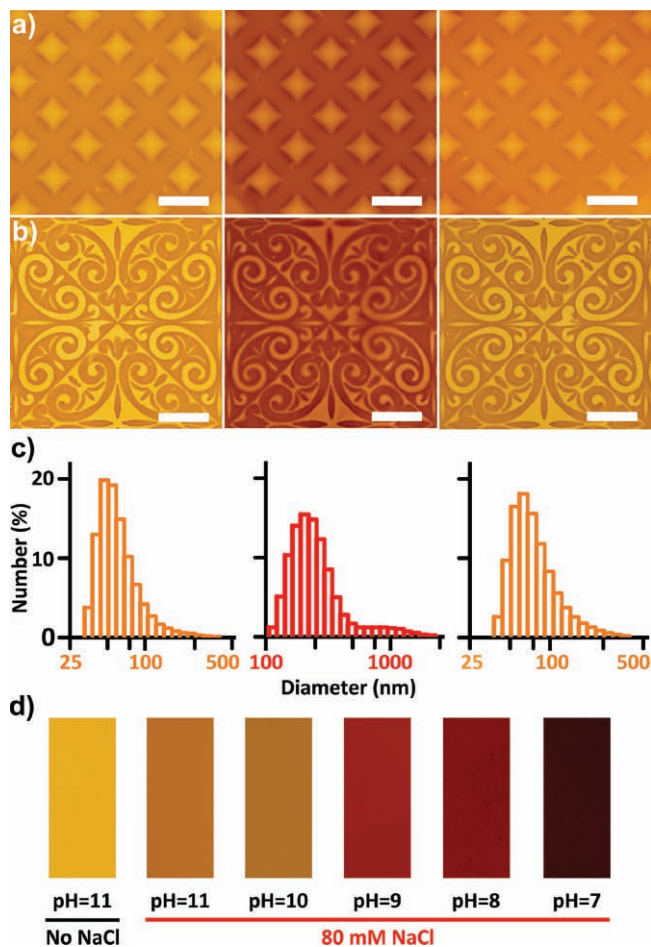
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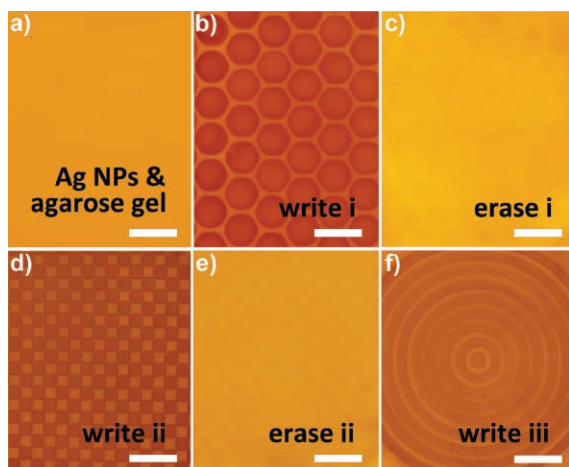
**Figure 1.** Wet Stamping of NP-aggregation patterns. a) Scheme of the experimental procedure. Here, an agarose stamp delivers a solution of HCl into a gel film containing dispersed AgMUA NPs (initially, at pH ~ 11). The protonation of MUA ligands over the patterned regions causes nanoparticle aggregation which manifests itself by a color change. b–d) show examples of micropatterns produced by Wet Stamping of 3 mM HCl solutions onto a gel containing 8 mM AgMUA NPs (effective pH in the patterned regions is ~6.5). After patterning and NP assembly, the gel films were dried without a noticeable loss of pattern quality/ resolution. The inset in panel d shows the diffraction pattern obtained by passing a 650 nm laser beam through the dried film. All scale bars correspond to 100  $\mu\text{m}$ . e) Experimentally observed colors of the gels at different values of effective pH after stamping and the corresponding hydrodynamic sizes of NP aggregates measured by DLS.

ten cycles can be performed in this way; above this limit, the patterns become increasingly ill-defined and cannot be completely erased, likely because the salt produced during acid/base neutralization screens electrostatic forces and prevents complete disaggregation of the NPs.

The screening effects due to high-salt concentration can be used to create permanent patterns which, however, can change color upon pH changes and act as primitive but multiple-use pH sensors (**Figure 3**). For example, when the agarose film at pH = 11 is Wet Stamped with 80 mM NaCl, the salt screens the electrostatic repulsions between the NPs resulting in particle aggregation and color change over



**Figure 3.** Nanoparticle patterns as pH sensors. The *leftmost* figures in (a) and (b) show patterns created in the gel film by stamping with 80 mM NaCl; effective pH in the patterned regions is ~11. The *middle* figures in (a) and (b) show the same patterns exposed to ~10  $\mu\text{L}$  of 50 mM HCl such that effective pH in the gel decreases to ~8. Under these conditions, the electrostatic repulsions are further weakened allowing for further NP aggregation and resulting in color changing to brown. In the *rightmost* figures of (a) and (b), the patterns' color reverts to orange when pH is adjusted to ~11 and MUA groups are deprotonated. Under these conditions the size of the aggregates decreases. All scale bars correspond to 1 mm. c) Size distributions of AgMUA NPs in solutions of 80 mM NaCl at different pH's (corresponding to the pH changes in (a) and (b)): ~11 (*left*), ~8 (*middle*) and ~11 (*right*). d) The experimentally observed colors of agarose films stamped with 80 mM NaCl and with pH adjusted by the addition of HCl. The color changes from orange at pH ~ 10–11, to red at pH ~ 9–8, to dark red/brownish at pH ~ 7.



**Figure 2.** Rewritable acid/base patterning in agarose gels containing AgMUA NPs. The images are written by Wet Stamping 10 mM HCl and are erased by washing the gel with 10 mM TMAOH. All scale bars correspond to 1 mm.

the stamped regions to dark orange (Figure 3a,b, *left*; also see UV-Vis spectra in Figure S2 in the SI). DLS measurements indicate that the sizes of these aggregates are in tens of nanometers (Figure 3c). The patterns remain intact but change color to dark red when the films are exposed to acid and pH decreases (e.g., pH ~ 8 in Figure 3a,b, *middle*) such that the electrostatic repulsions further weaken allowing formation of aggregates as large as ~200 nm. The color of the patterns can be changed back to dark orange by re-adjusting pH to 11. Of course, other colors are observed for other pH values between 6 and 11 (Figure 3d), and the sensors can be used reliably for up to ca. twelve pH measurements.

In summary, we demonstrated that Wet Stamping can be used to imprint rewritable and/or pH sensitive micropatterns based on nanoparticle “inks”. The pH range and colors of the nanoparticle inks depend on, respectively, the  $pK_a$  of the ligands coating the particles and the material properties of the metal cores (e.g., patterns comprising AuNPs change between red and violet-blue<sup>[15]</sup>). We believe our patterning method can be extended to other types of systems/sensors including those based on solvent responsive nanoparticles,<sup>[20]</sup> as well as NPs whose aggregation/dispersion is driven by host-guest chemistries<sup>[19,22,30,31]</sup> or DNA hybridization.<sup>[21]</sup>

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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