

Patterning precipitates of reactions in paper†

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This article describes a method for patterning certain solids—insoluble salts and reduced metals—in sheets of paper. Chemical reactions that produce these solids as precipitates occur when a stamp of patterned paper inked with an aqueous solution of reagent comes into contact with a paper substrate containing a second reagent. The pattern is determined by a hydrophobic barrier on the stamp that restricts delivery of the ink in two dimensions. The technique is one of the few methods available to generate two-dimensional patterns of solids within the bulk of sheets of paper. It can reliably produce features with lateral dimensions only down to 1 mm, but is convenient, inexpensive, and amenable to use in large-area patterning. The method can be used to introduce function to paper-based systems: (i) paramagnetic salts precipitated within paper allow pieces of it to be manipulated or separated from mixtures with a bar magnet, (ii) the precipitation of transition metals or enzymes can be used to position and store catalysts on paper for subsequent use, (iii) catalysts patterned in two dimensions in paper can be used to generate dynamic 3-D structures when exposed to appropriate substrates: for example, a ring of Pd⁰ deposited on a sheet of paper will generate a cylindrical “cage” of rising oxygen bubbles when exposed to an aqueous solution of hydrogen peroxide, and (iv) patterns of catalysts or colored precipitates can serve as deterrents to counterfeiting.

Introduction

This article describes a method for patterning precipitates—insoluble salts and colloidal metals—in sheets of paper. Templates of paper patterned with a hydrophobic barrier (*e.g.*, wax or toner deposited by an office printer) control the delivery of solutions of reactants to unpatterned sheets of paper that contain complementary reactants. The subsequent reactions generate solid precipitates that remain trapped within the pores of the paper. The technique can reliably produce features with lateral dimensions down to 1 mm, and this paper demonstrates that it can be used to introduce function to paper-based devices. Paramagnetic solids precipitated within the pores of paper allow the sheets to be manipulated with a bar magnet, and stamped patterns of catalysts can be used to generate dynamic 3-D structures on exposure to appropriate reactants. The technique can also be used to store proteins on paper as precipitates with ammonium sulfate, or to generate features in paper for applications such as deterring counterfeiting.

The ability to pattern functional materials in paper will be important as paper is exploited as a versatile platform for manufacturing devices such as low-cost, portable diagnostic assays.^{1–6} In spite of the widespread use of patterned paper (*e.g.*, in publishing, banknotes, and biomedical analysis), the methods available to pattern solid materials within the bulk of a sheet of paper (not just on its surface) are limited. These techniques include patterning polymers from liquid precursors that are

subsequently cured (*e.g.*, PDMS with heat, or SU-8 with UV light),^{1,7} patterning liquids that solidify on cooling (*e.g.*, wax),^{4,8,9} and patterning molecules from evaporating solvents (*e.g.*, pigments in ink).^{10,11} These methods are all direct-write or photolithographic techniques that are not well-suited to patterning solids that are insoluble in a mobile phase, including inorganic salts (*e.g.*, ZnS) and metallic heterogeneous catalysts (*e.g.*, Pd⁰). The method described here for patterning solids within paper can be used to introduce function to paper devices (*e.g.*, catalytic activity or a magnetic response) and has the potential to expand the use of paper in a variety of applications.

Background

Paper is available in many types and sizes, and with properties that make it an attractive material for use in a wide range of devices and other manufactured products.^{3,12} Paper can be inexpensive, lightweight, thin, flexible, and functionalized by simple chemical reactions to tune its permeability, hydrophobicity, and reactivity. The construction of paper-based devices, including assays for the detection of disease and contamination of water supplies, depends on both the ability to pattern the paper *and* to pattern functional materials within the paper.^{1,5,6,13}

Several methods are available to pattern hydrophobic solids within paper from liquid precursors. Wax printed onto the surface of paper will melt and flow into the sheet when heated.^{4,8,9} Upon cooling, the patterns of resolidified wax can serve as hydrophobic boundaries that block the passage of aqueous solutions. Polymers that cure thermally (*e.g.*, polydimethylsiloxane, PDMS) can be patterned in paper by printing the liquid prepolymer with a plotter.⁷ Polymers can also be patterned into paper photolithographically by impregnating a sheet with photoresist (*e.g.*, SU-8) and exposing it to light through a mask.¹

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Inkjet technology can print functionalized nanoparticles into paper from liquid dispersions.^{10,11}

A “delivery template” is a device that both stores a substance and delivers it, in a pattern, to a second medium (the acceptor or acquisition phase). One example of a delivery template is a rubber stamp, where a raised surface adsorbs or supports a solution (*e.g.*, ink) and transfers it in a 2-D pattern to an absorbent porous material (*e.g.*, paper). After the stamp has been designed and constructed, it can be used to replicate the pattern *ad infinitum*. Specific examples of methods that employ delivery templates in the fabrication of patterned materials include: (i) the use of PDMS stamps inked with alkyl thiolates to pattern self-assembled monolayers (SAMs) on surfaces of gold,^{14,15} (ii) the use of molded agarose stamps inked with bacteria or human osteoblasts to pattern cells on hydrophilic surfaces,^{16,17} and (iii) the use of hydrogel stamps in wet stamping (WETS) to introduce aqueous reagents to a hydrogel substrate where precipitation reactions occur to produce devices such as microlens arrays.^{18,19}

In previous work, we constructed delivery templates of paper for the fabrication of shaped films of ionotropic hydrogels.^{20,21} Hydrophobic barriers deposited onto the surface of paper controlled the diffusion of solutions of cross-linking ions off of the template and into a solution of un-cross-linked polymer. In the work presented here, we modify these templates to function as stamps for the delivery of an aqueous solution of a reagent to a second sheet of paper, where a reaction occurs that generates a solid that remains trapped within the pores of the substrate.

Experimental design

Our strategy to pattern solids within the bulk of sheets of paper was to generate the solids as the products of reactions between reagents adsorbed in sheets pressed against each other. When the layers of paper came into contact, a solution of a reactant on one layer (the stamp layer) flowed into a dry sheet (the substrate layer) that contained a second reactant. The reagents reacted and formed a precipitate that was trapped within a matrix of paper in the substrate layer. A hydrophobic barrier of wax or toner printed onto the stamp layer restricted mixing of the reagents to a predetermined two-dimensional design.

The substrate layer was initially dry to ensure a unidirectional flow of liquid from the stamp layer into the substrate layer. This property of the system ensured that the solid precipitate formed only in the substrate sheet. When both sheets were dry, the reagent on the stamp did not transfer and the precipitate did not form. When both sheets were wet, the precipitate formed on both of the sheets (the substrate and the stamp). To maximize the resolution of transferring the pattern from stamp to substrate, we selected reactions that produced precipitates rapidly upon mixing of the reagents. Slow reactions were poor candidates for use in this method; the reagents noticeably wicked distances greater than 1 mm across the paper before reacting, and this action reduced the fidelity of the pattern.

Some types of paper (*e.g.*, chromatography paper) have properties that make them particularly appropriate both as the planar vehicle for the delivery of liquid reagents, and as the substrate for supporting the patterned precipitates. Paper can be a convenient material to use—it is commercially available, and there is an extensive array of products that are designed

especially for working with paper (*e.g.*, printers, copiers, cutters, and adhesives). Many types of paper are absorbent, are not especially reactive, and will bend without fracturing. We selected Whatman-brand No. 1 chromatography paper for use as the stamp layer in our experiments because: (i) it is commercially available in sheets of convenient size, (ii) it has a high capacity for aqueous solutions— $11 \pm 1 \mu\text{L cm}^{-2}$,²¹ (iii) solutions wick through it faster than through many other types of paper, and (iv) we have previously developed a technique to pattern hydrophobic barriers on the sheets using a standard color laser printer.^{20,21} The standard use of Whatman-brand No. 1 paper is in the separation, isolation, and detection of proteins and other molecules by chromatography with water as the eluent (mobile phase).

Results and discussion

Fig. 1 illustrates the general method using a specific example: the precipitation of copper hydroxide within a sheet of chromatography paper. The stamp comprises three elements: (i) a piece of paper with a printed hydrophobic design in wax or color laser toner, (ii) one or more unpatterned pieces of paper that serve as reservoirs for the solution to be stamped, and (iii) a flat silicone surface on which the layers of paper are supported. The layers of paper are secured to the silicone with waterproof tape, and the stamp is inked with a solution of $\text{Cu}(\text{NO}_3)_2$ using a micropipettor (Fig. 1b). The substrate layer is prepared by wetting an unpatterned sheet of paper with a solution of NaOH and drying the sheet with a heat gun or oven. When the stamp comes into contact with the substrate, the solution of copper flows unidirectionally off of the wet sheet and into the dry sheet, where it reacts with the hydroxide ions present to form a cyan precipitate, $\text{Cu}(\text{OH})_2$.²² The stamping can be repeated until the stamp runs dry, and the excess (unreacted) NaOH can be washed off of the substrate layer with water (Fig. 1d). The copper hydroxide remains sequestered within the paper due to its low solubility in water ($K_{\text{sp}} = 2.20 \times 10^{-20} \text{ M}^3$).²²

The hydrophobic barrier of the stamp layer can be produced by two methods. The first method generates a 3-D hydrophobic barrier throughout the sheet by a previously described procedure where wax-based ink is printed onto the surface of the sheet and heated until it melts and flows into the paper.^{4,8} Alternately, a 2-D barrier localized to the surface of the paper can be printed in color laser toner.²¹ Both procedures are capable of producing functional stamps for our method, but we find the wax-based stamps to be superior on the basis of their durability. After extended use, if the 2-D layer of toner on the surface becomes compromised, the aqueous ink can leak past the barrier and blemish the substrate layer. This error was rarely observed for the wax-printed templates, presumably because the barrier is patterned in 3-D throughout the entire first layer of paper in the stamp.

The procedure works for any reaction that generates a solid precipitate quickly (*i.e.*, in seconds) from a mixture of water-soluble reagents (Table S1 in the ESI† summarizes solubility data for the compounds used in this study). We used the method to pattern insoluble salts (*e.g.*, $\text{Cu}(\text{OH})_2$ and PbI_2) from ion-exchange reactions, organic compounds (*e.g.*, fluorescein) from proton-exchange reactions, and colloidal metals (*e.g.*, Pd and

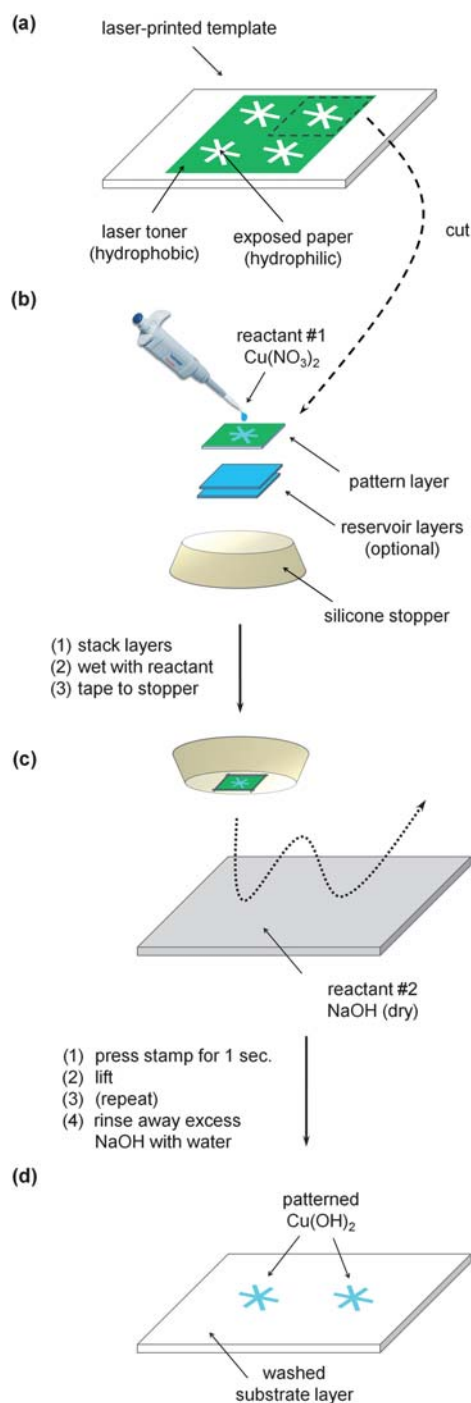


Fig. 1 Schematic representation of the method used to stamp patterns of a solid precipitate (here: cupric hydroxide) into a sheet of paper. A standard color laser printer produced the template (a) that was cut out and mounted on a flat silicone base (b). Extra pieces of paper stacked between the pattern layer and the silicone base served as a reservoir for the solution of Cu^{2+} used to ink the stamp. When the inked stamp came into contact with a dry sheet containing NaOH , the solution of Cu^{2+} flowed into the sheet and reacted to form $\text{Cu}(\text{OH})_2$, a cyan precipitate, in the shape of the stamp (c). A final rinse with water removed the excess unreacted NaOH from the substrate layer (d). The insoluble $\text{Cu}(\text{OH})_2$ remained trapped in the paper.

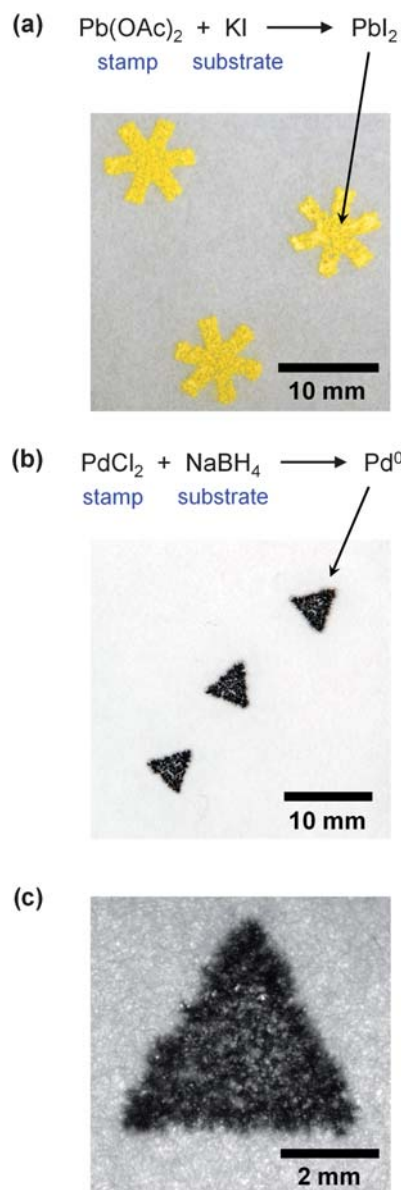


Fig. 2 Designs of precipitates patterned within paper by the stamping method. (a) Asterisks of PbI_2 (yellow) precipitated by stamping a solution of $\text{Pb}(\text{OAc})_2$ on a dry sheet that contained KI . (b) Triangles of Pd^0 deposited by stamping a solution of PdCl_2 on a dry sheet that contained NaBH_4 . (c) Magnified image of a stamped triangle of Pd^0 that depicts the roughness at the edges of the pattern.

Ag) from the reduction of metal cations. The precipitates did not just form on the surface of the paper, but within the bulk of the sheets. Presumably, the precipitates formed wherever the aqueous solution wet the paper—both in the pores of the fibers and the pores in between fibers. Fig. 2 depicts examples of shaped regions of precipitates patterned in paper by the stamping method.

The resolution of the technique was limited by two factors: (i) the resolution of the method used to print the hydrophobic barrier on the stamp, and (ii) lateral wicking of the ink into the paper substrate prior to formation of the precipitate. One of the advantages of the method is that it requires no specialized

equipment—the hydrophobic barriers can be printed with a standard color office printer. In order to produce a barrier thick enough to be impervious to aqueous solutions, we printed the patterns of wax or toner in triplicate on the same sheet of paper. Due to occasional errors in misalignment of the printed layers of toner and losses in resolution upon reflow of the printed wax during construction of the stamps, designs with feature sizes much smaller than 1 mm were difficult to generate with high fidelity. A second limitation to the resolution of the technique arose from wicking of the aqueous solution of reagent (*i.e.*, the “ink”) through the dried substrate when the stamp was pressed against it. This flow reduced the resolution of the imprint for slow reactions relative to fast reactions. To minimize the problem, we generally used a higher concentration of reagent to wet the substrate layer than the stamp layer. This stoichiometric excess helped ensure that the stamped reagent did not wick long distances into the paper for lack of sufficient reagent in the substrate layer.

While chromatography paper gave excellent results when used as both the substrate and stamp layers, some other types of commercial papers—such as bond paper and copier paper—proved unsatisfactory for the method. These types of paper had lower capacities for aqueous solutions than the chromatography paper, and the solutions wicked across these sheets at slower rates. These observations can potentially be explained by the effect of physical differences among the types of paper (*e.g.*, in thickness and pore size) on how aqueous solutions wick through the sheets, and interference from the presence of additives (*e.g.*, as whitening agents) in these types of paper that are not present in chromatography paper. The physical response of the paper to wetting must also be considered when selecting what paper to use in the method. Chromatography paper had sufficient mechanical strength such that it could be manipulated when wet without disintegrating. We also found chromatography paper to be more resistant to cockling—the formation of ripples across the sheets of paper upon wetting and drying—than bond or copier paper.

Patterning precipitates in paper to introduce function

We used the technique of precipitating solids within paper to introduce function. A solution of NaOH added to a dry paper substrate that contained GdCl₃ formed solid Gd(OH)₃ within the paper. Once washed with water and dried, these pieces of paper could be manipulated with an NdFeB bar magnet (Fig. S1 in the ESI†). The pieces adhered to the magnet both in air and underwater. Even when the pieces were immersed in water, the magnetic response persisted for days due to the low solubility of Gd(OH)₃ ($K_{sp} = \sim 10^{-26} \text{ M}^4$).²³

The technique can also be used to precipitate enzymes within sheets of paper. In biochemistry, proteins are commonly isolated as precipitates from aqueous solutions of salts such as ammonium sulfate.²⁴ Solutions of horseradish peroxidase (HRP) dispensed onto paper containing dried ammonium sulfate yielded precipitates of the enzyme.²⁵ Unlike the case for the insoluble inorganic compounds described above, the precipitation of proteins in concentrated solutions of ammonium sulfate is reversible,²⁴ and the enzyme redissolves from the paper in water that does not contain (NH₄)₂SO₄. The precipitation and redissolution of HRP, which is reddish-brown in color, can be

observed by eye. The enzyme precipitated in paper dissolves into pristine water in seconds, while it does not dissolve into saturated solutions of (NH₄)₂SO₄.

The ability to precipitate proteins within the pores of paper makes the method a potential tool for storing enzymes for subsequent use in solution or on paper-based devices such as lateral flow-based diagnostic assays.^{13,26} The method differs from systems where enzymes are covalently immobilized to paper or entrapped on the surface of a paper substrate, such as within sol-gel-derived silica or a matrix of trehalose.^{3,6,27} The activity of HRP can be monitored by the oxidation of iodide ions by hydrogen peroxide to form triiodide ions, which are yellow in color.²⁸ We have used this reaction as part of a colorimetric assay on paper-based devices for the detection of glucose in urine.¹ In comparison to the activity of an equal amount of HRP from the original stock solution (arbitrarily set to a value of 1.00), HRP dispensed onto chromatography paper with ammonium sulfate retained similar activity (0.43 ± 0.10) to HRP evaporated on paper with trehalose (0.44 ± 0.09). These values correspond to 90% confidence intervals based on four measurements taken within 1 hour of preparation of the paper samples. We have not studied the effect of ammonium sulfate precipitation on long-term shelf life of the enzyme.

We could also use the stamping technique to produce two-dimensional patterns of metal catalysts on paper that would generate three-dimensional dynamic structures when immersed in solutions of reactive molecules. Fig. 3 shows how a 3-D cylindrical cage of bubbles can be generated from a 2-D ring of Pd⁰ patterned

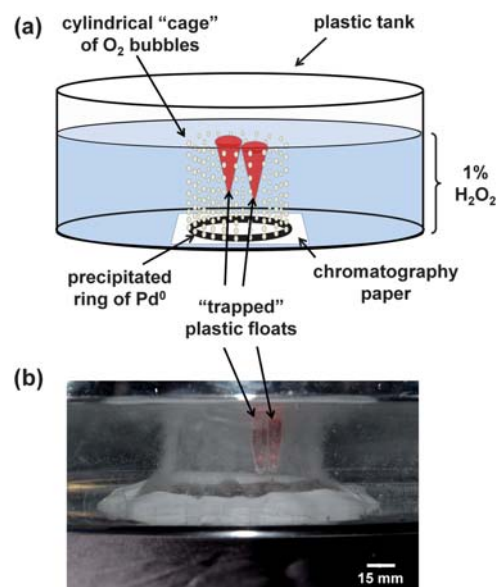


Fig. 3 Generation of a “cage” of bubbles. (a) Schematic diagram depicting the generation of a 3-D cylindrical “cage” of rising oxygen bubbles from a 2-D ring of Pd⁰ particles precipitated in a sheet of chromatography paper. The Pd catalyzes the disproportionation of H₂O₂ (1% aqueous solution) into water and oxygen. (b) Digital picture of two encaged floating vessels. When a vessel drifts into the wall, the rising bubbles impart a force that pushes the vessel back towards the center. During the course of the experiment, the paper substrate bulges due to the gas that builds up underneath the sheet, which is secured to the floor of the tank with adhesive tape. If the substrate is not taped down, it floats and cannot be used to generate the cage.

into a sheet of paper by stamping a solution of PdCl₂ onto a dry substrate containing NaBH₄.²⁹ Colloidal Pd is a heterogeneous catalyst for the disproportionation of hydrogen peroxide into oxygen and water.³⁰ When the paper was immersed in a 1% solution of H₂O₂, the regions with Pd⁰ effervesced and the bubbles of oxygen rose to the surface of the bath to result in the formation of a cylindrical wall of bubbles (Fig. 3). The cylinder was a dynamic (rather than static) structure composed of rising bubbles whose points of generation were controlled by the pattern of catalyst on the paper substrate. The frequency of generation of bubbles could be tuned, crudely, by changing the concentration of H₂O₂ in the bath. Floating vessels that drifted into the “wall” of the cylinder were pushed away by the force imparted by the rising bubbles. In this manner, the bubbles collectively functioned as a cage. A well known precedent for the use of bubbles to sequester swimming or floating objects occurs in marine biology, where humpback whales engage in a cooperative hunting behavior called “bubble feeding”.³¹ In this activity, the whales produce “bubble nets”—patterns of bubbles of exhaled air (typically, circles with diameters of 3–30 m)—in an effort to corral schools of small fish and krill into bait balls near the surface of the ocean.³² The whales plunge into these bait balls with open mouths to feed.

Applications of this method in anti-counterfeiting technology

One potential application of patterning precipitates inside of paper is in the area of document security as an anti-counterfeiting measure.³³ In the eighteenth century, Benjamin Franklin embedded flecks of mica, lustrous silicate minerals, in the paper used to print colonial American currency to serve as visual marks of authenticity.³⁴ The technique described here expands on this system by allowing the formation of inorganic compounds in defined patterns as opposed to random distribution. Many precipitates have distinctive colors that would be easy for the general public to identify and associate as authentic. Unlike dyes, many of the inorganic salts we can precipitate in the paper are impossible to bleach, wash away with solvent, or remove by scraping. Such a system might be useful in deterring counterfeiting.³⁵ Catalysts embedded within the pores of banknotes or official documents could serve as marks of authenticity that are validated by monitoring a chemical reaction. For instance, particles of Pd⁰ trapped in paper would produce bubbles when a banknote is treated with a dilute solution of H₂O₂ (Fig. S2 in the ESI†).

Conclusions

The procedure described here represents a method for patterning solids in two dimensions within the bulk of sheets of paper—instead of only on its surface—by generating the solids as precipitates of reactions within the pores of the paper. The method is simple, requires no specialized equipment beyond a color office printer, and should be amenable to scale up in roll-to-roll processes. Previously described methods for patterning solids into paper are limited mostly to polymers that cure from a liquid precursor. Our technique can be used to introduce functional materials into paper, such as catalysts or magnetic compounds. This technique could also be exploited to pattern chemicals in the paper used to print currency and official documents as a means of authentication.

Experimental

Preparation of the patterned paper

We designed 2-D patterns in Microsoft PowerPoint and printed them onto 20 cm × 20 cm sheets of Whatman No. 1 chromatography paper (Sigma-Aldrich) in either color laser toner or solid wax. For producing the templates with wax, we used a Xerox Phaser Model 8560 solid-ink printer and printed the design on the chromatography paper in duplicate. We then heated the wax with a heat gun (~150 °C) until it melted and flowed into the paper such that it permeated the entire 180 μm sheet (~10 to 20 s).

Assembly of the stamps

We used scissors to trim the desired template (from the printed sheet) and mounted it on a silicone rubber stopper (typically, size 8, VWR International) with adhesive tape (Scotch-brand transparent tape, 3M Company). To reduce how often the stamp required re-inking, several “reservoir” layers of chromatography paper were inserted between the patterned (stamp) layer and the stopper to hold an increased quantity of the ink. After one side of the paper stack was fixed with tape, we wet the sheets using a 100 μL micropipettor. Any excess solution—ink that did not seep into the stamp—was blotted with a lintless wipe, and the stack was sealed to the stopper on all four sides with waterproof tape to ensure that the stack was secure and that ink could not leak out of the sides. We performed the first several stamping repetitions on scrap paper in case the stamp was over-inked.

General procedure for patterning precipitates in paper by stamping

The substrate sheet was wet with the second solution of reagent using a surface coverage of roughly 10–15 μL cm⁻². A heat gun set to warm (~40 °C) was used to dry the substrate layer (this step typically required 2–3 min). To make each replicate of the pattern, we pressed the inked stamp against the dry substrate sheet for ~1 s. The stamping was repeated as desired or until the stamp ran dry. Once stamping was complete, the substrate sheet was rinsed with water and allowed to air dry.

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