Nanoparticle printing with single-particle resolution

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Bulk syntheses of colloids efficiently produce nanoparticles with unique and useful properties. Their integration onto surfaces is a prerequisite for exploiting these properties in practice. Ideally, the integration would be compatible with a variety of surfaces and particles, while also enabling the fabrication of large areas and arbitrarily high-accuracy patterns. Whereas printing routinely meets these demands at larger length scales, we have developed a novel printing process that enables positioning of sub-100-nm particles individually with high placement accuracy. A colloidal suspension is inked directly onto printing plates, whose wetting properties and geometry ensure that the nanoparticles only fill predefined topographical features. The dry particle assembly is subsequently printed from the plate onto plain substrates through tailored adhesion. We demonstrate that the process can create a variety of particle arrangements including lines, arrays and bitmaps, while preserving the catalytic and optical activity of the individual nanoparticles.

Today, printing is the most widespread technology to deposit small particles onto various surfaces. In book and fine-art printing, submicrometre pigment particles carry different colours, thus creating brilliant and bleach-resistant images. Small particles (often <100 nm in diameter) are increasingly used in other fields, too. In electronics, optics and biology, small particles are the target of intense research and are used in a number of commercial applications. Such applications exploit the particle’s confined electronic systems, their strong interaction with light, with their matrix and with each other, their well-defined surface properties, their high catalytic activity and—in sufficiently small particles—their quantum confinement properties.

A prerequisite for future applications using particles as functional entities is often control of their arrangement on a surface, between electrodes or in a device. Doing so with standard microfabrication techniques is difficult, and it is often time-consuming and inefficient to create sparse patterns of small particles using subtractive top-down processing. Printing techniques, in contrast, scale well to nanoscopic particle sizes. Figure 1 shows how gravure printing can be scaled to handle particles less than 100 nm in diameter. Using self-assembly processes to ink nanofabricated ‘printing plates’ and controlled adhesion for the transfer, we print nanocrystals at single-particle resolution. The process maintains the efficient parallel nature of self-assembly without requiring specially patterned substrates or elaborate surface treatments. Printing has been demonstrated on various targets, including soft and flexible materials that are challenging to handle by other microfabrication processes.

In conventional printing, the ink is treated as a continuous medium. Its wetting properties (as in offset printing) or the geometry of a template (as in gravure printing) define in which areas a printing plate is inked and from where the ink will later be transferred to the substrate. The arrangement of the final, embedded pigment particles in the print is stochastic. This principle holds even for molecular inks—many researchers have used micro-contact printing to transfer reactive molecules, proteins and catalytic colloids according to stamp geometries. The arrangement of the printed species itself is not imposed by a template, but is either irregular or imposed by the adsorption process.

In the process proposed here, discrete nanoparticles are arranged deterministically on structured surfaces using ‘directed assembly’. In contrast to conventional inking, directed assembly does not merely fill predefined structures with randomly dispersed pigment particles, but arranges nanoparticles at positions that are defined by the geometry of a template. These silicone templates are moulded with total areas in the order of 1 cm² from hard masters with feature dimensions between 40 nm and tens of micrometres. The template geometries adopted (Fig. 2) include lines, producing close-packed nanoparticle wires as used in molecular electronics, spaced regular arrays for nanowire growth and arbitrary arrangements, such as the sun designed by the seventeenth-century alchemist Robert Fludd, which is composed of about 20,000 single particles.

HIGH-PRECISION INKING

For inking, the meniscus of a colloidal suspension is moved over the patterned polymer layer so that the dispersed particles arrange inside the features. When the particles have assumed their desired positions, the liquid must be removed because brownian motion is sufficiently strong in nanoparticle suspensions...
to destroy the order. The dry, filled printing plates (Fig. 2) are then stable and can be stored until the particles are transferred onto substrates.

In capillary assembly, as the colloid moves over the surface, particles are deposited in the desired regions. Excess particles are removed through the Stokes drag exerted by the liquid meniscus (Fig. 3a), which fulfils a similar function as the doctor blade in gravure printing (Fig. 1). High yield, precise arrangement and high contrast require control of particle transport, which is intimately connected with the wetting behaviour of the colloidal suspension.

Providing sufficient particles from the bulk colloid to the assembly region near the contact line is a prerequisite for particle deposition. This mass transport can be achieved by the convective flux of liquid towards the meniscus caused by water evaporating from the meniscus\(^\text{16}\). For 60-nm gold particles, the timescale of inertial response is very short—on the order of nanoseconds—and the brownian timescale is very long compared with convective timescales, so that in the bulk part of the fluid, particles can be regarded as solutes that travel along the streamlines (see Supplementary Information, page 2). The streamlines depend on experimental parameters, notably the temperature, the humidity and the substrate velocity, and can be simulated. Figure 3b shows computational fluid dynamics simulations, taking into account the substrate motion, which drags liquid towards the meniscus, and the evaporation from the meniscus, which removes liquid that has to be replenished from the bulk.

Two main features appear in the laminar flow of the colloid according to our simulations (see Supplementary Information, page 5): a flow component that is directed towards the meniscus and a recirculation flow in the upper part of the liquid. As the evaporation rate increases, the recirculation zone moves away from the meniscus. Higher colloidal temperature and lower outside humidity increase particle flux to the assembly region both by increasing flow rates from the bulk and by decreasing the particle recirculation. For the liquid flow rate \(V_{\text{colloid}}\) that occurs at a colloid temperature of 27°C and a bulk particle concentration of \(c_p = 2 \times 10^{14} \text{ l}^{-1}\), a flux of \(N_{\text{p}} = c_p V_{\text{colloid}} \approx 1.5 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}\) is transported to the assembly region. This particle flux is larger than the flux required to form a full particle monolayer,\(^\text{6}\)

\[
N_{\text{ML}} = v_{\text{substr}} \frac{\pi/(3\sqrt{2})}{r_p^2 \pi} \approx 1.96 \times 10^7 \text{ m}^{-1} \text{ s}^{-1}
\]

at a substrate velocity of \(v_{\text{substr}} = 0.3 \text{ µm s}^{-1}\). Thus, sufficient particles to fill any feature on the printing plate are supplied. However, to ink with high yield and good contrast, additional prerequisites need to be satisfied.

In addition to the particle flux, the particle concentration in the assembly zone has to be sufficient. We can analyse the requirements for high-yield assembly using a microscopic model of particle transport. Whereas gaussian statistics describe the transport of particles to the accumulation zone, Poisson statistics apply when small numbers of particles need to move into specific positions. The immobilization of a single particle in a capture site of the template can be modelled by assuming that any particle from a certain volume \(V_c\) above this site will be captured (Fig. 3c). If no additional force exists, the average number \((n)\) of particles in \(V_c\) depends solely on the particle concentration, \((n) = c_p V_c\). Thus, the probability of capturing at least one particle becomes

\[
P(n \geq 1) = 1 - e^{-(n)}
\]

Figure 1 From traditional gravure printing to high-resolution particle printing. a, In gravure printing, a doctor blade fills the recessed features of a printing plate with ink. Pigment particles are randomly dispersed in the ink, which is transferred from the plate onto the substrate. b, In high-resolution particle printing, a self-assembly process controls the arrangement of nanoparticles on the printing plate. The entire assembly is printed onto the substrate, whereby the particle positions are precisely retained at a resolution that is three orders of magnitude higher than in conventional printing.
so that the minimum concentration required to achieve a 90% yield across many capture sites is \( c_p \geq 2.3/V_c \), which is large when compared with the original colloidal concentration. We therefore have to induce local particle accumulation without destabilizing the colloid to provide high assembly yield.

When contact angle and particle stabilization are adjusted properly, the excess particles that flow into the assembly region form a stable zone of high concentration close to the contact line (Fig. 3c). This ‘accumulation zone’ is self-limiting: it does not grow in size even if the meniscus is moved over an unstructured substrate, where no particles are deposited. A steady state between leaving and entering particles results when the accumulation zone has reached a certain size. The zone is reminiscent of the well-known concentration polarization in ultrafiltration\(^\text{17}\), where the Stokes drag on the particles is balanced by interparticle forces (mainly hydrodynamic forces, electrostatic and entropic repulsion). This dynamic diffusion–convection equilibrium is tunable through temperature, which strongly affects the evaporation rate and mainly changes the Stokes drag on the particles, and through colloid composition, which changes the particle interaction forces.

More accurate descriptions of the assembly mechanism need to take into account the dewetting dynamics, particle–surface interaction and particle–particle forces. It was observed that the template geometry not only defines the particle arrangement, but also governs the mechanism leading to this arrangement. Larger features, for example the lines shown in Fig. 3d, create microscale flows. Particles can flow into the features and the actual arrangement often takes place at some distance from the main assembly front. In contrast, arrays that capture single particles pin the meniscus only very slightly, and the assembly takes place very close to the contact line. In all cases, the wetting behaviour is critical—the transition from the mobile to the assembled state takes place only upon dewetting.

Both the microscopic dewetting and the bulk liquid motion depend on the contact angle; inking at high yield and high precision requires its tuning. It is possible to modify the template surface to this end\(^\text{15}\). However, in a printing process, higher-energy surfaces are not an option because particles would strongly adhere to them, inhibiting the transfer step. Instead, we use surfactant systems to tune the wetting behaviour with more flexibility, as is frequently done in conventional printing, and to tune particle–surface interactions simultaneously. A surfactant system for particle inking has to change the contact angle of the colloidal suspension with the hydrophobic poly(dimethylsiloxane) (PDMS) to an angle between 50° and 60°, where we find the highest assembly yield. The surfactants should not, however,
destabilize the colloidal particles, not even in the accumulation zone with its high particle concentrations, and it should only leave a very thin film on the inked plate. Less obvious are the effects of the surfactant on the particle–substrate interactions. We find that some surfactants hinder the assembly, possibly by creating a repulsive force between substrate and particles, whereas others (such as polyvinylpyrrolidone) form deposits that embed the particles on the substrate. A mixture of a non-ionic, rather hydrophobic surfactant—namely Triton X-45, an octylphenol ethoxylate with a short polyethyleneglycol chain—and the anionic dodecyl sulphonate appears to avoid all these issues, leaving the colloid stable even at high concentrations.

The surfactant system ensures a proper receding contact angle on an unstructured surface, but the local contact angle during assembly also depends on the pinning caused by the structures on the template’s surface. To achieve high yields without unspecific deposition, both an appropriate geometry and a sufficient depth of the capture sites have to be chosen. The results shown in Fig. 2 stem from arrays of single particles assembled in 40- to 45-nm deep holes and lines of particles assembled in 70- to 100-nm deep lines. The deeper the lines are, the more robust the assembly process, at the cost of a lower transfer yield. To produce sufficiently precise templates, masters patterned through electron-beam or optical lithography and etched into silicon or silicon oxide were used. They can be used to cast many templates in a high-elastic-modulus polydimethylsiloxane rubber. First, a prepolymer mixture is poured onto the silicon master, then a flexible glass backplane is placed on top, and the polymer is cured. The backplane and polymer layer are peeled off, and the template is finally extracted with ethanol to remove residues before the inking of the printing plate (see Supplementary Information for details of printing plate fabrication).

Figure 3 The inking process that arranges the particles. a, The meniscus of a colloidal suspension containing 60-nm Au particles is moving over the patterned PDMS surface of a printing plate. b, Simulation of the evaporation (colours indicate concentrations) and the streamlines (red lines) of the laminar flow that drags along particles towards the three-phase contact line, where they form an accumulation zone. The main panel is a simulation at a relative humidity (RH) of 50% and the inset for a RH of 95%. c,d. The accumulation zone, visible in the micrographs as a bright yellow line, moves over the printing plate. Depending on the geometry they encounter, particles at the contact line form sparse patterns, for example, arrays (c) or dense arrangements such as lines (d).

PARTICLE TRANSFER

Inking is followed by transfer in the printing process. During transfer, the printing plate and substrate are brought into conformal contact, facilitated by the elastomer layer that adjusts to the topography of the substrate surface. On removal of the printing plate, adhesive forces hold the particles on the substrate, thereby creating the desired arrangement (Fig. 4). Traditional printing technologies use liquid inks, and ink transfer is based on wetting differences between the printing plate and the substrate, thereby creating the desired arrangement (Fig. 4). In this work, the ink solely consists of dry nanoparticles, which are far less mobile than liquids. Particles therefore can be positioned more precisely, but they are harder to print. Their transfer is based on the different levels of particle adhesion on the printing plate and the substrate. Such adhesion differences have already been used to transfer larger particles and large molecules.

Wetting differences are caused by differences in interfacial energy. Likewise, the adhesion of small particles strongly depends on the interfacial energy of the particle–substrate joint. In contrast to solid–liquid interfaces, however, the particle–substrate interface is often not conformal, and its geometry can be complex. When surfaces with different energies are used to transfer particles, it is also necessary to control the interfacial area, in particular when working with individual nanocrystals. Such crystals often have irregular surfaces with sharp crystal edges. The adhesive force acting on one particle with a planar geometry can be much stronger than that acting on spherical ones. Moreover, solutes from the colloidal suspension frequently form adlayers on the metal surface while drying, thereby changing the chemical identity of the interface and increasing the particle–substrate distance. We
find that dry transfer of isolated spherical gold nanoparticles with 60 nm diameters leads to very low yields on silicon, quartz, and even fresh gold layers with strong van der Waals attraction to gold particles. The transfer of cubes and plates leads to much larger yields. Likewise, lines and layers of 60-nm gold spheres could be printed with good yield onto a hard silicon surface with a clean native oxide layer (Fig. 4). It appears that both a large crystal face in contact with the hard substrate and multiple smaller contact points increase adhesion and transfer yield, whereas organic adlayers on the particles decrease adhesion and yield. This is consistent with standard microscale models of adhesion, which stress the importance of the actual interfacial area and of contact splitting for adhesive strength. Inside the lines, particles strongly adhere to each other, and each particle adheres to the substrate. Thus, to break the adhesive bond to the substrate, multiple particle–substrate contacts have to be broken, which requires a larger force than for each single adhesive contact.

A reliable transfer process thus requires both surface-energy differences and defined interfacial areas. The PDMS layer on the printing plate that we use provides a low-energy surface, well known for its capacity to release biomolecules onto more hydrophilic substrates. The geometry of the PDMS layer was designed such that the particles come into contact with the substrate when the printing plate is placed on the target. This sometimes conflicts with the inking process, which for some particle arrangements (for example, for lines) requires that the template be deeper than the particle’s diameter. In such cases, the gap was kept as small as possible. A height difference of 5–10 nm can be overcome when pressure is applied on the stamp during the transfer process. Figure 4a shows particle lines of different widths printed on oxidized silicon using this geometry.

In contrast to lines, arrays of individual spherical nanocrystals cannot be transferred onto hard substrates, even if they protrude significantly from the template (Fig. 2e,f). However, transfer with high yields is possible onto thin polymer layers, for example, spin-coated resists. A polymethylmethacrylate (PMMA) layer with a thickness of 10–30 nm increases the transfer yield to above 95%. Transfer takes place at a temperature of 110–120 °C, slightly above the glass transition temperature of PMMA. The polymer embeds the protruding segment of the crystal, thus providing a sufficiently large area of contact to create the adhesion necessary for transfer. Figure 4 shows arrays of individual nanocrystals printed on PMMA. If necessary, the PMMA can then be removed in hydrogen plasma, where it cleanly decomposes.

The position of the nanocrystals is preserved during the transfer with a local accuracy better than 100 nm (see also Fig. 5b). The long-range accuracy of the transfer is comparable to that of microcontact printing with thin-film stamps, for which relative average positioning errors below 20 p.p.m. have been demonstrated across 4-inch wafers. Our printing plates feature the same combination of hard backplanes with soft elastomer layers to reduce the deformations of the stamp that cause long-range inaccuracies in soft lithography techniques.

Figure 4 Particle structures printed on unpatterned Si substrates. Lines are directly printed onto the native oxide layer of Si wafers, and single-particle arrays are printed onto additional 30-nm PMMA adhesion layers. a, AFM and b, SEM images of lines from 60-nm Au particles. The bottom row in b is made from 100-nm Ag particles, which are mostly cubical in shape. c, Larger area of 200-nm-wide lines from 60-nm Au particles. d, AFM detail and e, SEM overview of 1-µm-spaced array of 60-nm Au particles. f, Detail (left eye) from a printed sun pattern composed of 60-nm-diameter Au particles with 260 nm pitch.
It is crucial that printed nanoparticles retain their useful properties during integration. Here, a surface-sensitive application was chosen to demonstrate that the individual gold nanocrystals are still catalytically active. Figure 5a shows silicon nanowires (SiNW) that were grown from an array of 60-nm particles using a vapour–liquid–solid (VLS) process. The particles were printed onto a 30-nm-thick PMMA layer on top of a hydrogen-passivated silicon (111) substrate. The PMMA adhesion layer was removed by thermal decomposition at 300 °C in vacuum, assisted by hydrogen plasma. SiNW growth was then initiated at 460 °C in a reactor using silane as the precursor gas. Nanowires nucleated and grew from the gold particles, and their arrangement was preserved. The epitaxial relationship of the SiNW with the substrate is evident from the wires growing along both the vertical and the three inclined (111) growth directions. Such nanowires are regarded as novel building blocks for future transistors, memory cells and sensors, for example.

Metal nanocrystals also interact strongly with electromagnetic waves, a property that is exploited in applications such as glass staining, surface-enhanced Raman spectroscopy (SERS) and surface plasmon resonance-based agglomeration assays. It has been noticed that the characteristics of single particles can vary considerably, and the printing technique adopted here can create samples that allow investigating such single-particle effects in detail. When the particles are arranged in regular arrays, it is easy to find extraordinarily active particles and analyse them using a variety of methods. Figure 5b shows how some particles scatter visible light more strongly than others, both when immobilized in the PDMS template and when printed onto a silicon substrate. Comparison of the dark-field micrographs with the atomic force microscopy (AFM) and scanning electron micrograph (SEM) images reveals that this is not simply a function of size or overall shape (although doublets of particles often scatter the light strongly), and it will be interesting to apply single-particle SERS and high-resolution electron microscopy to identify the features that distinguish strongly scattering particles or SERS 'hot spots'.

CONCLUSIONS AND OUTLOOK

In conclusion, we have developed an efficient process to fabricate lines, arrays and complex arrangements of nanoparticles with high accuracy and single-particle resolution that retains individual particle functionality. Our printing approach is compatible with different particles, including not only metals, but also polymers, semiconductors and oxides. It can handle bulk-synthesized particles directly in their original colloidal state even when they have been modified with functional molecules. Thanks to its high resolution, nanoparticle printing can efficiently define the critical dimensions for nanoscale devices. The long-range accuracy is similar to that of microcontact printing methods and reaches about 12 p.p.m. Reaching higher accuracies of 1 p.p.m., as required for large-scale integration in microelectronics, is a challenge that remains to be addressed.

Printing processes are adaptable to continuous processing and large areas. Particle handling is based on adhesion, which scales favourably with particle size, so that the printing step can handle much smaller particles, and both self-assembly and directed assembly techniques have been reported to arrange particles down to 2 nm in diameter. Many such techniques, including dry processes based on surface charging and processes based on biological systems could be combined with nanoparticle printing. This should enable not only the integration of much smaller objects but also the development of printing plates that can be programmed for any desired particle arrangement without requiring new templates.

METHODS

PARTICLE AND TEMPLATE PREPARATION

Metal nanocrystals were either purchased (gold colloid, 60 nm nominal diameter, British Biocell International) or synthesized through reduction from...
their respective salts. The polydispersed gold particles shown in Fig. 2 were obtained following a method from Brown et al., in three steps, starting with small crystals produced according to Frens’ method, which were used to seed the next stages. The silver nanocubes shown in Fig. 4 were obtained through polycrystalline silver nitrate and polyvinylpyrrolidone were injected into ethylene glycol at 140 °C under acidic conditions, and 100-nm cubes were obtained after 17 h of growth. Those were then transferred into water and used for inking.

Templates for assembly were cast in PDMS using nanostructured silicon masters. See Supplementary Information, for details of the electron-beam writing and the processing of these masters. The masters were used to cast large numbers of silicone templates. The PDMS used is a variation of the commercially available product. It has a higher elastic modulus and can be patterned at higher fidelity. All templates were fabricated on backplanes cut from display glass (175 μm, Schott AG).

**PARTICLE TRANSFER**

Particle transfer was carried out on both bare silicon surfaces (lightly doped, p-type, polished silicon wafers, Siltronic) and on PMMA-coated silicon surfaces (spin-coated with a 10–30 nm PMMA layer, having a molecular weight of 950 kDa, Microchem). In both cases, the printing plates with the particles were brought into contact with the substrates either manually or in a printing tool that allows microscopic inspection and alignment with existing structures as well as force and temperature control during the transfer. In the case of the uncoated substrates, the printing plate was pressed firmly onto the target and removed immediately after. In the case of the substrates with PMMA adhesion layers, the printing plate was placed on the target, the temperature was increased to 120 °C, pressure was applied on the backplane, the temperature was decreased, and the printing plate was removed as the temperature had dropped to 40 °C.

**BULK COLLOID-FLOW SIMULATION**

The laminar flows occurring in the inking process were simulated with a standard finite element modelling discretization of the Navier–Stokes equations using a commercial code (COMSOL, FEMLAB GmbH), in which the evaporation was calculated simultaneously to produce boundary conditions for the flow into the meniscus. (See Supplementary Information for details and results for a range of simulation parameters.)

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**Competing financial interests**

The authors declare no competing financial interests.

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