

## Self assembled nanoparticle wires by discontinuous vertical colloidal deposition

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We report a simple, one-step method for assembling spherical nanoparticles into wires without the need for lithographic templating. It is effective for a variety of conducting and nonconducting nanoparticles and substrates, and the only material requirement is that the nanoparticles be placed in a colloidal suspension that is wettable on the desired substrate. The shape of the meniscus defines the wire's geometry, and we report the synthesis and physical properties of wires several millimeters long by a few micrometers wide. As we demonstrate here, the technique is fast and easily controlled, and can be used to make integrated nanoparticle wire arrays. © 2005 American Institute of Physics. [DOI: 10.1063/1.2042637]

Nanostructured materials have received substantial attention due to their high potential for technological applications. The large surface to volume ratio of nanomaterials gives rise to electrical, chemical, optical, and thermal properties that are sometimes markedly different from those of their bulk counterparts.<sup>1-4</sup> As Xia and co-workers have reviewed,<sup>5</sup> these differences make nanostructures desirable for use in a variety of technologies.

While important advances are still being made regarding the fundamental properties of nanoparticles,<sup>6,7</sup> the ability to synthesize nanoparticles into wires, films, and bulk geometries will bridge their unique properties to macroscopic applications. To this end, efforts to assemble onto substrates via molecular linkers in patterned<sup>8</sup> and unpatterned<sup>9</sup> geometries have been reported. Patterning can be achieved either pre- or post-deposition by optical or electron-beam lithography or by inkjet printing.<sup>10</sup> These methods possess relative merits with respect to simplicity, scale, resolution, and cost. Single-step assembly methods such as dielectrophoresis are attractive,<sup>11</sup> although the control of the resulting structures is limited, and care must be taken to tune the dielectric contrast between particle and solvent in order to achieve the best results. To avoid assembly entirely, nanowires have been grown, *in situ* by CVD or solution chemistry, a satisfactory solution when the physical properties of the nanorod can be matched to the application. For example, semiconducting nanorods have been grown to form electrically active connections between devices and sensors.<sup>12</sup> These and similar approaches to nanoparticle assembly promise to create advanced materials<sup>13-15</sup> and have attracted significant interest for applications such as nanocoatings and sensors.<sup>8,11,16,17</sup>

In this letter, we present an approach for assembling wires from spherical nanoparticles: discontinuous vertical colloidal deposition (VCD). Since VCD is a recently developed technique, we will first briefly describe the theoretical and experimental basis for assembling films by this method. The technique does not require special chemical synthesis, and we have demonstrated that nanoparticle wires can be

formed on a variety of substrates, conducting or nonconducting; with the choice is driven by the desired application. We will describe the fabrication of wires as a one-step process which avoids lithographic pre- or post-patterning, and we will summarize the electrical properties of gold nanoparticle wires formed in this way.

In our experiments, we assemble 0.02 weight percent,  $12 \pm 1$  nm diameter gold nanoparticles that are synthesized by citrate reduction.<sup>18</sup> The VCD synthesis proceeds at room temperature and at atmospheric pressure by immersing a substrate vertically in a low-viscosity, colloidal, nanoparticle suspension and then gradually exposing it to air by slowly removing the suspension. Simply allowing the solvent to evaporate is particularly effective, resulting in evaporation-driven vertical colloidal deposition (EVCD), for preparing nanoparticle thin films (see Fig. 1), though any other method of solute removal, such as low-speed pumping may be

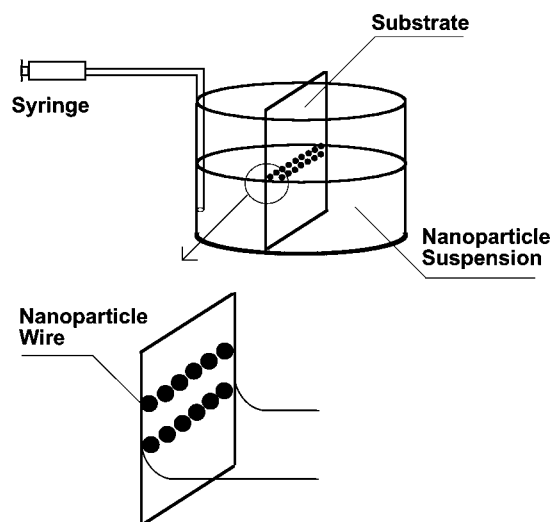


FIG. 1. Illustration of nanoparticle assembly at the meniscus of the air-water-substrate interface. VCD formation of nanoparticle wires proceeds by allowing the solvent to slowly evaporate for a given time, followed by rapidly withdrawing a fixed volume of the suspension and then returning to the evaporation step.

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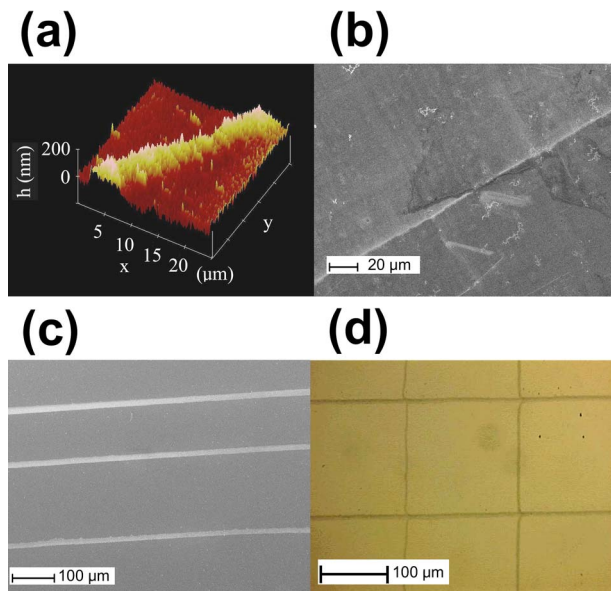


FIG. 2. Images of nanoparticle wires produced by discontinuous VCD: (a) an atomic force microscope image of a  $6\ \mu\text{m}$  wide latex nanosphere wire from a 1 min deposition, (b) a scanning electron micrograph (SEM, LEO 1460VP) of a  $2\ \mu\text{m}$  wide wire following a 15 s deposition, (c) an SEM image of parallel,  $10\ \mu\text{m}$  wide wires, and (d) an optical micrograph a two-dimensional square array of crossed  $10\ \mu\text{m}$  wide wires.

used.<sup>19</sup> Due to interfacial forces, nanoparticles at the liquid-air-substrate interface deposit in a continuous line on the substrate along the meniscus.<sup>20</sup>

The VCD process depends upon the thermal motion of the colloidal particles. Within the suspension itself, the nanoparticles diffuse randomly and their thermal energy is sufficient to desorb any particles that attach to the substrate. However, those diffusing into the meniscus region are trapped where the meniscus narrows to a width less than the mean-free path for colloidal motion. During evaporation, the distance between the particles and the substrate is further reduced by the loss of water content and the particles trapped in the meniscus are deposited on the substrate.

The results of our previous theoretical study show that the areal density of deposited nanoparticles is  $N = \alpha C/v$ , where  $C$  is the concentration of the suspension,  $\alpha$  is the deposition constant for a given nanoparticle, substrate, solvent, and temperature, and  $v$  is the decent speed of meniscus.<sup>20</sup> This theoretical model for the deposition process along with supporting data, allow one to predict the morphology of films synthesized at different evaporation rates from solutions of varying densities.

In order to form wires, the deposition process is interrupted by rapidly removing a small quantity of the suspension so as to drop the meniscus to a new level. In this way, a number of morphologies are obtained from latex spheres or gold nanoparticles, as illustrated in Fig. 2. The wires shown here are formed with their widths determined by the evaporation rate and the deposition time: speeds of about one hundred nanometers per second and times of several seconds to minutes. Up to this point, our narrowest wires are  $2\ \mu\text{m}$  wide [Fig. 2(b), from a 15 s deposition]—this is comparable or superior to the best results from inkjet printing of wires. The separation between adjacent wires is conveniently controlled by removing a fixed volume of liquid between each deposition episode. In this way, parallel arrays of wires can be formed such as those pictured in Fig. 2(c). The length of the

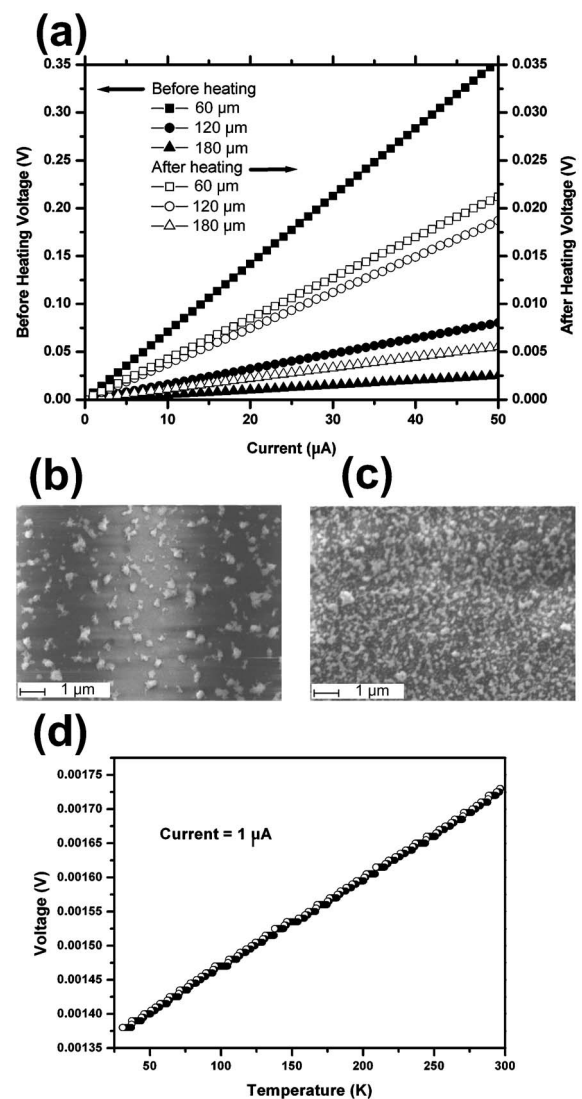


FIG. 3. (a) The current-voltage curves for a selection of 4 mm long by 100 nm thick gold nanoparticle wires with 60, 120, and  $180\ \mu\text{m}$  widths, with and without post-heating. (b) before- and (c) after-heating SEM images of a nanoparticle wire. (d) The voltage-temperature response from 30 to 300 K for a  $240\ \mu\text{m}$  wide wire. The open and closed circles represent the forward and reverse current measurements.

wires is limited only by the substrate size, which can easily be several centimeters. The wires deposited in this way are robust, probably because of the strong tendency for 12 nm gold nanoparticles to aggregate, and so the wires can be re-immersed into the colloidal solution to deposit additional layers of wires like the two-dimensional array pictures in Fig. 2(d).

By using metallic nanoparticles, VCD allows for simple and quick electrical connections at ambient conditions. To demonstrate this, we connected the 4 mm gap between a pair of 100 nm-thick planar electrodes with 12 nm gold nanoparticles. The current-voltage (I-V) responses of these wires, are measured in a four-wire configuration, after connecting the nanoparticle wires to the electrodes with a small amount of silver paint. 10, 20, and 30 min depositions resulted in 100 nm thick by 60, 120, and  $180\ \mu\text{m}$  wide wires, respectively. Their IV curves are plotted in Fig. 3(a) with solid symbols. The linear dependence demonstrates ohmic behavior, and the resistivity of the wires ranges from  $1 \times 10^{-5}\ \Omega\ \text{m}$  to  $2 \times 10^{-6}\ \Omega\ \text{m}$ , about three orders of magni-

tude higher than that of bulk gold but comparable to that of nanoparticle wires prepared by other methods.<sup>15</sup> After several hours of heating at moderate temperatures (2 h at 120 °C followed by 2 h at 170 °C), the conductivity of the wires increases by about a factor of 10. The resulting I-V curves for the heat-treated wires are also plotted in Fig. 3(a) but with hollow symbols. More significantly, the heating process enables spontaneous electrical connection between the wires and the electrodes, eliminating the need for silver paint. The temperature-dependent resistivity for the gold nanoparticle wires exhibits the metallic dependence shown in Fig. 3(d).

SEM micrographs of the wires indicate that the improvement in resistivity results from local aggregation, driven by the breakdown of the functionality of the capping ligands. This aggregation is already visible in the pre-annealed image, Fig. 3(b), with the appearance of clusters of nanoparticles on top of a smooth background of assembled nanoparticles. After annealing, the original structures have disappeared and the underlying gold particles are observed to clump into a more highly textured film imaged in Fig. 3(c). TEM microscopy corroborates this description by showing that the particles aggregate but remain distinct: bright field images show no change in the size or shape of the particles, and electron diffraction is characterized by rings arising from a sample of randomly oriented crystallites. The annealed films do adhere much more firmly to the glass substrates than the unannealed ones, consistent with experiments on self-assembled, gold-thiol multilayers.<sup>21,22</sup> Further studies are underway to investigate the assembly of nanoparticles capped with molecules other than citrate groups.

Discontinuous VCD technique is shown to be a simple and versatile method for assembling nanoparticle wires. We report the synthesis of gold nanowires 10  $\mu\text{m}$  wide and as long as one centimeter: aspect ratios impractical for electron-beam lithography but consistent with inkjet printing. Our best results have produced wires that are two microns wide, which would be difficult to synthesize with an inkjet. We are currently investigating the formation of defects that prevent the fabrication of submicron-width wires by synthesizing wires in dust-free environments and by studying the effects of jamming in the assembly process. Work will continue in our laboratory to explore the means to tune the coupling

between individual nanoparticles within the wires, so as to study a range of material properties, from bulk attributes to those unique to the nanoscale. More details about discontinuous VCD and the physical properties of nanoparticle wires will be presented in forthcoming work.

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- <sup>1</sup>Y. Huang, X. F. Duan, Q. Q. Wei, and C. M. Lieber, *Science* **291**, 630 (2001).
- <sup>2</sup>Y. Cui, Q. Q. Wei, H. K. Park, and C. M. Lieber, *Science* **293**, 1289 (2001).
- <sup>3</sup>S. J. Limmer, T. P. Chou, and G. Cao, *J. Phys. Chem. B* **107**, 13313 (2003).
- <sup>4</sup>S. J. Limmer and G. Cao, *Adv. Mater. (Weinheim, Ger.)* **15**, 427 (2003).
- <sup>5</sup>Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, and H. Yan, *Adv. Mater. (Weinheim, Ger.)* **15**, 375 (2003).
- <sup>6</sup>V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, *Nature (London)* **370**, 354 (1994).
- <sup>7</sup>C. P. Collier, R. J. Saykally, J. J. Shiang, S. E. Henrichs, and J. R. Heath, *Science* **277**, 1978 (1997).
- <sup>8</sup>S. J. Park, T. A. Taton, and C. A. Mirkin, *Science* **295**, 1503 (2002).
- <sup>9</sup>M. D. Musick, C. D. Keating, L. A. Lyon, S. L. Botsko, D. J. Pena, W. D. Holliday, T. M. McEvoy, J. N. Richardson, and M. J. Natan, *Chem. Mater.* **12**, 2869 (2000).
- <sup>10</sup>Y. Wang, J. Bokor, and A. Lee, *Proc. SPIE* **5374**, 628 (2004).
- <sup>11</sup>O. D. Velev and E. W. Kaler, *Langmuir* **25**, 3693 (1999).
- <sup>12</sup>F. Patolsky, G. Zheng, O. Hayden, M. Lakadamyali, X. Zhuang, and C. M. Lieber, *Proc. Natl. Acad. Sci. U.S.A.* **101**, 14017 (2004).
- <sup>13</sup>C. A. Mirkin, R. L. Letsinger, R. C. Mucic, and J. J. Storhoff, *Nature (London)* **382**, 607 (1996).
- <sup>14</sup>W. Shenton, S. A. Davis, and S. Mann, *Adv. Mater. (Weinheim, Ger.)* **11**, 449 (1999).
- <sup>15</sup>K. D. Hermanson, S. O. Lumsdon, J. P. Willimas, E. W. Kaler, and O. D. Velev, *Science* **294**, 1082 (2001).
- <sup>16</sup>K. H. Bhatt and O. D. Velev, *Langmuir* **20**, 467 (2004).
- <sup>17</sup>D. J. Norris and Y. A. Vlasov, *Adv. Mater. (Weinheim, Ger.)* **13**, 371 (2001).
- <sup>18</sup>R. G. Freeman, M. B. Hommer, K. C. Grabar, M. A. Jackson, and M. J. Natan, *J. Phys. Chem.* **100**, 718 (1996).
- <sup>19</sup>J. J. Diao, F. S. Qiu, G. D. Chen, and M. E. Reeves, *J. Phys. D* **36**, L25 (2003).
- <sup>20</sup>J. J. Diao, J. B. Hutchison, G. Luo, and M. E. Reeves, *J. Chem. Phys.* **122**, 184710 (2005).
- <sup>21</sup>L. Supriya and R. O. Claus, *J. Phys. Chem. B* **109**, 3715 (2005).
- <sup>22</sup>B. G. Prevo, J. C. Fuller, and O. D. Velev, *Chem. Mater.* **17**, 28 (2005).