Formation of asymmetric one-sided metal-tipped semiconductor nanocrystal dots and rods

TALEB MOKARI1, CLAUDIA G. SZTRUM2, ASAF SALANT1, ERAN RABANI2,* AND URI BANIN1,*

1Department of Physical Chemistry, The Farkas Center for Light Induced Processes, and The Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 91904, Israel
2School of Chemistry, The Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel
*e-mail: rabani@tau.ac.il; banin@chem.ch.huji.ac.il

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Multicomponent nanoparticles represent a new approach for creating smart materials, requiring the development of the growth of different material types on one particle. Here, we report the synthesis of asymmetric metal–semiconductor heterostructures where gold is grown on one side of CdSe nanocrystal quantum rods and dots, creating nanostructures offering intrinsic asymmetry for diverse device functionalities such as diode elements, along with one-sided chemical accessibility through the gold tips. Surprisingly, one-sided growth is preceded by two-sided growth and is generally observed in different particle shapes. Theoretical modelling in a lattice-gas model and experimental analysis show that a ripening process drives gold from one end to the other, transforming two-sided growth to one-sided growth. Ripening is therefore occurring on the nanostructure itself, leading to a phase-segregated structure. This thereby extends the realm of ripening phenomena and their significance in nanostructure synthesis, in particular for nanocrystals composed of different materials.

Ostwald ripening is a universal phenomenon in which particles larger than a critical size grow on account of the smaller particles owing to their relative stabilization by the surface energy term. This well-known process occurs on surfaces as well as in solution and has been extensively studied for a variety of material systems in diverse environments. The Ostwald-ripening process typically leads to a coarsening of the size distribution, and hence in nanocrystal synthesis one usually aims to suppress it by having excess precursors in solution. At long times, Ostwald ripening leads to a decreased number of particle domains.

An important frontier in nanocrystal synthesis is the growth of composites of different materials in the same nanostructure as a means of increasing functionality. Ripening processes in such complex systems may have profound effects on the outcome of the synthesis. A key question is whether one could achieve a core/shell structure of two materials or, rather, will the materials phase segregate on the nanostructure or even separate to form two different particles. An important combination of materials is that of a metal and semiconductor in the same nanocrystal, where metal tips can provide anchor points for electrical connections and for self-assembly. Metal (Au) tips were grown in ref. 8 on the apexes of semiconductor rods (CdSe), forming ’nano-dumbbells’ (NDBs). From the viewpoint of self-assembly, they are equivalent to bi-functional molecules such as the di-thiols manifesting two-sided chemical connectivity.

A challenging problem is the formation and control of asymmetric metal–semiconductor heterostructures. Several attempts were reported using a photochemical route, seeded growth or a site-selective lithographic approach. Here we report the growth of a metal (Au) tip on one side of semiconductor (CdSe) dots and rods, termed ’nano-bell-tongues’ (NBTs). These represent a new class of asymmetric nanostructures for diverse device functionalities, such as diode elements. NBTs are analogous to a mono-thiol providing one-sided chemical connectivity in self-assembly schemes. Self-assembly of nanocrystals has already yielded a diverse set of structures and
could be enriched by the availability of nanostructures manifesting a single anchor point. For example, a metal (Au) tip could be used for connection to a biomolecule, whereas the semiconductor side will yield fluorescence\(^{13}\). A magnetic tip could also be used for aligning or manipulating the nanostructure with an external field.

In this work we focus on the detailed understanding of the growth process leading to the formation of symmetric or asymmetric heterostructures. Surprisingly, we find that one-sided growth of a gold tip on a semiconductor quantum dot or rod is preceded by two-sided growth. Experimental analysis and theoretical modelling show that a ripening process drives gold from one end to the other, transforming the NDBs to NBTs. Ripening is therefore occurring effectively on the nanostructure itself, leading to a phase-segregated structure and thus extending the realm of ripening phenomena and their importance in nanostructures.

The growth of gold on CdSe dots\(^{29}\) and rods\(^{30}\) follows our earlier strategy\(^{8}\) for growing NDBs with AuCl\(_3\) as the gold precursor, didodecylidammoniumbromide (DDAB) as a surfactant for the gold salt and dodecylamine (DDA) as a stabilizing agent for the nanocrystals and a reduction agent (see Methods). Figure 1 presents transmission electron microscopy (TEM) images of one-sided gold tips grown on CdSe dots and rods of different dimensions. In the dots (diameter 10 nm, Fig. 1a) and the shorter rods (length \(\times\) diameter, 18 \(\times\) 3.5 nm, Fig. 1b; 25 \(\times\) 4 nm, Fig. 1c), gold, identified by the dark contrast in the TEM owing to its high electron density, grows with high selectivity on one side. In long rods (50 \(\times\) 4 nm, Fig. 1d), a large gold particle grows on one end with some gold still visible on the other side or on extra sites along the rod.

The effect of increasing Au/rod molar ratio on the growth is shown in Fig. 2. One-sided growth involves using higher relative ratios of gold to the dots/rods as compared with the two-sided growth conditions (see Table 1). Figure 2a shows the original rods of dimension 25 \(\times\) 4 nm and mole number (\(\sim 1.5 \times 10^{-10}\) mol). After adding 1.3 \(\times\) 10\(^{-6}\) mol of gold precursors we obtain NDBs (Fig. 2b), on further addition of an amount of 1.3 \(\times\) 10\(^{-6}\) mol of gold, highly selective one-sided growth was achieved (Fig. 2c). Surprisingly, NDBs are an intermediary for one-sided growth, but the end product is a highly asymmetric Au–CdSe heterostructure.

This intriguing behaviour is also observed in the results of a theoretical model presented in the lower panels of Fig. 2 (see Methods for details). In our model, we represent the system on a two-dimensional lattice (Fig. 2d)\(^{31,32}\). In Fig. 2e and f we plot snapshots of final morphologies at low and high gold densities (\(\rho_g\)). The similarity with the experimental results shown in Fig. 2b,c is striking. At lower gold concentrations, two-sided growth is evident in the simulation (Fig. 2e), in agreement with the experimental observation (Fig. 2b). As the gold concentration is increased a marked change is observed, leading to one-sided growth and formation of NBTs both theoretically (Fig. 2f) and experimentally (Fig. 2c). We note that the model does not include any initial asymmetry in the interactions between the gold and either rod apex. In fact, even when asymmetric interactions were included in the model, the probability for a transition to one-sided growth
Figure 2 Effect of increasing Au/rod molar ratio on the growth. Top panels show the experimental results. a, Original rods of dimension 25 × 4 nm. b, NDBs after adding 1.3 μmol of gold precursors to a. c, NBTs after adding 1.3 μmol of gold precursors to b. Lower panels show the theoretical results. d, Presentation of the system on a two-dimensional lattice. e, Snapshot of final morphology at low gold concentration (the two-dimensional gold density is ρ₀ = 0.001) yielding two-sided growth. f, Snapshot of final morphology at high gold density (ρ₀ = 0.01) showing one-sided growth.

Table 1 Summary of growth conditions in different samples.

<table>
<thead>
<tr>
<th>Shape</th>
<th>Size (nm)</th>
<th>Product after Au growth and figure</th>
<th>Amount of nanocrystals (mol)</th>
<th>Concentration of nanocrystals (M)</th>
<th>Amount of Au (mol)</th>
<th>Concentration of Au (M)</th>
<th>Au/nanocrystal mole ratio</th>
<th>Au/nanocrystal concentration ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rods</td>
<td>25 × 4</td>
<td>NDBs (Fig. 2b)</td>
<td>1.5 × 10⁻¹⁰</td>
<td>7.5 × 10⁻⁹</td>
<td>1.3 × 10⁻⁶</td>
<td>4.3 × 10⁻⁴</td>
<td>9,000</td>
<td>57,800</td>
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<tr>
<td>Rods</td>
<td>25 × 4</td>
<td>NBTs (Fig. 2c)</td>
<td>1.5 × 10⁻¹⁰</td>
<td>7.5 × 10⁻⁹</td>
<td>2.6 × 10⁻⁶</td>
<td>8.6 × 10⁻⁴</td>
<td>18,000</td>
<td>115,000</td>
</tr>
<tr>
<td>Dots</td>
<td>10</td>
<td>Two sided (Fig. 3a)</td>
<td>5.5 × 10⁻¹⁰</td>
<td>5.5 × 10⁻⁸</td>
<td>2.7 × 10⁻⁶</td>
<td>9 × 10⁻⁴</td>
<td>4,900</td>
<td>16,400</td>
</tr>
<tr>
<td>Dots</td>
<td>10</td>
<td>One sided (Fig. 3b)</td>
<td>5.5 × 10⁻¹⁰</td>
<td>5.5 × 10⁻⁸</td>
<td>8.2 × 10⁻⁶</td>
<td>2.7 × 10⁻³</td>
<td>14,900</td>
<td>49,000</td>
</tr>
<tr>
<td>Rods</td>
<td>50 × 4</td>
<td>NDBs (Fig. 3d)</td>
<td>2.35 × 10⁻¹⁰</td>
<td>1.17 × 10⁻⁶</td>
<td>2.4 × 10⁻⁶</td>
<td>8 × 10⁻⁴</td>
<td>10,200</td>
<td>68,000</td>
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<tr>
<td>Rods</td>
<td>50 × 4</td>
<td>Nanobeads (Fig. 3e)</td>
<td>2.35 × 10⁻¹⁰</td>
<td>1.17 × 10⁻⁸</td>
<td>4.8 × 10⁻⁶</td>
<td>1.6 × 10⁻³</td>
<td>20,400</td>
<td>136,000</td>
</tr>
<tr>
<td>Rods</td>
<td>50 × 4</td>
<td>NBTs (Fig. 3f)</td>
<td>2.35 × 10⁻¹⁰</td>
<td>1.17 × 10⁻⁸</td>
<td>8.2 × 10⁻⁶</td>
<td>2.7 × 10⁻³</td>
<td>35,000</td>
<td>231,000</td>
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<tr>
<td>Tetrapods</td>
<td>25 × 4</td>
<td>Fig. 5</td>
<td>1.53 × 10⁻⁹</td>
<td>1.53 × 10⁻⁷</td>
<td>3.3 × 10⁻⁵</td>
<td>0.811</td>
<td>21,800</td>
<td>72,000</td>
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<tr>
<td>Defected rods</td>
<td>(45 × 4)</td>
<td>Fig. 6a-e</td>
<td>1.4 × 10⁻¹⁰</td>
<td>1.4 × 10⁻⁸</td>
<td>9.8 × 10⁻⁶</td>
<td>2.4 × 10⁻³</td>
<td>93,000</td>
<td>315,000</td>
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</table>

was equal for both tips. The transition to one-sided growth could therefore only be understood if a fluctuation in the density of the gold on the tips leads to growth and relative stabilization of gold on one tip and, subsequently, to its further growth, along with consumption of the other tip (that is, a ripening process). However, it is important to note that the ripening phenomena observed here has very different consequences compared with the more common Ostwald ripening in the sense that on its completion, each and every nanostructure contains one gold tip, whereas in Ostwald ripening coarsening results in a decrease in the number of particles, asymptotically, to a single large island.

Similar behaviour was also observed in nearly spherical particles. Figure 3a shows the initial growth that typically led to the creation of two gold patches (see Table 1 for synthesis details). CdSe nanocrystals grow in a wurtzite structure and are not spherically symmetric. Thus the gold grows on certain facets, in particular on the polar facets along the c axis as seen in the high-resolution TEM (HRTEM) of these dots (inset of Fig. 3a). After increasing the
Figure 3 Behaviour of growth onto dots and long rods as a function of gold concentration. a, CdSe dots (10 nm) showing two-sided growth. Inset shows a HRTEM of a single dot. b, One-sided gold growth on the CdSe dots shown in a. Inset is a HRTEM of a single dot. c–f, Original rods 50 × 4 nm (c), two-sided growth (d), bead growth (e) and one-sided growth (f). See also Table 1 for more details.

amount of gold we observe a transformation to one-sided growth similar to that observed in the rods (Fig. 3b).

A different dependence on gold concentration is seen in longer rods (50 × 4 nm, Fig. 3c). Here, following early two-sided growth of NDBs (Fig. 3d, see Table 1 for reaction details), adding more Au precursor leads to growth of gold deposits along the rod, appearing as 'nano-beads' (Fig. 3e). Further addition of Au precursor results in nearly complete transformation to one-sided growth (Fig. 3f). A closer examination of the NBTs using HRTEM showed a CdSe lattice in the rod centre along with gold on the tips (see Supplementary Information, Fig. S1). The intermediate nano-bead formation is probably owing to the nucleation of gold at defect sites that are more abundant in long rods. However, the final product is also characterized in this case by a tip of gold
Figure 4 Simulation of the growth dynamics of the gold on the nanocrystal.  

**a.** A random initial configuration of the gold (time $t = 1$ in Monte Carlo steps).  
**b.** The gold grows on both ends of the rod, leading to the formation of NDBs ($t = 260,000$).  
**c.** The system reaches the dissolution limit ($t = 2,100,000$).  
**d.** At longer times the right tip grows larger than the left ($t = 8,400,000$).  
**e.** Formation of a NBT ($t = 33,500,000$). The larger and more stable right tip continues to grow, while at the same time the left tip is nearly fully consumed.  
**f.** Plot of the size of both gold tips showing how, initially, they grow together, followed by growth of one tip along with a decrease in the size of the other.

A microscopic picture of the ripening process is depicted in Fig. 4, where a typical simulated trajectory of one-sided growth is shown. We assume a random initial configuration of the gold (orange colour, Fig. 4a). First, the gold grows on both ends of the rod, leading to the formation of NDBs (Fig. 4b,c). At longer times a fluctuation in the density on the length scale of the rod is clearly observed and in this case the right tip grows larger than the left (Fig. 4c,d). Following this, the larger and more stable right tip grows even more, while at the same time the left tip is nearly fully consumed leading to the formation of the NBT (Fig. 4e). In Fig. 4f we plot the size of both gold tips showing how, initially, they grow together. At $\sim 10^5$ steps, both tip sizes reach a transient plateau indicating that the system has reached its dissolution limit. Following this plateau, at $\sim 10^6$ steps, the size of the left tip starts to decrease, while at exactly the same time the right tip continues to grow and the sum of the size of both tips is nearly conserved. This provides clear evidence for two-sided growth preceding one-sided growth.

As already discussed above, the transition from two- to one-sided growth is analogous to the well-known Ostwald ripening phenomena. In fact, our experimental and theoretical observations manifest a similar phenomenon, where ripening is constrained to the rod itself and occurs when the two tips reach a critical size as described in common Ostwald ripening theories. As observed experimentally, this constraint leads to a relatively uniform size distribution of gold tips on each and every rod, strongly suggesting that the rod body itself plays a role in the ripening process.

To better understand the mechanism of ripening we consider the contributions to the stabilization of the larger metal tip versus the smaller tip. First, surface energy will stabilize the larger particles. Second, the standard reduction electrode potential for metal nanoparticles was found to negatively shift in smaller size. Therefore, smaller gold nanoparticles are more easily oxidized compared with the larger nanoparticles and, hence, are relatively destabilized. Both the surface energy term and the latter term depend inversely on particle radius. The electrochemical Ostwald ripening of colloidal silver particles on conductive substrates based on these driving forces was reported in ref. 5. They found that the ripening process could only occur on a conductive substrate facilitating electron transfer from small to large particles.

In our case, excess of the gold growth solution is added drop-wise so that gold growth can in part be ascribed to a process similar to that yielding growth in the first place, namely, its reduction on the rod aided by the amine. However, at the same time we observe the consumption of the smaller gold tip. We note in this context that experiments of gold growth in dark conditions showed a similar behaviour of one-sided growth suggesting that the source of electrons for reduction is not from a photochemical process.
as reported for ZnO rods\textsuperscript{33}. Alternatively, this process is assigned to the electrochemical Ostwald ripening phenomenon discussed above in the following manner. In the small particle, Au\textsuperscript{0} must be oxidized to be released to solution and the electrons released are transferred through the rod to the large particle on which a gold ion is reduced leading to growth on that side. A valid question concerns the electron transfer process through the semiconductor rod body, a process not included explicitly in the theoretical model. We suggest that the rod is involved in this process and the electron is transferred to the growing side by means of hopping through surface states. The presence of such surface states is evident in particular for larger rods that show an intermediate stage of ‘nano-beads’, where gold deposits on the sites along the rod. Fluctuating charge on such surface states is also believed to lead to spectral wandering observed in single nanocrystal optical spectroscopy studies\textsuperscript{34} and also in rods\textsuperscript{35,36}.

This mechanism of electron transfer from one tip to the other to explain the gold oxidation process on the small tip is strongly supported by a study of the temporal evolution of the growth. This was performed by taking aliquots and analysing them with TEM at different times after the initial Au precursor injection, in this case without further Au addition. After a rapid transition from two- to one-sided growth occurring on a timescale of one minute or less (Fig. 5a,b, respectively), the system reaches a steady state sustained for hours (Fig. 5c). This shows that ripening is suppressed after all the rods have reached the NBT structure, with gold on one side. In usual ripening we would expect coarsening to continue between different rods, but this could not take place because Au\textsuperscript{0} oxidation is blocked as electrons could not transfer from one rod to another. This provides compelling evidence for the crucial role of the rod body itself in this electrochemical intra-rod ripening. An electron freed by Au\textsuperscript{0} oxidation on one side is transferred by the rod body to the other side where reduction of a Au ion from solution could be facilitated.

The process of electron transfer through the rod body that is required for the transition from two- to one-sided growth has interesting implications on the outcome of this process in other nanostructures. Interestingly, this leads to diverse behaviour for the gold growth on tetrapods as shown in Fig. 6. In about 40\% of the tetrapods (a total of 25 were examined), adding more Au does not lead to one-sided growth but rather to concerted growth of all tips (Fig. 6a,b). In the same reaction, rods show distinctly different behaviour of one-sided growth as seen in Fig. 6c. About a third of the tetrapods also show such tendency for one-sided growth (Fig. 6c,d), observed at conditions where we can also see independent gold-particle nucleation. The rest of the tetrapods show either growth on the junction point or growth on the tip pointing out from the plane of the grid (Fig. 6e). This diversity in gold growth behaviour on different tetrapods is assigned to a barrier at the junction point of the tetrapod that impacts the electron transfer essential for gold-tip consumption. The barrier at the tetrapod junction point could result from structural defects at the connection point between the arm, which has a wurtzite lattice, and the central part of the tetrapod, with a zinc-blende lattice\textsuperscript{37}. When the barrier is high, electron transfer is suppressed and this will block the oxidation process to consume the tips, leading to concerted growth on all tips. This is analogous to the suppression of ripening of silver particles on insulating substrates reported in ref. 5. In the other cases, the barrier is low and electron transfer can take place leading to one-sided growth. Transport measurements on single tetrapods indeed show two distinct transport behaviours assigned to the presence or lack of a barrier at the junction point\textsuperscript{38}.

Further support to the blocking of the electron transport as being the reason for the lack of one-sided growth in a large fraction of the tetrapods is provided by the simulation shown in Fig. 6f–k. The tetrapod is modelled in the two-dimensional square lattice by an inverted T-shaped nanostructure, with equal distances between the three arms. When the oxidation/reduction of gold is not blocked, the transition from multi-sided growth to one-sided growth occurs, as can be seen in Fig. 6. First, there is gold growth on all three apexes (Fig. 6f–h). At later times the top tip starts to disappear whereas the other two grow (Fig. 6i,j). Finally, the left tip disappears whereas the right tip grows further, leading to one-sided growth (Fig. 6k). We emphasize that a theoretical modelling of the exact pathway for the electron transport must be based on atomistic calculations\textsuperscript{39–42} and will be addressed in a future study.

The role of a barrier in the gold growth and ripening processes is also demonstrated by an experiment on rods in which we purposely grow a defect point to serve as a barrier. Figure 6l shows a TEM image of rods onto which a defect point, manifested by a larger dot along the rod, was grown (see Supplementary Information for

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Gold growth kinetics. a, A TEM image of NDBs at $t=0$. b, c, Taken after 3 min (b) and 8 h (c), without further addition of gold monomers. See Table 1 for details.}
\end{figure}
Figure 6 Gold growth experiment on tetrapods, experiment versus simulation and on rods with a defect. a, b, TEM images of tetrapods after gold growth, showing growth on all tips. c, d, TEM images of single rod and tetrapod showing asymmetric growth. e, TEM image of a tetrapod showing growth on the junction point. The width of images b–e is 70 nm. f–k, Simulation of growth dynamics of gold on a model three-branched inverted T-structure (f) as a function of time. Note the evolution from three-sided growth (g)–(i) to two-sided growth (j) and finally to one-sided growth (k). Time in Monte Carlo steps from f to k: $t = 1$, $t = 16,000$, $t = 525,000$, $t = 2,100,000$, $t = 8,400,000$ and $t = 16,800,000$. l, Rods with a directed structural defect. m, Same sample at the end of the gold growth process. Defected rods (circled in black) show growth on the defect point, whereas rods without defect (circled in red), show the usual one-sided growth.
growth details). Due to the crude control, some rods do not show the defect. Gold growth was performed on this sample and initially we observed the usual two-sided growth. On increasing the gold concentration we observe a transition to a single gold patch on the rods. Rods without defects show the usual behaviour of one-sided growth, whereas for those with a defect the patch is located on the defect-site as this is a sink for the electrons and hence the preferred site for ripening to occur.

There are kinetic and energetic contributions to the fluctuations leading to ripening and one-sided growth. For low gold concentrations, gold density fluctuations (on the length scale of the rod size) are suppressed by the strong coupling to the rod and cannot lead to ripening resulting in the formation of NDBs. As the gold concentration is increased, the magnitude of these density fluctuations can also increase, providing the driving force for ripening. This increase in density fluctuations with the monomer density also leads to faster ripening kinetics. For these reasons, experimentally, we can stop the reaction when NDBs are formed at low monomer concentrations, whereas at high concentrations the two- to one-sided growth transformation is rapid and more difficult to control.

The mechanism of one-sided growth of a metal on a semiconductor nanocrystal is of general importance for the growth of a variety of nanostructures composed of two different materials. Experimental results show that this phenomenon generally applies to different particle shapes. The agreement of the experiments with the theoretical model, which is not system specific, suggests that the reported phenomenon is universal and could therefore explain further experimental observations of phase-separated growth in other nanocrystal systems. The one-sided metal–semiconductor NBTs grown here are interesting nanostructures offering intrinsic asymmetry along with one-sided chemical functionality through the gold tips.

**METHODS**

**MATERIALS**

Tri-n-butylphosphine (TBP, 99%) and dimethyldichloride (CdCl₂) were from Strem. CdCl₂(Cd₃Cl), was transferred from its original cylinder to remove impurities and stored in a refrigerator inside a glovebox. Tetraethylammonium hydroxide (TEA) was from Afa. Hexylphosphonic acid (HPA) was prepared by reacting hexylphosphonic dichloride with water. Solid HPA was then extracted with diethyl ether and isolated by evaporation of the solvent. AuCl₃ (99%), DDAB (98%) and DDAO (90%) were from Aldrich.

**SYNTHESIS OF CdSe DOTS, RODS AND TETRAPODS**

CdSe dots, rods and tetrapods, serving as templates for gold growth, were prepared by known procedures as described in Refs. 31, 44. Defected rods were synthesized as described in Supplementary Information.

**SYNTHESIS OF CdSe–Au NBTs (TABLE 1)**

In a typical one-sided gold growth reaction, a gold solution was prepared containing 2.5 mg AuCl₃ (0.008 mmol), 20 mg of DDAB (0.04 mmol) and 35 mg of 1:6 (28.15 × 10⁻³ mol of rod) of CdSe quantum rods of size 50 × 4 nm were dissolved in 20 ml of toluene in a three-neck flask under argon. In the case of 25 nm x 4 nm rods, 0.9 mg (4.8 × 10⁻³ mol) of rods) was dissolved in 20 ml toluene keeping the same gold solution amount. The gold solution was added drop-wise over a period of 3 min. During the addition, carried out at room temperature, the solution colour gradually changed to dark brown. In the NBT synthesis as mentioned here, the molar ratio of gold to nanorods is significantly higher compared with the NDB (two-sided growth) case. The separation of the NBTs from the growth solution was carried out by adding 1 ml of methanol, which leads to precipitation, and centrifuging for 5 min.

**PARTICLE CHARACTERIZATION**

TEM images were obtained using a Tecnai 12 microscope operated at 100 kV. HRTEM images were obtained using a Tecnai F20G microscope operated at 200 kV.

**THEORETICAL MODEL**

We briefly review the approach used to model the growth of gold on semiconductor tips. The density of gold, solvent and nanorod are represented by binary variables. We represent the system on a two-dimensional (size 512 × 512) lattice (Fig. 2d). Each cell of the square lattice, with a size typical to atomic dimensions, can be occupied by the gold or by the solvent. For simplicity we assume that these species are of similar dimensions using the Au–Au bulk bond length (0.28 nm) for scaling. The density of gold and solvent is represented by two binary variables ρ = 0, 1 and l = 0, 1, respectively. These binary variables are proportional to the gold and solvent densities at site i, respectively. The semiconductor nanorod is also modelled by a binary variable, r = 0, 1.

We consider non-equilibrium initial conditions appropriate for the experiments discussed above. The initial uniform random distribution of the gold precursor is described in our model by

\[ \rho = \begin{cases} 1 & \xi < \xi_1 \\ 0 & \phi \end{cases} \]

where \( \xi \) is a uniform random number in the range \([0,1] \) and \( 0 \leq \xi_1 \leq 1 \) is the two-dimensional gold density. A single nanorod with dimensions \( L \times D \) (here \( L \) and \( D \) are the length and diameter in lattice units at the centre of the simulation box) is defined as \( r = 1 \). Otherwise, half-circled caps are added to the two ends of the nanorod to prevent early growth of rectangular-shaped gold tips resulting from the choice of the symmetry of our lattice.

The dynamics in our model are stochastic. Gold particles react on a random walk on the lattice, biased by their interactions with the solvent, with the nanorod and with each other. Such a move is accepted with a Metropolis probability \( P_m = \min(1, \exp(\Delta H/k_B T)) \), where \( k_B \) is Boltzmann’s constant, and \( \Delta H \) is the resulting change in energy. The hamiltonian of the system is described by

\[
H = -\sum_{<ij>} \epsilon_{ij} l_i l_j - \sum_{<ij>} \gamma_{ij} (l_i r_j - l_j r_i) - \sum_{<ij>} \delta_{ij} (r_i - r_j)
\]

The sums in the above equation include only nearest-neighbour cells. In all of the results reported in this paper we take the liquid–liquid attractions to be \( \gamma = 1/(3T) \), with reduced-gold–gold attractions to be \( \gamma = 1/(3T) \), gold–liquid attractions to be \( \epsilon = 1/(4T) \) and gold–rod attractions to be \( \epsilon = 25T \), where \( T \) is the temperature. Gold–rod attractions are spatially limited to only the tips to mimic the tips higher interaction parameter. The parameter \( \gamma = \sum_{<ij>} \epsilon_{ij} \) is used to represent the dependence of the gold–gold interaction strength on the oxidation state of the gold, \( \gamma > 5 \) for \( \gamma > 5 \) and \( \gamma = 1 \) otherwise. Qualitatively the results are insensitive to the choice of these parameters within a reasonable range as long as (i) the gold–gold sticking probability in solution is negligibly small (\( \epsilon > \epsilon_a \) and (ii) the gold–rod sticking probability is high \( \epsilon > \epsilon_a \).

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Correspondence and requests for materials should be addressed to E.R. or U.B.

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