NANOMATERIALS

Controlled growth and shape-directed self-assembly of gold nanoarrows

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Self-assembly of colloidal nanocrystals into complex superstructures offers noteworthy opportunities to create functional devices and artificial materials with unusual properties. Anisotropic nanoparticles with nonspherical shapes, such as rods, plates, polyhedra, and multipods, enable the formation of a diverse range of ordered superlattices. However, the structural complexity and tunability of nanocrystal superlattices are restricted by the limited geometries of the anisotropic nanoparticles available for supercrystal self-assembly. We show that uniform gold nanoarrows (GNAs) consisting of two pyramidal heads connected by a four-wing shaft are readily synthesized through controlled overgrowth of gold nanorods. The distinct concave geometry endows the GNAs with unique packing and interlocking ability and allows for the shape-directed assembly of sophisticated two-dimensional (2D) and 3D supercrystals with unprecedented architectures. Net-like 2D supercrystals are assembled through the face-to-face contact of the GNAs lying on the pyramidal edges, whereas zipper-like and weave-like 2D supercrystals are constructed by the interlocked GNAs lying on the pyramidal (111) facets. Furthermore, multilayer packing of net-like and weave-like 2D assemblies of GNAs leads to non-close-packed 3D supercrystals with varied packing efficiencies and pore structures. Electromagnetic simulation of the diverse nanoarrow supercrystals exhibits exotic patterns of nanoscale electromagnetic field confinement. This study may open new avenues toward tunable self-assembly of nanoparticle superstructures with increased complexity and unusual functionality and may advance the design of novel plasmonic metamaterials for nanophotonics and reconfigurable architectured materials.

INTRODUCTION

The self-assembly of intricate superstructures from inorganic nanocrystals is an attractive route toward functional nanoarchitectures with enhanced collective properties and provides insights into the behavior of atomic and colloidal crystals as well as biological self-assembled systems (1–7). The geometry of nanoscale building blocks plays key roles in the hierarchical assembly of ordered superstructures showing properties dependent on the shape, orientation, and spatial arrangement of the building blocks. Anisotropic nanocrystals with varied shapes, such as rods (8), plates (9), polyhedra (10–13), and multipods (14), have been widely used for constructing superstructures with symmetries that are unattainable with conventional spherical particles. Dense packings are favored for nanocrystal superlattices because the self-assembly of hard particles is usually dominated by entropy-driven maximization of the packing density (15). In particular, the self-assembly of nanoscale convex polyhedra into supercrystals (SCs) with the densest packings has been experimentally observed (10, 16) and theoretically predicted (11, 16). Non–close-packed superlattices with tunable structures can be achieved by using depletion attraction (10) or exploiting the semiflexible layer of organic surface ligands through control of surface coverage (9), tuning of surface wettability (17), polymer grafting (18), and DNA functionalization (12, 13). Note that branched nanocrystals with a concave geometry have been organized into ordered superlattices of increased complexity (14, 19–21) or binary superlattices coassembled with shape-complementary building blocks (12, 22). Nevertheless, it remains a great challenge to fabricate well-defined nanoarrows with more complicated concave geometries for constructing SCs with structural complexity and conformational diversity.

Geometrically perfect metal nanocrystals are excellent building blocks for plasmonic nanostructures with strong and tunable field confinement and enhancement (23, 24). In particular, considerable progress has been made in the assembly and applications of SCs built of uniform metal nanocrystals in the shape of polyhedra (10, 16, 17, 25–27) and rods (28–31). Although the synthesis of metal nanocrystals with concave geometries, such as faceted concave polyhedra, has been reported (32), their self-assembly into ordered SCs has yet to be realized, owing to the unsatisfactory uniformity or unfavorable geometric features. Here, we developed an efficient synthesis of uniform gold nanoarrows (GNAs) with a peculiar concave geometry through delicate overgrowth of gold nanorods (GNRs). The GNAs exhibited unique packing and interlocking ability and could be readily assembled into diverse two-dimensional (2D) and 3D SCs with unprecedented conformations, significantly expanding the structural complexity and tunability of self-assembled superlattices. The elaborate self-assembly of GNAs may advance the design of novel plasmonic metamaterials for nanophotonics (33) and reconfigurable architectured materials (34).

RESULTS

As shown in Fig. 1, the controlled overgrowth of normal GNRs into the GNAs consisting of two pyramidal heads and a four-wing shaft was readily achieved through kinetic control induced by cetyltrimethylammonium chloride (CTAC) coupled with selective surface passivation via Ag underpotential deposition (UPD), and the shape-directed self-assembly of the GNAs into a variety of loosely packed or tightly interlocked SCs was realized through solvent evaporation involving continuous movement of the three-phase contact line. Uniform GNAs were synthesized by controlled overgrowth of GNRs (~102 nm in length and ~23 nm in diameter; fig. S1) in the presence of CTAC and AgNO3.
The shape evolution from the original GNR to the final GNA is schematically illustrated in Fig. 3A, where four key parameters [the length \( L \) and width \( D \) of the arrow and the length \( l \) and width \( d \) of the four wings] are used to describe the geometric features. With the overgrowth of GNPs, two pyramidal heads with the exposed [111] facets and four truncated [100] facets are grown on the two ends of the nanorods, and this process is accompanied by the extrusion of four plane wings parallel to the [110] planes along the four <110> directions. Time-dependent morphology evolution of the GNAs shows that two small swelling heads were formed on both ends of the GNAs initially and four thin wings in the center gradually appeared, which quickly developed into near-perfect GNAs with enlarged pyramidal heads and wider wings within 5 min (fig. S2). After 4 hours of growth, well-developed GNAs with an aspect ratio \( L/D \) of 2.0 were obtained, which essentially remained unchanged after a prolonged period of time. Examination of the effects of the concentrations of Ag\(^{+}\) ions and CTAC on the formation of GNAs indicates that the presence of CTAC promoted the formation of concave shapes, whereas the presence of Ag\(^{+}\) ions favored the formation of the pyramidal heads with the [111] exposed facets (figs. S3 to S5). It has been documented that the Ag UPD during the growth of Au nanocrystals can lead to selective passivation of the [111] facets and that the presence of CTAC involving the Cl\(^{-}\) ions is beneficial to kinetic growth pathways related to the accelerated reduction rate owing to the higher reduction potential of Au\(^{-}\)-Cl complexes, higher Au\(^{+}\) ion availability, and lower halide binding strength (32). Because a high relative magnitude of deposition rate \( (V_{\text{deposition}}) \) and surface diffusion rate \( (V_{\text{diffusion}}) \) would lead to kinetic growth pathways (40), it may be reasonably proposed that the four-wing shaft resulted from the preferential growth along the four <110> directions under kinetic control induced by a high concentration of CTAC (fig. S6). Therefore, the formation of the unique GNAs consisting of two pyramidal heads and a four-wing shaft could be attributed to kinetic control coupled with selective surface passivation through a delicate combination of appropriate Ag\(^{+}\) and CTAC concentrations. Nevertheless, considering the intrinsic complexity of the gold nanocrystal growth (41), further advanced imaging techniques and thorough theoretical modeling would be required to fully elucidate the growth mechanism.

The geometric parameters of the GNAs can be readily adjusted by controlling the GNR overgrowth process through changing the reactant concentrations in the growth solution (Fig. 3, B to D, table S1, and fig. S7). When the HAuCl\(_4\) concentration was increased, the two pyramidal heads gradually grew larger and closer, whereas the arrow length \( L \) stayed almost constant, leading to an increase in \( D \) and a decrease in \( l \). The absorption spectra of the GNAs are characterized by two local surface plasmonic resonance (LSPR) peaks (Fig. 3E). The decrease in the aspect ratio \( (L/D) \) accompanying gradual overgrowth results in a small red shifting in the transverse mode and a significant blue shifting in the longitudinal mode.

A unique feature of nanocrystals with a concave geometry is that they exhibit the promising potential as building blocks to construct novel interlocked superstructures, which has been demonstrated in several nanocrystal systems, such as octapods (14) and concave cubes (12). The current concave-shaped GNAs are able to form unusual superstructures...
through interlocking between neighboring GNAs (movie S2). In particular, the unique packing and interlocking ability of the distinct GNAs with a concave geometry allows for the shape-directed assembly of sophisticated SCs. A simple bulk solvent evaporation method (42) was used to realize the self-assembly of GNAs into 2D and 3D SCs (fig. S8). Figure 4 shows representative 2D SCs on Si substrates assembled from GNAs (L/D = 2.3) and 1.7 (C). (D) Structural parameters of GNAs plotted as a function of the concentration of HAuCl₄ for the GNA growth. (E) Absorption spectra of GNAs with different aspect ratios. Inset shows the photograph of the solutions containing GNAs. Note that the red and blue arrows indicate the red shift and blue shift of two plasmonic absorption peaks, respectively. a.u., arbitrary unit.

If the GNAs lie on the pyramidal {111} facets with the longitudinal direction oriented horizontally with respect to the substrate, resulting in net-like 2D assemblies with face-to-face contact via two opposite {111} facets of each pyramid. In the Net-I SCs, all the GNAs are oriented along the same direction (Fig. 4, A1 to A4), whereas in the Net-II SCs, the GNAs are oriented in two alternate directions (Fig. 4, B1 to B4). TEM observations of the Net-I SCs suggest that the nanogap size between adjacent GNAs with a face-to-face contact is around 3 nm (fig. S9), which is in good agreement with the thickness of the incompressible organic layer between two neighboring GNAs. Despite the existence of some cracks, the Net-I SCs larger than several square micrometers in area are well ordered, as confirmed by the hexagonal fast Fourier transform (FFT) pattern. The GNAs in Net-I can slip along their glide planes to some extent (fig. S10), thus generating Net-I SCs with tunable lattice parameters. Considering the two limiting configurations (that is, the closest arrangement along the longitudinal and radial directions), the packing efficiency can be varied within 41.1 to 51.3% (fig. S11 and table S2). In contrast, the orthogonal Net-II SCs have a fixed lattice structure with a packing efficiency of ~42.6%, and they usually coexist with Net-I SCs with minor frequencies and smaller areas.

If the GNAs lie on the pyramidal {111} facets with the longitudinal direction oriented slantwise, more densely packed 2D SCs consisting of interlocked GNAs can be obtained. The face-to-face contact between adjacent GNAs via two neighboring {111} facets of each pyramid and the plunge of the pyramidal heads into the concavities of adjacent GNAs lead to the formation of intriguing zipper-like assemblies or Zipper SCs (Fig. 4, C1 to C4), which have an orthogonal lattice structure with a packing efficiency of ~53.0%. Meanwhile, linearly aligned GNAs with face-to-face contact via one {111} facet of each pyramid can be packed regularly through partial insertion of the pyramidal heads into the depressions of adjacent GNAs, leading to the closely packed weave-like superstructures with similar packing efficiencies (fig. S11). The adjacent lines of aligned GNAs can be either parallel for Weave-I SCs (Fig. 4, D1 to D4) or antiparallel for Weave-II SCs (Fig. 4, E1 to E4).

An increase in the concentration of the GNA dispersion from 3 to 12 nM resulted in the formation of ordered multilayer assemblies as the dominant superstructures, as shown in Fig. 5. The regular packing of the monolayers of the Net-I SCs can produce multilayer Net-III SCs with face-to-face contact via all the four {111} facets of each pyramid (Fig. 5, A1 to B4). The close-packed Net-III SCs with a 2D hexagonal structure on the horizontal plane have a 3D monoclinic structure with a high packing efficiency of 60%. Note that the Net-III SCs have varied geometric shapes including planar films (Fig. 5, A1 and A2) and faceted polyhedra (Fig. 5, B1 to B3, and fig. S12), which could be related to the spatially nonuniform fluctuations in solvent evaporation. Besides, another type of 3D SCs was less commonly observed. Similar to the planar packing of linearly aligned GNAs standing slantwise on the substrate for 2D Weave-I SCs, 3D packing of linearly aligned GNAs through face-to-face contact via all the four {111} facets of each pyramid results in 3D Weave-III SCs (Fig. 5, C1 to C4). These SCs with a 2D orthogonal structure on the horizontal plane also adopt a 3D monoclinic structure but have a relatively lower packing efficiency of ~54%.

Therefore, multiple 2D and 3D SCs with unprecedented architectures have been achieved by delicate self-assembly of a single type of geometrically distinct gold nanocrystals. This shape-directed self-assembly may be driven by the entropic forces favoring dense packing and the shape complementarity promoting stable interlocked structures. Although it remains difficult to realize selective formation
of specific 2D or 3D SCs currently because the self-assembly of the competitive superstructures with minor differences in the free energy may be very sensitive to the nonequilibrium evaporation process, we have achieved the preferential formation of certain SCs by adjusting the geometry parameters of GNAs and the assembly conditions (fig. S13). By controlling the aspect ratio (L/D) and the concentration of GNAs, the area fraction of different types of SCs can be adjusted and some types of SCs can be synthesized with a high yield (fig. S14). Generally, 2D SCs were dominant at a lower GNA concentration, whereas 3D SCs were dominant at a higher GNA concentration. Note that the area fraction of Net-III SCs reached ~ 99% when the GNAs with an L/D ratio of 2.0 were used as building blocks with a relatively high nanoparticle concentration, illustrating the high stability of the assembled structures with the highest packing efficiency of 60%. It may be noted that a slow evaporation rate at a relatively high humidity in the vessel of the GNA solutions is essential to the formation of the Net-III SCs with a high yield (fig. S15), indicating that humidity plays an important role in the self-assembly process. Notably, the relative sizes of the pyramidal heads and the concave cavities of the GNAs play a key role in the self-assembly of SCs; in particular, the Zipper SCs do not appear at an L/D ratio of less than 1.8, and 3D SCs are difficult to form at a high L/D ratio of 2.3. Therefore, the loose packing through face-to-face contact and the tight interlocking through plunging the pyramidal heads into the concavities provide plenty of possible packing fashions. The aspect ratio and the GNA concentration played key roles in determining the competitive formation of various types of SCs. In general, GNAs with a lower aspect ratio would promise a larger proportion of the pyramidal heads, favoring the formation of the packing types of SCs, whereas GNAs with a higher aspect ratio would offer more room (concavity) for accommodating arrowheads to form the interlocking connection.

Fig. 4. 2D SCs assembled by GNAs. SEM images (A1, A2, B1, B2, C1, C2, D1, D2, E1, and E2) and geometric models (A3, A4, B3, B4, C3, C4, D3, D4, E3, and E4) of Net-I (A1 to A4), Net-II (B1 to B4), Zipper (C1 to C4), Weave-I (D1 to D4), and Weave-II (E1 to E4) SCs. Insets show the corresponding FFT patterns. The red rhomboids in (A3) represent the unit cell of Net-I SCs with lattice parameters of a and b, and the black dashed lines denote the glide planes. Two Net-I SCs with the limiting conformations are also shown in (A3). Facets lying against the facets of neighboring GNAs are painted in saffron in (A4), (B4), (C4), (D4), and (E4).
The sophisticated 2D and 3D SCs assembled from GNAs represent novel plasmonic nanostructures with structure-dependent field confinement and enhancement. The nanoscale electric field distribution of individual GNAs and their SCs was simulated with finite element method (FEM). Under polarized irradiation along the radial and axial directions of a single GNA, the electrically enhanced position on the surface transferred from the edges to the four wings and two arrow tips, with two simulated extinction peaks matching well with the experiment result (fig. S16). Figure 6 shows the electric field distribution of different SCs, exhibiting patterned plasmonic hot spots generated from strong LSPR coupling among adjacent GNAs. The average normalized electric field intensity $|E|/|E_0|$ was estimated to be 2.9 and 8.6 for the flat 2D Net-I and Net-II SCs, respectively (Fig. 6, A and B). The electric field intensity is much stronger for the Net-II SCs because the arrow tips were closer. Considering the gliding nature of the Net-I SCs, the $|E|/|E_0|$ was calculated to be 7.4 and 3.8 for Net-I-wide and Net-I-narrow, respectively, that is, the one with the shortest distance along the length axis owned the strongest enhancement owing to the immense electric coupling between the tips (fig. S17). As for the densely packed SCs consisting of slanting GNAs, the $|E|/|E_0|$ was calculated to be 2.0, 2.2, 11.3, and 2.8 for Zipper, Weave-I, Weave-II, and bilayer Weave-III, respectively (Fig. 6, C to F). The strongest electric field enhancement for the Weave-II SCs suggests that the enhancement of electric field mainly depends on the spatial arrangement of the tips, edges, and facets rather than the packing efficiency, indicating flexibility and complexity in controlling over the hot spots.

The obtained planar SCs may be considered as metasurfaces with unique nanoscale light-matter interactions. Note that the simulated absorption, scattering, and extinction spectra of monolayer SCs show a clear structure dependence of optical properties; in particular, the Zipper SCs display two extinction peaks at wavelengths of 610 and 790 nm, indicating complex coupling and hybridization of plasmon resonance modes caused by the symmetry breaking in the novel packing structure (fig. S18 and note S1). The GNA SCs exhibit pronounced polarization-dependent scattering properties (fig. S19 and note S2). For the planar Net-I SCs, the main scattering peak exhibits a red shift as the polarization changes from 0° to 90°, and the difference between the scattering maxima ($\Delta \lambda$) can be systematically tuned from ~250 to ~190 nm by adjusting the configuration of the Net-I SCs. The $\Delta \lambda$ values are much larger than the reported $\Delta \lambda$ value (~10 nm) for the superlattices consisting of gold nanoctahedra (43). Furthermore, the Zipper structure exhibits two well-resolved SPR peaks in the scattering spectra, and both the position and relative intensity of the peaks show marked changes upon changing the polarization. The polarization-dependent properties may lead to several applications, such as polarization-dependent optical metamaterials, plasmonic color generation, and sensing (43, 44).

On the other hand, it has been documented that the nanogaps among plasmonic nanoparticles are favorable for surface-enhanced Raman scattering (SERS) enhancement; in particular, the SERS enhancement is generally increased with decreasing the nanogap size from 10 to ~2 nm or smaller (45–47). For example, the effects of the nanogap size and shape on SERS signals have been extensively investigated in a variety of plasmonic systems, such as diagonally aligned Au nano-blocks (48), square lattices of Ag nanodomes (49), and Au nanocube-nanosphere dimers (50). Therefore, the GNA SCs with plenty of nanogaps (~3 nm) between adjacent nanoarrows with a face-to-face contact, as well as many tips, edges, facets, and interstices among them, would be promising SERS substrates. Considering the availability of large-area assembly, preliminary investigation on the SERS of the Net-I SCs was performed, revealing an enhancement factor around 15 times higher than that for the monolayer SCs of GNRs (fig. S20 and note S3). In addition, a comparative investigation of the SERS performance of Net-I
and Zipper was carried out, which suggests that Net-I shows a 2.9-fold higher Raman intensity than Zipper, in good agreement with the average normalized electric field intensity (fig. S21 and note S3). This result indicates that despite the similar nanogap sizes between two GNAs with a face-to-face contact, the assembled structures with a larger face-to-face contact area would bring about more hot spots and thus a higher SERS enhancement. Much better SERS performance may be expected for Net-II and Weave-II, if their large-area assembly can be realized because they have considerably higher electric field intensity.

**DISCUSSION**

In summary, we have achieved controlled growth of uniform GNAs with a fascinating concave geometry and succeeded in the shape-directed self-assembly of these novel building blocks into diverse non-close-packed SCs with unprecedented architectures. The formation of the unusual GNAs may be ascribed to kinetic control coupled with selective surface passivation under the delicately controlled growth conditions. This approach highlights the key effects of shape, especially the concave geometry, in determining nanoparticle self-assembly through the specific packing and interlocking ability. Even more complex superstructures or reconfigurable architectured materials may be assembled from these arrow-like building blocks, if elaborate adjustment of their structural parameters is achieved and other assembly strategies, such as surface modifications (12, 13, 17, 18), shape-complementary particles (12, 22), and external templates (24), are introduced. Our numerical simulation results show that the diverse GNA SCs with high porosity and structural stability exhibit exotic patterns of electromagnetic field confinement, indicating their potential applications as promising plasmonic metamaterials. This work may open new avenues toward the controlled growth of nanocrystals with unconventional concave geometries and the tunable self-assembly of nanoparticle superstructures with increased complexity and novel functionality.

**MATERIALS AND METHODS**

**Seed-mediated synthesis of GNRs**

The synthesis of GNRs was carried out using a seed-mediated method following a previously reported procedure (51) with minor modification. The seed solution was prepared by adding an aqueous HAuCl₄ solution (0.25 ml, 10 mM) into a cetyltrimethylammonium bromide (CTAB) solution (10 ml, 0.1 M) in a glass vessel. A freshly prepared ice-cold NaBH₄ (0.6 ml, 10 mM) was then injected into the mixture under vigorous stirring. After 10 s of stirring, the resultant seed solution was aged for 30 min at 27°C before use. For the preparation of the growth solution, 100 ml of sodium oleate (NaOL) solution (20 mM) was mixed with 74 ml of CTAB solution (0.1 M) and 26 ml of water in a beaker flask under mild stirring and thermostated at 30°C in a water bath, which was followed by injection of 3.84 ml of AgNO₃ (10 mM). The mixture was kept undisturbed for 15 min at 30°C, and an aqueous HAuCl₄ solution (10 ml, 10 mM) was then added. After 90 min of undisturbed standing, the solution became colorless, and 1.2 ml of HCl (37 weight %, ~12.1 M) was introduced. After another 15 min of undisturbed stirring, an aqueous ascorbic acid (AA) solution (1.2 ml, 20 mM) was added, and the mixture was vigorously stirred for 30 s. Finally, the growth of GNAs was started by adding 0.08 ml of the seed solution into the growth solution. The reaction mixture was left undisturbed overnight at 27°C, resulting in the formation of a GNR dispersion with a GNR particle concentration of approximately 0.6 nM, which was estimated by the Lambert-Beer law with a molar extinction coefficient of 5.5×10⁹ M⁻¹ cm⁻¹ for GNRs (52). The resultant GNR dispersion was centrifuged, and the GNAs were redispersed in 1 mM CTAB solution for further overgrowth.

**Overgrowth of GNRs into GNAs**

The GNAs were synthesized via overgrowth of the prepared GNRs in the presence of CTAC, Ag⁺, HAuCl₄, and AA. Briefly, a certain volume of 10 mM HAuCl₄ solution (typically, 3 ml) was first added into a CTAC solution (100 ml, 0.1 M) under stirring. After the sequential addition of AgNO₃ (1.5 ml, 10 mM) and HCl (2 ml, 1 M), a certain volume of 100 mM AA solution (typically, 1.5 ml) was added, and the solution was vigorously stirred for 30 s. Finally, 5 ml of 20-fold concentrated GNR seed solution was injected into the growth solution. The resultant mixture was stirred for 10 s and left undisturbed for 4 hours at 27°C for the growth of GNAs. The final products were isolated by centrifugation and redispersed in 1 mM CTAB solution for the following assembly. Typically, a GNA dispersion (~3 nM) was obtained through 5-fold concentration, and a GNA dispersion (~12 nM) was obtained through
20-fold concentration. The aspect ratio of the obtained GNAs can be adjusted by changing the concentrations of HAuCl4 and AA in the growth solutions (table S1).

**Self-assembly of GNAs into SCs**

The controlled self-assembly of GNAs was realized by using a bulk solution evaporation method, which was developed previously in our laboratory (42). For a typical self-assembly process, a clean Si square wafer (~4 mm × 4 mm × 0.5 mm) was flatly placed at the bottom of one vessel (~6.5 mm in inner diameter) of a plastic 96-well tissue culture plate. Subsequently, 0.2 ml of GNA dispersion with a certain concentration was injected to the vessel. The vessel was covered by a piece of filter paper and the lid of the well to slow down solvent evaporation. The 96-well tissue culture plate was placed in an incubator and kept undisturbed for about 7 days at 25°C until the completion of evaporation. Then, the dry Si plates with GNA SCs were immersed successively in a Na2S2O3 solution (100 mM) for 30 min and water for 1 min to remove the residual Ag impurities and excessive surfactants.

**Electromagnetic simulation**

We used FEM to simulate the optical response of the individual GNAs and the GNA SCs, with the nanogap size between adjacent GNAs set as 3 nm. The permittivity of gold was taken from the example data (53), and a minimum mesh size of 0.1 nm was used to refine the tip area of the GNAs. In all simulations, the plane wave normally interacting with these arrow structures was used. To get unpolarized results, we performed two separate simulations, with the incident electric field polarized along the x axis and y axis, respectively. Then, the unpolarized electric field was extracted with 

$$E_{\text{unpolarized}} = \frac{1}{2}E_x + \frac{1}{2}E_y.$$

All electric fields represented in this study have been normalized to the incident electric field.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/10/e1701183/DC1

**REFERENCES AND NOTES**


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