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Journal:	Journal of the American Chemical Society			
Manuscript ID	ja-2023-00503g.R2			
Manuscript Type:	Article			
Date Submitted by the Author:	n/a			
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Tuning Geometric Chirality in Metallic and Hybrid Nanostructures by Controlled Nanoscale Crystal Symmetry Breaking

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ABSTRACT: Understanding and controlling chirality in inorganic crystalline materials at the nanoscale is crucial in elucidating fundamental chirality-dependent physical and chemical processes as well as advancing new technological prospects, but significant challenges remain due to the lack of materials control. Here we have developed a facile and general bottom-up synthetic strategy for achieving chiral plasmonic Au nanostructures, including nanocubes and nanorods with fine chirality control. The underlying chiral mechanism enabled by the chiral boundary morphology is substantiated by theoretical modelling and finite element method simulation. Because of the robustness of induced handedness and their small size, these as-synthesized chiral nanostructures can be further employed as building blocks towards formation of complex chiral nanostructures. We have demonstrated a new class of chiral hybrid metal-semiconductor nanostructures that can allow integration of chirality with other properties and functionalities. All these together have paved the way to engineer nanoscale inorganic chirality and thus study various emerging chirality entangled effects with practical technological applications.

INTRODUCTION

Chirality (or handedness) represents a pervasive and fundamental geometric character of an object whose space group contains no improper symmetry operations. While organic chiral molecules containing cyclic or dihedral point groups and their induced chirality-dependent phenomena have been extensively studied¹, exploration of inorganic chiral objects has been limited until recently due to their structural complexity with involvement of many atoms as well as lack of understanding of underlying chiral mechanisms. Nevertheless, if chirality of inorganic objects can be induced or even controlled, it should open up many foreseeable opportunities for emerging exotic physics and applications. For example, merging chirality with metal nanostructures could potentially induce chiral plasmons with tunable and enhanced chirality and the emerging chiral vortical effects (e.g., negative refractive materials)²⁻⁵. A few mechanisms have been proposed to induce inorganic chirality. For example, there exist a small group of inorganic crystals such as quartz, mercury sulfide and tellurium that can possess a chiral atomic lattice along certain crystallographic axes, leading to intrinsic handedness^{6,7}. Although intrinsic lattice handedness is absent in achiral inorganic metals

and semiconductors, extrinsic handedness can be induced by either electromagnetic coupling or interparticle assembly via chiral templates⁸⁻¹². Nevertheless, such extrinsic handedness is in general not robust and has limited applications. From the crystallographic viewpoint, the kinked site of step edges can act like a chiral center in an organic molecule to break mirror symmetry in an inorganic achiral lattice, rendering two high Miller index crystallographic planes enantiomorphous (see more details in Supporting Information). Fig. S1 shows the unit sphere of a facecenter cubic (fcc) lattice that can be divided to different regions designated by two distinct colors, representing two sets of left- and right- handed chiral planes, respectively. Although the racemic mixture of chiral high Miller index planes should not induce handedness in a bulk crystal, when they are exposed and controlled on the surface of a crystal the enantiomeric excess favoring chiral facets with definite handedness can be induced by chiral symmetry breaking, leading to the formation of chiral boundary morphology and thus extrinsic chirality of an achiral crystal. Importantly, a few theoretical studies have shown enantiospecific interactions between chiral molecular adsorbates and inorganic chiral facets, which has also been

experimentally confirmed by scanning tunneling microscopy¹³⁻¹⁶. This can potentially offer a general and effective pathway to enable symmetry breaking of crystallographic chiral facets towards new chiral materials design and enantioselective control of inorganic chiral nanostructures.



Figure 1. Schematic of controlled bottom-up growth of chiral inorganic materials and their enabled chiral hybrid nanostructures. Red and blue represent high Miller index chiral *S*- and *R*- crystallographic planes, respectively. Small chiral organic molecules are employed to break structural symmetry and to enable enantiomerically pure chiral boundary morphology to induce crystallographic handedness in inorganic materials. The robustness of chiral boundary morphology of inorganic materials can allow integration of multiple components (yellow block) by the formation of hybrid nanostructures, possessing interfacial chirality coupling (green arrows).

RESULTS AND DISCUSSION

Fig. 1 shows schematics of how to employ small organic chiral molecules to preferentially occupy enantioselective chiral facets during the synthesis of achiral inorganic nanostructures. This enantioselective interaction leads to a biased kinetic growth rate favoring crystallographic overgrowth with opposite handedness, thus dictating the prevailing coverage of one handedness of chiral facets on the surface to induce robust chiral boundary morphology of an inorganic nanostructure (see more details in Supporting Information). One significance of such chiral inorganic nanostructures is to serve as building blocks to allow creation of novel chiral hybrid nanostructures through interfacial epitaxial and non-epitaxial growth to form various chirality coupling at the nanoscale¹⁷. We choose Au nanostructures as an example to demonstrate the proposed strategy in Fig. 1 based on a few considerations: First, the Au possesses an achiral fcc lattice and synthesis of achiral Au nanostructures with versatile controls have been achieved, which make Au an excellent testbed for understanding role of chiral morphology in an achiral crystal¹⁸⁻²⁰. It is worth noting that a gigantic chiral Au structures with a size of a few hundred nanometers have been achieved recently²¹⁻²³, however small sized chiral Au nanocrystals with robust

chirality that can be potentially utilized as chiral functional building blocks have been absent, which is the impetus of our current work; Second, Au nanostructures have been demonstrated to possess strong localized surface plasmon resonance (LSPR), which is uniquely determined by the size and morphology of nanostructures²⁴. Therefore, chirality of crystalline boundary morphology should have a direct implication in the LSPR due to delocalization of plasmonic electrons, which plays an important role in the emerging field of chiral plasmonics and in understanding the interplay between chirality and plasmonics; Last but not the least, it has been demonstrated that functional hybrid nanostructures consisting of metal and semiconductor subunits can be synthesized by non-epitaxial approach with enhanced and tunable light-matter coupling^{17,25,26}. Consequently, if the standalone chiral Au nanostructures can be achieved with robust chirality, chirality of metal subunits might be imprinted to semiconductor subunits to create unique chiral hybrid nanostructures with exotic functionality and properties. In following the proposed synthetic strategy outlined in Fig. 1, we start with Au nanostructures with well-defined achiral morphology (e.g., nanocubes, NCs or nanorods, NRs) as seeds, followed by surface treatment with chiral molecules (e.g., L-/D- cysteine). After the removal of excessive chiral molecules from the surface treatment, overgrowth of chiral Au nanostructures is initiated and kinetically controlled by a slow injection of an Au precursor with a mild reducing agent such as ascorbic acid. The notation of handedness of as-synthesized chiral Au nanostructures is described in the Supporting Information.

Chiral Au Nanocubes. Fig. 2a shows a typical transmission electron microscopy (TEM) image of chiral S-Au NCs with average size of 50 nm by using Lcysteine molecules, which were grown from achiral seed NCs shown in Fig. S2. A large-scale scanning electron microscopy (SEM) image is presented in Fig. S3 to highlight the yield of as-synthesized chiral Au NCs without any post-processing of samples. Different from achiral Au NCs possessing uniform morphology with flat surface, high-resolution TEM image of a single chiral NC as presented in Fig. 2b show inhomogeneous identities on the surface with a few highlighted by red arrows. Importantly, the circular dichroism (CD) measurement of as-synthesized S-Au chiral NCs in Fig. 2a shows the presence of a clear bisignate spectra feature (red data points in Fig. 2c), i.e., a positive peak at 532 nm and a negative peak at 592 nm. For the chiral *R*-Au NCs that are synthesized by using D-cysteine molecules while other synthetic conditions remain the same, their corresponding CD spectrum is also presented in Fig. 2c (blue data points) for comparison, in which the CD peaks occur at the same wavelengths but with opposite sign. For both *R*- and *S*- chiral Au NCs,

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their optical extinction spectra are almost identical (Fig. 2d), similar to the case of molecular enantiomers.



Figure 2. Synthesis and characterizations of chiral Au NCs. (a) Typical large-scale TEM image of chiral *S*-Au NCs. Scale bar, 100 nm. (b) Typical TEM image of individual *S*-Au NC. A few inhomogeneous features on the surface are highlighted by red arrow. Scale bar, 20 nm. (c) Experimental CD spectra of *S*- (red) and *R*- (blue) Au NCs. (d) Experimental extinction spectra of *S*- (red) and *R*- (blue) Au NCs.

A few mechanisms have been proposed to account plasmonic nanoparticles, for chiral including electromagnetic interaction between chiral molecules and plasmonic resonance on the surface and formation of chiral oligomers^{9,10,27}. We have performed one control experiment by passivating the surface of achiral Au NCs with chiral molecules but without overgrowth, however no detectable CD is found from such samples. This is also consistent with theoretical study that for the high symmetric plasmonic nanostructure like nanosphere or NCs, the chirality induced by electromagnetic coupling between embedded/coated chiral molecules and nanostructures could be cancelled out, and the effect of chiral molecules in this scenario is negligible⁸. Furthermore, although chiral-templatemediated inter-particle interactions in a plasmonic oligomer has been observed in literatures²⁸, such chiral oligomers have been absent in our current study based on TEM and SEM characterizations, and the concentration of chiral molecules utilized in our chiral synthesis is much smaller than those required for the formation of chiral oligomers.

In order to understand the inhomogeneous morphological features as highlighted in Figs. 2a and 2b and to elucidate the origin of their optical characteristics shown in Figs. 2c and 2d, we have performed a thorough angle-dependent high-resolution SEM characterization of single *S*-Au NC with three examples presented in Fig. 3a (and more in Fig. S4). A few structural features can be immediately

identified: First, although the overall shape of chiral Au NC remains cubic, its surface becomes concave after the overgrowth, which is consistent with TEM observation in Fig. 2b and can be attributed to the edge- and cornerfavored growth under the kinetically controlled condition²⁹. The fact of formation of concave surface further suggests the exposure of high Miller index facets during the growth^{20,30}. Second, the boundary edges of chiral Au NC are twisted as is evident from the twisting sites highlighted by the four small green circles in Fig.3a. From the crystallographic viewpoint (Fig. S1 and Fig. 1), the surface of a regular achiral concave Au NC can be modeled as a racemate of chiral high Miller index facets, which is schematically shown in the middle of Fig.3b. In the presence of chiral molecules like L-cysteine, the preferential occupancy of chiral molecules onto specific chiral facets (e.g., R-facets for Lcysteine) inhibits their successive outward growth and thus leads to preferential kinetic growth of chiral facets with opposite handedness. As a result, the predominant coverage of chiral facets with exclusive handedness is achieved on the surface of a chiral NC, resulting in chiral morphology with feature of twisting boundary edges, as schematically shown in Fig. 3b. The small green filled circles on both the right and left NCs in Fig. 3b highlight the twisting sites on the edge, which are formed by simply considering the prevailing overgrowth of one type of chiral facets from a concave surface. Based on the proposed mechanism illustrated in Fig. 3b, we have constructed a structural model (see Supporting Information) and compared it with SEM images acquired at the different tilting and rotating angles (Fig. 3a), which shows excellent agreement with experimental results and can elucidate chiral characteristics of morphology as manifested in the SEM characterization. It is worth noting that due to their small size, direct structural differentiation between two different handedness, S- and R- Au NCs can become subtle. However, the twisting boundary edges observed in Fig. 3 can often offer a useful means to discriminate two different handedness by the electron microscopy imaging (Figure S5), with one example presented in Figure S6 to compare images of S- and R-Au NCs. More importantly, we have utilized the constructed models presented in Fig. 3a to compute optical properties of chiral Au NCs by using finite element method (FEM) simulation³¹, and presented both theoretical CD and extinction spectra in Fig. 3d, which also shows excellent agreement with experimental data in Figs. 2c and 2d. This offers a sanity check of our model and assignment, and supports the proposed CD mechanism of assynthesized chiral Au NCs. Furthermore, we would like to emphasize that our as-synthesized chiral Au NCs represent a different chiral entity from the existing works beyond just size difference. For example, our chiral Au NCs possess concave morphology, while more complex convex-like shape has been demonstrated in much larger chiral cubic Au structures²¹. This can be

attributed to different growth kinetics of chiral Au NCs (see Supporting Information). Additionally, although same chiral molecules (L-cysteine) were employed to induce chirality in the gigantic Au NCs, the *R*-facets were found to exist on their surfaces and contribute to the handedness²¹, while the chiral *S*-facets are the dominant chiral high Miller index facets in our current work. A thorough understanding of how chiral organic molecules play a role in the growth of inorganic chiral nanostructures at the different length scale and different growth conditions/dynamics will require more substantial work, and should offer invaluable insights and controls to engineer inorganic chirality.

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Figure 3. Angle-dependent high-resolution SEM characterizations and modeling of chiral Au NCs. (a) (Top) SEM images of single *S*-Au NC under three different viewing angles. Scale bar, 20 nm. (Bottom) Corresponding structural model. (b) Schematic showing the formation of *S*- (left) and *R*- (right) chiral NCs facilitated by the prevailing chiral high Miller index facets on the surface due to chiral symmetry breaking from an achiral NC (middle). Small green filled circles as guide to the eye highlight the twisted edges on the boundary. (c) & (d) Computed CD and extinction spectra of *S*- (red) and *R*- (blue) chiral Au NCs by using the structural model presented in (A), respectively.

Chiral Au Nanorods. We would like to emphasize that our model and understanding of the CD origin in a

chiral Au NCs, which is based on the symmetry breaking of chiral high Miller index facets on the surface, is general and can be immediately applied to other nanostructures to induce and control similar extrinsic handedness. Fig. 4 presents another example of chiral Au NRs by following a similar mechanism and growth process. As compared with Au NCs, Au NRs are more complicated from the structural viewpoint, but possess more tunability to engineer their properties and functionalities. For example, a few structural parameters including the aspect ratio (AR) and the surface facets on both sides and ends of a NR often play a crucial role in determining various physical and chemical properties and functionalities.

We choose achiral Au NRs that are synthesized by using the well-known seed-mediated growth method as the starting structures³², and then perform overgrowth after treatment using chiral molecules to control the handedness of overgrown Au NRs. Typically, a regular achiral NR can be modeled as a four-sided elongated rhombic dodecahedron (middle in Fig. 4a)³³⁻³⁶, whose side surfaces manifest achiral low index facets (110), while the high surface curvature at the apexes often makes chiral high Miller index facets (red and blue regions) more accessible at both ends. This can provide an invaluable opportunity to induce intriguing chirality of NRs by controlling the prevalence of chiral high Miller index facets at the end of NRs, as schematically shown in Fig. 4a. Figure 4b shows one typical TEM image of overgrown chiral Au NRs assisted by the chiral L- cysteine molecules in the growth. Both high-resolution TEM (Fig. 4c) and SEM characterizations (Fig. S7) have confirmed that our assynthesized chiral Au NR remains an overall four-sided elongated rhombic dodecahedron but with concave morphology in the boundary facets. The atomic image and its Fast Fourier Transform (FFT) pattern show the undistorted (110) facets on the sides, which is evident by typical FFT pattern along Au [110] direction and indexing the $(\overline{1}11)$ and (002) planes in Fig. 4c. The concave morphology can be clearly observed at both ends of NRs, that is similar to the concave characteristics and chiral high Miller index facets of chiral NCs in Fig. 2. Furthermore, we have performed angle-dependent TEM characterization of single chiral NR, confirming straight and undistorted sides (Fig. S8).

We have found that the as-synthesized chiral Au NRs manifest CD features in the visible regime. In particular, Fig. 4d (red data points) shows experimental CD (left) and extinction (right) spectra of the *S*-Au NRs from the Fig.4b which is grown by using L-cysteine molecules. For comparison, the optical data acquired from the *R*-Au NRs that possess the same dimensions but were grown using D-cysteine instead are also presented (blue data points). Both *R*- and *S*- chiral Au NRs exhibit almost identical optical extinction features, and two absorption peaks at 525 nm and 660 nm can be



Figure 4. Synthesis, characterizations and modeling of chiral Au NRs. (a) Schematic showing that by breaking the symmetry of enantiomeric high Miller index facets (red and blue colors represent chiral crystallographic *S*- and *R*- facets, respectively) at the ends of achiral NR (middle), chiral *S*- (left) and *R*- (right) NRs can be formed by the prevailing chiral facets at the ends, while its elongated side consists of symmetric low Miller index facets (gray color) as those of achiral NR. (b) Typical large-scale TEM image of chiral *S*-Au NRs. Scale bar, 100 nm. (c) (Left) High-resolution TEM image of single chiral *S*-Au NR. (Middle top) Atomic resolved TEM image of the green region on the left image. Scale bar, 2 nm. (Middle bottom) the FFT pattern of the side of NRs. The side facets of the chiral NR are identified by both imaging and indexing the FFT pattern. (Right) Constructed structural model of chiral *S*-NR. (d) Experimental CD (left) and extinction (right) spectra of chiral *S*- (red) and *R*- (blue) Au NRs. (e) Computed CD (left) and extinction (right) spectra of chiral *S*- (red) and *R*- (blue) Au NRs by using the structural model in (C).

attributed to the transverse and longitudinal LSPR modes of the Au NRs, respectively³⁷. Meanwhile, their CD spectra show the opposite signs with peaks at 530 nm and 660 nm.

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In order to elucidate the underlying mechanism of observed chirality in the Au NRs, we have performed two control experiments. First, we have removed surface ligand molecules after growth of chiral Au NRs by a ligand exchange process with achiral oleylamine molecules, and redispersed the chiral Au NRs in toluene, and we have observed that the CD features remain almost unchanged. This observation excludes the role of possible residue chiral molecules on the surface^{38,39}. Second, we have modified chiral overgrowth conditions (see Supporting Information) and coated additional Au layers onto chiral Au NRs by binary surfactant mixture using а of cetyltrimethylammonium chloride and sodium oleate (Fig. S9). This modified overgrowth condition led to an even morphology of NRs, and those inhomogeneous structural features that are originally observed from the chiral Au NRs disappear (Fig. 4c and Fig. S7). Correspondingly, the CD features measured after this second overgrowth almost completely disappear. This control experiment unambiguously suggests that our observed CD in Fig. 4d originates from the boundary morphology itself, rather than other mechanisms. Similar to the CD mechanism observed in chiral Au NCs that is attributed to the existence of prevailing chiral high Miller index facets on the surface, we propose that the prevailing chiral high Miller index facets exist on both ends of the chiral Au NRs as schematically shown in Fig. 4a. The exposure of chiral high Miller index facets at the ends of NRs originates from the kinetically controlled overgrowth reaction, and the adsorption of chiral molecules onto enantioselected chiral high Miller index facets breaks the symmetry and thus promotes the formation of each enantiomorph dependent upon the molecular chirality. Based on this proposed mechanism, a structural model of a chiral Au NR is constructed (see Supporting Information) and presented in Fig.4c to compare with its corresponding TEM image, showing an excellent agreement. More importantly, we have computed the CD and extinction spectra by using the structural model in Fig. 4c, and presented the results in Fig. 4e. The excellent agreement between our experimental (Fig. 4d) and simulation (Fig. 4e) results has validated our proposed CD mechanism as well as our structural model in Fig. 4c.

Understanding and Tuning Chiroptical Response of Au Nanorods. Our experimental observations and proposed mechanism of induced chirality in both Au NCs and NRs immediately suggest that such nanoscale chirality can be further engineered by designing and tailoring their dimensions and boundary morphology. Fig. 5 highlights two examples of such chirality control.



Figure 5. The dependence of chiroptical response of chiral Au NRs on the AR and the apex protrusions. (a) & (b) Evolution of peak wavelengths in CD and extinction spectra with the AR, respectively. Both transverse (green spheres) and longitudinal peaks (orange spheres) are presented and compared. The green and orange lines are data from simulation for transverse and longitudinal peaks, respectively. (c) & (d) Evolution of peak wavelengths in CD and extinction spectra with the average number of protrusion features at the ends of chiral NRs, respectively. Both transverse (green spheres) and longitudinal peaks are presented and compared. The cyan upper and down triangles are simulation data for longitudinal and transverse peaks, respectively. The experimental 1σ uncertainty of the AR is determined by counting more than 500 nanostructures from TEM images of each sample. The experimental uncertainty of peak wavelength is estimated by the Gaussian peak fit error.

For regular achiral Au NRs, their optical properties have been demonstrated to be dependent on the AR⁴⁰. By using our proposed CD mechanism and model of chiral Au NRs in Fig. 4, we have evaluated theoretically the evolution of both CD and extinction spectra with the AR of chiral Au NRs while keeping the other structural parameters the same, and we present the results in Figure S10. Experimentally we have achieved chiral Au NRs with different AR but similar width of 18.3 ± 0.5 nm (Fig. S11), and we have measured their CD and extinction spectra with results presented in Figure S12. It can be seen that although all samples with different AR show similar characteristics in both CD and extinction spectra and both transverse and longitudinal LSPR modes are observed, the longitudinal mode in both CD and extinction spectra manifests strong dependence on the AR but the transverse mode does not. In order to compare experimental with computational results, we have extracted peak wavelengths of both transverse and longitudinal LSPR modes from the CD and extinction spectra, and summarized their results in Figs. 5a and 5b, respectively. It can be clearly seen that the variation tendency seen in our experimental results agrees very

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well with the theoretical prediction, and both the CD and extinction wavelengths of the longitudinal mode show strong dependence on the AR, while the corresponding peak wavelength of the transverse mode remains almost unchanged, as it is mainly determined by the width of chiral Au NRs.

Our observed CD of chiral Au NRs originates from the prevailing chiral facets exposed at the ends of chiral NRs, suggesting that if such chiral facets (and thus the end morphology) can be tailored it should offer an important way to finely tune chiroptical response and enhance its induced chirality. Indeed, by employing a layer-by-layer overgrowth process onto the starting chiral Au NRs, we have found that the boundary morphology at both ends of NRs evolves from a simple chiral concave rhombic dodecahedron (Fig. 4) to a more intricate shape with multiple protrusions at the end, and the average number of such structural protrusions can be controlled from single protrusion to a bone-shaped morphology with more than six protrusions (Fig. S13). The appearance of protrusions can be understood by the kinetically controlled overgrowth condition, in which the overgrowth at corners is favored over facets. We have performed optical measurements on a series of samples with different numbers of protrusions, and summarized the results in Figs. S14a and S14b. Based on the morphologies of protrusion structures, we have also constructed corresponding models (Fig. S13) and computed their chiroptical responses to account for the effect of such morphological protrusions (Figs. S14c and S14d). In order to compare experimental with theoretical results and to validate the underlying CD origin and model, we have acquired peak wavelengths from experimental and simulated CD and extinction spectra, and summarized results in Figs. 5c and 5d. It can be seen that both the CD and extinction spectra of resultant chiral Au NRs with protrusions vary consistently with total number of protrusions at the ends, which can be fully rationalized by our modeling. Our work has demonstrated for the first time that the chiral mechanism based on chiral high Miller index facets can be applied to NRs to induce chirality, and to further tailor corresponding chiroptical response at the nanoscale by combining with various structural controls. Thus far, the consistency between our experimental results and theoretical computations and modeling for all different chiral Au NCs and NRs has validated our proposed chiral mechanism in this important class of plasmonic chiral metal nanostructures, offering a general guideline to further tailor CD characteristics of chiral nanostructures from the bottom-up.

Chiralhybridmetal-semiconductornanostructures.It is worth noting that different fromother mechanisms for inducing chirality in plasmonicnanostructures by either electromagnetic coupling or

assembly, the boundary morphology induced handedness of metal nanostructures has been demonstrated in Fig. 5 to be very robust with various controls, thus offering a viable bottom-up chiral materials platform for developing more complex and functional chiral hybrid nanostructures that can potentially integrate different functionalities within a single nanoscale entity to enable synergistic couplings (Fig. 1), and to explore the emerging chiralitydependent physics and chemistry. For example, exotic nanoscale resonant plasmon-exciton coupling has been achieved in achiral hybrid metal-semiconductor nanostructures^{25,26,41}. If similar hybrid nanostructures can be achieved with chiral plasmonic nanostructures, like the chiral Au NCs and NRs from our current work, chirality should provide a new degree of freedom to control nanoscale spin or enantioselective photocatalysis by a chiral local plasmonic field. Fig. 6 demonstrates the feasibility to develop a new class of chiral hybrid nanostructures and to investigate the evolution of structural and optical characteristics in such hybrid nanostructures. We start with chiral S-Au NRs with bone-shaped end morphologies that retain strong CD (Fig. S13a). A plasmonic Ag shell is first grown onto these chiral Au NRs, followed by the chemical conversion of the metal Ag shell to semiconductor Ag₂S and CdS shells, while maintaining the chiral Au core NRs unchanged during the whole multiple-step process. Fig. 6a and Fig. S15 show the step-by-step structural and compositional evolution characterized by TEM imaging, with a schematic model, and the corresponding variation of the Ag shell while the bone-shaped Au NRs remain intact and visible in the TEM images. The subsequent chemical conversions from the metal Ag to dielectric semiconductor shells (both Ag₂S and CdS) do not alter either the overall cuboid morphology or the central bone-shaped Au core, highlighting the robustness of as-synthesized chiral Au NRs.

We have studied the evolution of CD characteristics (Fig. S15), and compared the corresponding dimensionless dissymmetry factor (g-factor) in Fig. 6b. There are a few important observations that can be immediately identified from Fig. 6b: First and foremost, the hybrid Au-Ag₂S and Au-CdS nanostructures manifest strong CD that originates from the chiral Au core NRs. This observation is consistent with our TEM result confirming that chiral Au NRs remain intact even after multiple overgrowth and harsh chemical conversion processes. This again can be attributed to the robust chirality mechanism by chiral boundary morphology in Fig. 1; Second, the CD of the Au-Ag coreshell NRs almost disappears after overgrowth of the Ag shell, but is recovered once the Ag shell is converted to the semiconductor Ag₂S shell in the Au-Ag₂S hybrid NRs. The revival of CD features in the Au-Ag₂S hybrid NRs suggest that the chirality of Au NRs is sustained



Figure 6. Development and characterization of chiral hybrid nanostructures. (a) Step-by-step chiral structural evolution (top to bottom in figure) from chiral metal Au NRs with bone-shape morphology, to Au-Ag core-shell, to Au-Ag₂S and to Au-CdS metal-semiconductor core-shell NRs by chemical conversion. For every step, solution in a glass vial showing good sample dispersion and color (left), TEM image of individual nanostructure with scale bar of 20 nm (middle) and its corresponding model (right) are presented. (b) Experimental dissymmetry g- factor measured at each step. Purple, pink, gray and yellow data curves were acquired from the Au, Au-Ag, Au-Ag₂S and Au-CdS NRs, respectively. For comparison and clarity purpose, the curves of the Au-Ag, Au-Ag₂S and Au-CdS NRs are vertically shifted by -0.006, -0.0105 and -0.0155, respectively.

in the process, however the disappearance of CD in the Au-Ag core-shell NRs can be attributed to the fact that both Au and Ag are conductive and the overall morphology of the Au-Ag core-shell NRs becomes even, and the plasmonic electrons are delocalized on the surface of entire core-shell NRs. As a result, the effect of the chiral boundary morphology of Au NRs becomes negligible to the delocalized plasmonic electrons; Lastly, although the CD features are recovered in the hybrid Au-Ag₂S and Au-CdS metal-semiconductor NRs, both the CD peak wavelengths and intensities are varied as compared with the starting chiral Au NRs. Qualitatively, such variation can be attributed to the difference in the dielectric constant of semiconductor shell in the hybrid nanostructures. A more thorough and quantitative comparison is currently under investigation and is beyond the scope of current work.

CONCLUSIONS

We have developed a facile synthetic method to induce and engineer chiroptical response of small-sized plasmonic Au NCs and NRs from the bottom-up, having an achiral crystallographic lattice. Both experimental and theoretical results have suggested that the observed chirality originates from the nanoscale chiral boundary morphology induced by the broken symmetry of chiral high Miller index facets and is very robust. Because of their small size and robustness of chirality, these as-synthesized nanoscale chiral plasmonic structures can serve as chiral functional building blocks. We have demonstrated a new class of chiral hybrid nanostructures that can integrate multifunctionalities, including chirality, plasmons and excitons at the nanoscale. Our current work opens up a few emerging research avenues. For example, although we have utilized Au as an example, the chiral mechanism based on broken symmetry of chiral high Miller index facets should be general and be readily applied to other achiral inorganic metals. As compared with existing mechanisms for inducing chirality at the nanoscale, chiral boundary morphology in inorganic nanocrystals should offer a robust mechanism for preserving CD characteristics for many practical applications with unique tunability, including enantioselective catalysis and chiral plasmonic chemistry. For example, by tuning structural parameter such as the AR, the chiroptical response of chiral NRs can be finely tailored to match different energy landscape in a chemical reaction, while the local chiral

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plasmonic field can be significantly enhanced in a chiral NR with controllable apex protrusions due to its induced large local curvature to facilitate asymmetric reactions³. Additional importantly, the availability of hybrid chiral metal-semiconductor nanostructures as demonstrated in our work should offer a new and unique pathway to study various entangled chirality effects, including chirality induced spin selectivity and chiral hot electrons at the nanoscale^{42,43}.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxx.

Synthesis, simulation and characterization details, Notes on hardness notation of chiral boundary, supporting TEM, SEM images and CD data (PDF)

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ACKNOWLEDGEMENTS

Work at UMD was supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Science and Engineering (DESC0010833) for materials synthesis and characterization. We acknowledge facility support from Maryland Nanocenter and its AIMLab for sample characterization.

Notes

The authors declare no competing financial interest.

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