

Micelle-Directed Chiral Seeded-Growth on Anisotropic Gold Nanocrystals

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Abstract:

The surfactant-assisted seeded-growth of metal nanoparticles can be engineered to produce anisotropic gold nanocrystals with high chiroptical activity, through the templating effect of chiral micelles, formed in the presence of dissymmetric co-surfactants. Mixed micelles adsorb on anisotropic gold nanorods forming quasi-helical patterns, which direct a subsequent seeded growth into nanoparticles with pronounced morphological and optical handedness. Sharp chiral wrinkles were obtained, leading to chiral plasmon modes with high dissymmetry factors (~20%). Through variation of the dimensions of such chiral wrinkles, the chiroptical properties can be tuned within the visible and near-infrared regions of the electromagnetic spectrum. The micelle-directed mechanism readily allows extension to other systems, as confirmed by the seeded growth of chiral platinum shells on gold nanorods. This colloidal fabrication approach thus provides a reproducible, simple and scalable method toward the fabrication of nanoparticles with high chiral optical activity.

One Sentence Summary: Seeded growth of gold nanorods in the presence of micelles with chiral co-surfactants results in nanoparticles with high chiroplasmonic activity.

Chirality is a key signature of nature that can be found across length scales, from subatomic particles, through molecules and biological systems, to galaxies (1–3). In technology, imparting handedness to selected materials may provide important advantages in terms of their interaction with living organisms, allowing the development of enantioselective catalysts, or obtaining spin selectivity in electron transport (4–6). For example, the demonstration of chiral plasmon modes in noble metal nanocrystals has drawn significant interest in the field of metamaterials and the design of enantioselective sensing probes (7–9). The fabrication of plasmonic nanostructures has thus become an active field of research (10–16).

However, growing crystalline noble metals with dissymmetric morphology remains a significant challenge (10–12). The formation of chiral plasmonic nanomaterials is usually achieved by means of the assembly of achiral plasmonic gold and silver nanoparticles, using molecular templates (DNA, proteins, polymeric fibers, etc.) (13–15). Although lithographic approaches have been successfully applied to fabricate chiral gold nanoparticles, their scalability remains limited (9, 16). On the other hand, the significant advances in the colloidal synthesis of noble metal nanoparticles achieved during the past decades point toward realistic prospects for the production of plasmonic nanocrystals with diverse morphologies, including chiral ones (17–19). The presence of chiral aminoacids during nanoparticle growth has been shown to guide the formation of nanocrystals with distinct handedness. The most prominent example is the synthesis of helicoidal nanostructures assisted by cysteine and glutathione (11,20). The enantioselective interaction of amino acids with chiral geometrical elements naturally appearing at certain facets of the nanocrystals has been claimed to induce the observed shape evolution into twisted geometries with high dissymmetry factors.

Aside from the presence of chiral additives, the synthesis of colloidal chiral nanoparticles additionally requires the presence of other ligands adsorbing onto the nanoparticles to prevent undesired aggregation (11, 21). However, most of the usually employed capping agents also play a relevant role in the growth process and the resulting nanocrystal morphology (17, 22). Among the wide variety of ligands used for the synthesis of noble metal nanocrystals, quaternary alkylammonium halide (CTAX, X = Cl, Br) surfactants are some of the most extensively investigated ones. Through the adsorption of CTAX micellar aggregates on certain crystallographic facets, a wide variety of nanoparticle morphologies have been obtained (nanorods, nanotriangles, Platonic geometries, etc.) (17–19, 22–24). Recently, the addition of co-surfactants such as aromatic molecules, fatty acids, or long chain alkyl alcohols, has been shown to further improve the quality of colloidal gold nanoparticles, nanorods in particular (25–27). The ability of co-surfactants to intercalate within CTAX surfactant aggregates has been proposed to increase the rigidity of the micelles and/or induce phase transitions. Interestingly, the impact of co-surfactants on the aggregation behavior of surfactant molecules can also be extended to the formation of chiral micelles. It has been recently demonstrated that (*R*)-(+)-1,1'-bi(2-naphthol) ((*R*)-BINOL), a co-surfactant with axial chirality (i.e., atropisomerism), can induce the formation of chiroptically active giant worm-like micelles (28).

Considering the role of surfactants on the synthesis of gold nanocrystals and the possibility of producing chiral micelles in the presence of BINOL-like co-surfactants, we envisioned the surfactant-assisted seeded-growth of chiral gold nanocrystals. We hypothesized that elongated rod-like particles would have the ideal shape to guide the adsorption of twisted, worm-like micelles on the gold surface into helix-like chiral structures. To investigate both hypotheses, we first carried out a computational analysis on an ideal

system comprising cetyltrimethyl ammonium chloride (CTAC) and BINOL. Molecular dynamics (MD) simulations revealed that BINOL molecules are able to induce the assembly of surfactants into chiral worm-like aggregates. Such elongated micelles tend to coil around gold nanorods, which can thus be considered as templates for the seeded growth of anisotropic nanoparticles with chiral features. Although experimental evidence of the proposed idea was obtained using BINOL as a co-surfactant, the results of chiral growth were largely improved by using its derivative (*R*)-(+)-1,1'-binaphthyl-2,2'-diamine ((*R*)-BINAMINE)). The growth of plasmonic gold nanorods patterned with a complex chiral surface was indeed confirmed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) tomography. By tuning the dimensions of the final nanostructures, high anisotropy factors (g-factor ~ 0.20) were achieved within a wide wavelength range (from 500 to beyond 1350 nm). Theoretical modeling of the optical properties highlight the importance of growing well-defined chiral wrinkles to obtain intense circular dichroism (CD) responses.

MD simulations confirmed that, in the presence of BINOL as a co-surfactant, CTAC can form giant cylindrical micelles, which span across the simulation boxes (i.e., up to 60 nm in length; Fig. 1A, fig. S1). Regarding their chiral nature, we observed that unit vectors between the local micellar center and the principal micellar axis were distributed helically, the handedness being dictated by the choice of co-surfactant stereoisomer. This effect can be shown by measuring the average angle formed between pairs of vectors (fig. S2). An achiral helix does not have any tendency to coil into a particular direction, so that the angle formed between such vectors averages out to zero. In our simulations, we found that the average angles not only were finite but appeared sinusoidally correlated and displayed a clearly defined handedness (Fig. 1B). Due to the marked atropisomerism of BINOL, we can assume that it has the potential to induce helical chirality onto the surfactant aggregates, likely by a sergeants and soldiers mechanism (29, 30). In this case, the adsorbed chiral micelles would be able to assist chirality transfer during further deposition of metal atoms onto the nanorods surface. We tested this effect by simulating a gold nanorod, immersed in an aqueous mixed solution of CTAB and BINOL. Visual inspection of the simulation results reveals that CTAB and BINOL adsorb into worm-like micelles coiled around the gold nanorod surface (Fig. 1C and 1D). Although no preferred orientation of the assembly was observed by the use of different BINOL enantiomers in this case, we found that in the absence of co-surfactant, the coil-like morphology was largely lost. Instead, small aggregates and a high fraction of individual surfactant molecules would adsorb on the gold surface (fig. S3). The simulations indicate that chiral wormlike micelles are likely formed first, and subsequently adsorbed onto the gold nanorod. Therefore, a complex cooperative chiral transfer mechanism would convey the atropisomerism from BINOL into the giant micelles and ultimately to gold nanorods.

On the basis of the simulation results, we implemented experimentally the growth of chiral nanorods. (*R*)-BINOL was solubilized by surfactant micelles in aqueous solution, at an optimum molar ratio of 40, and used to template the growth of pre-formed gold nanorods (130 ± 10 nm long, 29 ± 2 nm thick, see Fig. 2A and SM for details). It should be noted that BINOL is insoluble in water in the absence of surfactant. Preliminary characterization by CD spectroscopy revealed the appearance of moderate chiral LSPRs bands (figs. S4 and S5, g-factor ~ 0.002). HAADF-STEM analysis of the nanoparticles grown in the (*R*)-BINOL/surfactant mixture revealed a complex morphology characterized by the presence of wrinkles on the nanorod surface (Fig. 2B). Previous theoretical and experimental studies demonstrated that intense CD responses are exhibited by nanoparticles with distinct chiral distortions and/or stellated-like morphologies (9, 11, 31). Encouraged by the appearance of plasmonic bands in the CD spectra, our efforts focused on improving chiral seeded growth.

We hypothesized that the use of stronger stabilizing agents would help directing the growth of better structured chiral wrinkles (32). (*R*)-BINAMINE, an analogue of (*R*)-BINOL in which the hydroxyl functionalities are replaced by amine moieties, was then investigated as a co-surfactant to template the growth of chiral nanorods. Although the interaction of amines with gold surfaces is moderately strong (Au–N bond energy ~ 6 kcal/mol), the presence of two amines in a chelating configuration should ensure a greater affinity (33, 34). MD simulations of the BINAMINE/CTAC system confirmed the formation of chiral worm-like aggregates, similar to those for BINOL/CTAC, with a helical distribution of unit vectors (fig. S6).

HAADF-STEM analysis of the particles obtained by seeded-growth in (*R*)-BINAMINE/CTAC revealed the presence of gold nanorods displaying a highly complex surface morphology, resembling an intricate network of wrinkles (Fig. 2C,D, figs. S7-10). Scanning electron microscopy (SEM) imaging of the same nanoparticles also revealed a complex surface structure (fig. S11). Notwithstanding, proper understanding of such complex structures demands a more detailed characterization than that provided by either HAADF-STEM or SEM, which only retrieve 2D and surface information, respectively. We therefore employed HAADF-STEM tomography, which has been shown to be a powerful technique to investigate the three-dimensional morphology of complex nanocrystals. Similar particles, but with increasing dimensions, were prepared using 130×29 nm gold nanorods as seeds and characterized by HAADF-STEM (see SM for synthetic details). Electron tomography reconstructions of nanorods with the smallest degree of growth, i.e. 165 nm long and 73 nm thick, revealed the presence of sharp wrinkles oriented in a seemingly radial direction and displaying tilt angles between 0° and 45° with respect to the short axis (Fig. 3A and fig. S7). Detailed analysis of the internal structure suggested that the wrinkles grow from the surface of the gold nanorod seed, in a quasi-radial direction, up to ~ 15 – 20 nm in height and with a constant width of 3–4 nm. The average inter-groove separation was measured to be 2–3 nm (Fig. 3B,C), which is close to the 3.75 nm width of worm-like micelles obtained from MD simulations. This finding would point to a micelle-directed chiral growth of the gold nanorods, as we initially hypothesized. It should be noted that the width of the wrinkles is compatible with the diffusion of metal ion-loaded CTAC micelles from solution (35), leading to reduction at available gold sites in between CTAC/BINAMINE micelles on the nanorod surface. By varying the concentration of nanorod seeds in the growth mixture, chiral nanorods were obtained with increased dimensions of 210 nm in length and 112 nm in thickness, and their surface was found to become more entangled (Fig. 3D and fig. S8). Nonetheless, the presence of tilted wrinkles was still clearly visible and angles between 0° and 45° were again observed (between 0° and -45° in the case of (*S*)-BINAMINE, fig. S9). Analysis of the internal structure revealed wrinkles of ca. 35–45 nm in height and a similar width to those in the smaller rods (Fig. 3E,F). Finally, even larger chiral nanorods (270 nm long and 175 nm thick) were investigated. Although the surface appeared more undefined in this case, analysis of the internal structure showed the characteristic features described for the previous samples (Fig. 3G–I and fig. S10). 3D animations are provided as Supplementary Material (Movies S1–S20)

It is well-known that diffraction of ideal helical structures results in X-shaped patterns (36,37). Therefore, we applied fast Fourier transformations (FFT) to our 3D reconstructions. As illustrated in Fig. 4C, X-shaped patterns are indeed visible; further details are provided in the SM, as well as comparison with an idealized model (fig. S12 and Movies S28–S32), with a smooth nanorod and with a BINOL-grown nanorod (fig. S13 and Movies S13, S35 and S38). Next, the spots in reciprocal space can be linked to the corresponding features in real space by manually segmenting the 3D FFT (see supplementary movie S45) to minimize noise. By using the segmented 3D FFT as a mask (see details in SM), an inverse FFT (38) was

computed and overlaid (pink fringes) with the original reconstruction, as exemplified in Fig. 4D, so that the helical features are visually highlighted. From Fig. 4D, fringes with a right handed angle can be observed. It should be noted that the wrinkles growing on the sides of the gold nanorod seeds seemed to display a better-defined chiral arrangement than those located at the hemispherical tips. The observation of a curvature-dependent growth was confirmed by a control experiment, in which seeded-growth was carried out on 30 nm gold nanospheres (figs. S14, S15) Although some chiral features can still be observed, the spheres yield a more random wrinkle organization, as revealed by the corresponding HAADF-STEM tomography reconstruction (Fig. 3J) and further supported by their 3D FFT and corresponding inverse FFT (fig. S14 and movies S42-S44). Accordingly, more intense plasmonic CD bands were recorded when gold nanorods were used as seeds (g-factor ~ 0.2 , Fig. 5A) as compared to spheres (g-factor ~ 0.003 , fig S15).

An additional evidence behind the general validity of this chiral growth method and the proposed mechanism is provided by experiments in which we varied the nature of the metal deposited during seeded growth. We thus implemented the seeded growth of Pt on BINOL/CTAC-covered gold nanorods, using identical dimensions and similar growth conditions. Representative results are shown in Fig. 4E-H, where it is obvious that seeded growth resulted in strikingly regular wrinkled platinum coating. The smaller dimensions of the wrinkles, as well as the different electron configuration between platinum and gold (see a 3D EDX reconstruction in fig. S16), allow a better distinction of the obtained pattern. Although the tilting angle is obviously lower than that measured for gold, a helical character is demonstrated by the 3D-FFT analysis (Fig. 4E). Unfortunately, the lossy character of platinum does not allow to record meaningful plasmonic optical activity for these samples.

We next demonstrate that the optical activity (CD bands) can be modulated by varying the dimensions of chiral nanorods (by varying the amount of seeds in the growth solution). In all cases, an intense negative Cotton effect was recorded for the (*R*)-enantiomer (29). As the size of the nanorods was increased from 165×73 nm to 270×175 nm, the positive band was found to redshift from 700 up to 1300 nm, while the maximum of the negative band shifted from 1100 to beyond 1350 nm (fig. S17). Analysis of the anisotropy factor showed values ranging from 0.1 to 0.2 (Fig. 5A), which are among the highest values reported for colloidal plasmonic nanoparticles in the visible and NIR ranges (10, 11). By extending the analysis further into the NIR, up to the limit of our CD spectrometer (1600 nm), we recorded even higher dissymmetry factors (fig. S18). However, the noise in the 1400-1500 nm range precluded us from obtaining more compelling evidence to confirm the precise values. When gold nanorods of different dimensions and degrees of anisotropy were used to seed the chiral growth (fig. S19 and S20), similar trends in optical activity were observed. However, the anisotropy factor was significantly influenced by the nanorod dimensions. In general, slightly lower g-factor values were obtained when shorter and thinner gold nanorods were used as seeds (100×12 nm; i.e., higher aspect ratio), while a significant decrease was observed for seeds with similar length to the optimal one but thicker in diameter (130×52 nm; i.e., lower aspect ratio).

The relationship between the chiral features observed by electron microscopy and the chiroptical activity measured by CD spectroscopy was further investigated by electromagnetic modeling. We used an accurate full-wave solver based on Maxwell's surface integral equations and the method of moments to model the plasmonic properties of chiral gold nanorods (see SM for details) (39-41). Three-dimensional computer-aided design (CAD) models were constructed on the basis of the information provided by the experimental electron tomography reconstructions (Fig. 5B). Although suitable reproduction of the

observed morphologies appeared challenging, owing to the intricate network of wrinkles covering the chiral gold nanorod surface, we were able to create models for the three different dimensions characterized by electron microscopy: 165×73 nm, 210×112 , and 270×175 nm. To mimic the regions with wrinkles displaying different angles, each rod was built with sixteen helices having four leveled and four inclined steps per pitch (pitch of 90 nm). The wrinkle width was fixed at 3.5 nm and the separation distance between wrinkles was 2.5 nm. The simulations revealed chiral plasmonic bands that shifted toward longer wavelengths with increasing nanorod dimensions, in agreement with the experimental results (Fig. 5C, fig. S21–S23). Differences in the anisotropy factors can be attributed to the polydispersity in size and shape of the real sample, as well as the difficulty in modeling the exact morphology of the nanoparticles. Overall, our theoretical model confirms the origin of the plasmonic chiroptical activity and the importance of sharp wrinkles for the emergence of strong CD responses. Importantly, we found that replacement of BINAMINE by L-cysteine did not induce any clear modification on the CD signal obtained for chiral nanorods synthesized with either (*R*)-BINAMINE or (*S*)-BINAMINE. A significant modification would be expected if the chiroptical properties would stem from the coupling of the chiral molecules with the nanoparticle plasmon, rather than from the chiral structural features (fig. S24). (42)

We have experimentally demonstrated that chiral gold nanostructures can be readily obtained by seeded-growth of gold nanorods in BINOL/surfactant mixtures, whereas nanoparticle colloids with intense CD responses were obtained using BINAMINE/surfactant mixed micelles. The chiroptical properties stem from the formation and stabilization of steep chiral wrinkles. These findings point to a dual role of mixed micelles: (i) templating the growth of steep wrinkles and (ii) the subsequent stabilization of such morphological features. We propose that the formation of wrinkles during seeded-growth can be explained by the presence of elongated micelles coiled on the gold nanorod seeds, which act as patterns directing the diffusion of micellar aggregates containing gold ions, from the aqueous solution toward the core nanocrystal at inter-micellar regions. Indeed, the size of micelles in solution would fit the inter-wrinkle distance on the nanorod surface. However, wrinkle formation is only induced when the rate of gold ion deposition is faster than their diffusion on the surface (43). We observed that, upon lowering the concentration of reducing agent (ascorbic acid, from 160 down to 1.6 mM), the CD intensity decreased by an order of magnitude and less defined surface roughness was observed in STEM (fig. S25). It should be noted that an additional source of surface stabilization is required to preserve the wrinkles after growth. In this case, BINAMINE plays such a role during the growth process, likely due to its two amine moieties in chelating conformation (33). When one of the amine groups in BINAMINE was replaced by a hydroxyl moiety, the passivation effect was suppressed and the growth of chiral features was hindered, which resulted in a decrease of CD intensity (fig. S26). Once the growth is completed, addition of a stronger stabilizing agent (e.g., cysteine) is necessary because the adsorption of surfactant micelles is not sufficiently strong and the nanoparticles may slowly reshape, as reflected by the loss of chiroptical properties (fig. S27).

The approach described here for the synthesis of chiral plasmonic anisotropic nanocrystals is simple, reproducible, and holds great potential for large scale production, intrinsic to colloid chemistry methods. Compared with the growth of inorganic chiral nanostructures based on the direct chemisorption of small additives on the nanocrystal surface to induce chiral growth, the micelle-directed growth method relies on the ability of the chiral-co-surfactant to direct the formation of helical micelles. Such supramolecular assemblies have plenty of interaction points with the nanoparticles, thus, they can effectively transfer their chirality to the nanoparticles during the growth step via a multivalency effect. Notwithstanding, with these

results at hand, we additionally foresee that the scope of micelle-directed chiral growth can potentially go beyond the synthesis of chiral gold nanocrystals. Owing to the important role of surfactants in the synthesis of a wide variety of colloidal nanoparticles, we expect that this approach will be generalized toward shaping diverse nanomaterials (e.g. other noble metals and metal oxides, even polymer nanoparticles) with chiral morphologies, and other related applications (44) A wide variety of nanostructures can be imagined by varying the nature of the co-surfactant additives. Moreover, the unique curvature of the obtained chiral rods and nanospheres, covered with network of wrinkles and interstitial spaces could potentially serve as platforms for biomimetic chiroplasmonic catalysis or chiral bias of molecules.

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Figures

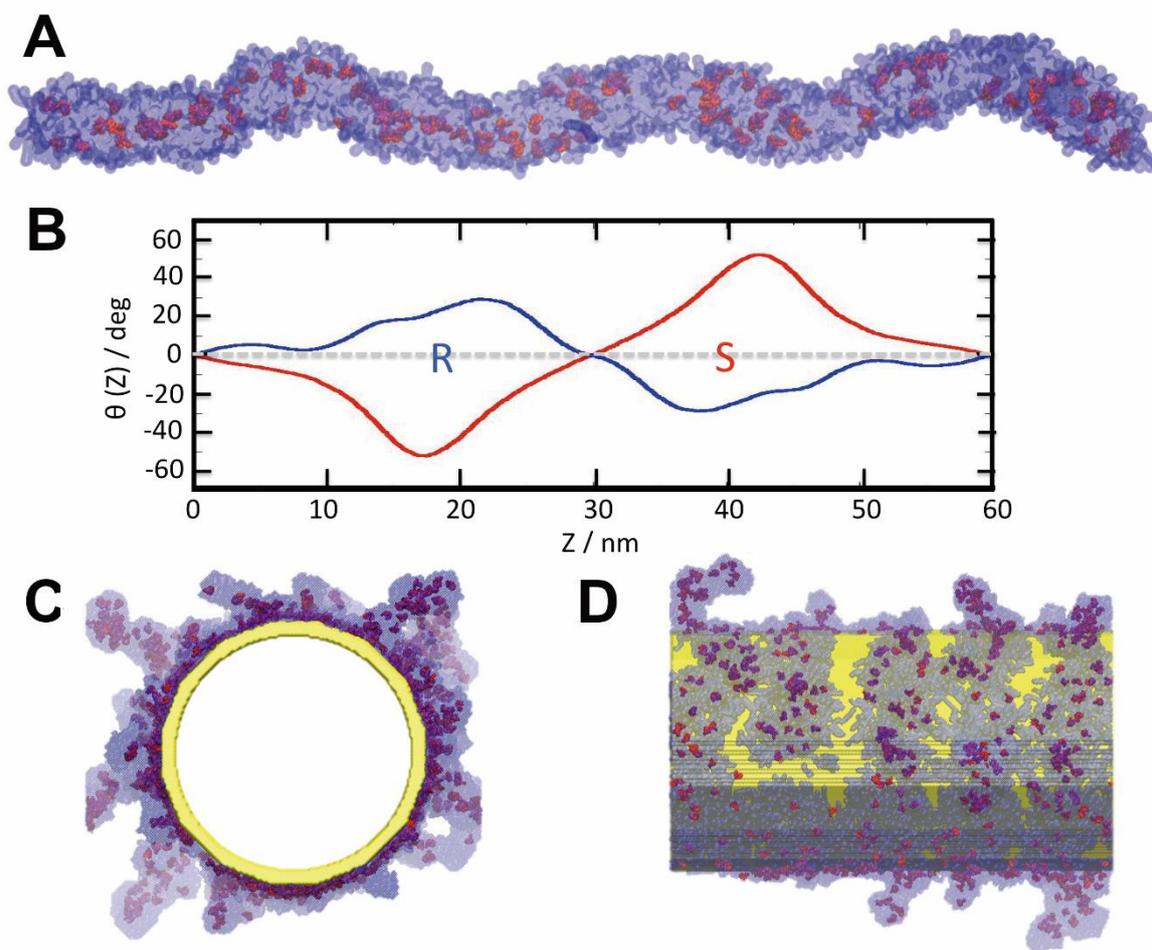


Figure 1. MD simulations of BINOL/CTAC micellar system and their assembly on gold nanorods. (A) MD Simulations for (*R*)-BINOL/CTAC in solution. The aggregation of CTA⁺ (blue) in the presence of (*R*)-BINOL (red) results in chiral worm-like aggregates spanning the whole simulation box: 60 nm in length. (B) The shape of the micellar coil is described by a set of vectors along the principal micellar axis. The average angle between vectors is plotted as a function of their vertical distance for 60 nm long rod-like micelles. The presence of (*R*)- or (*S*)-co-surfactant enantiomers in the micelles leads to coiling in opposite directions, as revealed by the sign of the average angle. (C, D) MD simulations for (*R*)-BINOL /CTAC adsorbed onto a gold nanorod in axial and lateral views, respectively.

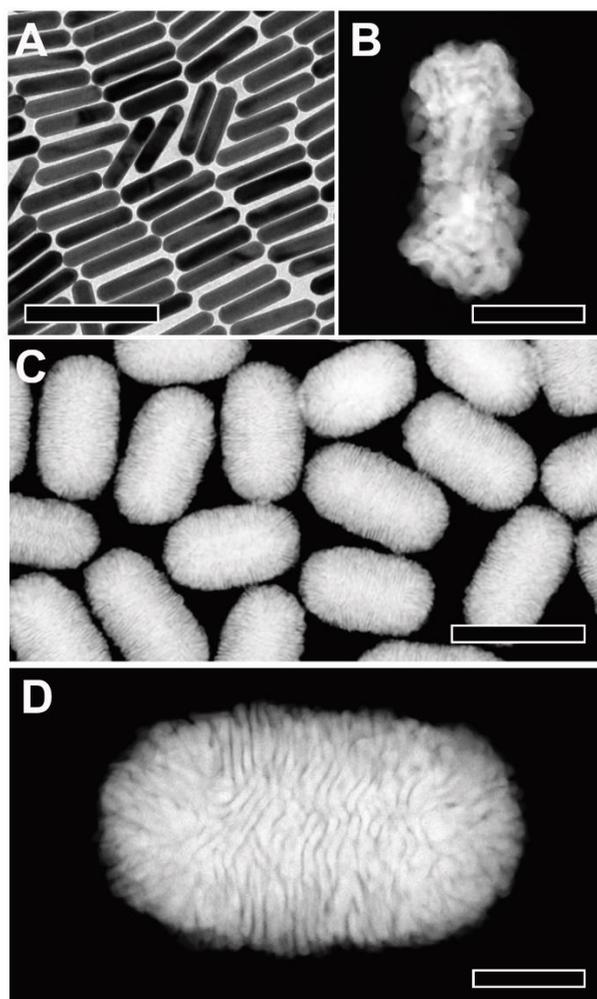


Figure 2. Growth of chiral gold nanorods in the presence of BINOL/CTAC and BINAMINE/CTAC micellar systems. (A) TEM image of gold nanorods of 130 nm in length and 29 nm in width, used as seeds. (B) High magnification HAADF-STEM image of a chiral gold nanorod grown in (*R*)-BINOL, displaying a complex surface containing wrinkles. (C,D) HAADF-STEM images at low (C) and high (D) magnification of gold nanorods obtained in the presence of (*R*)-BINAMINE, displaying a complex surface containing sharp wrinkles. Scale bars: 200 nm (A,C), 100 nm (B), 50 nm (D).

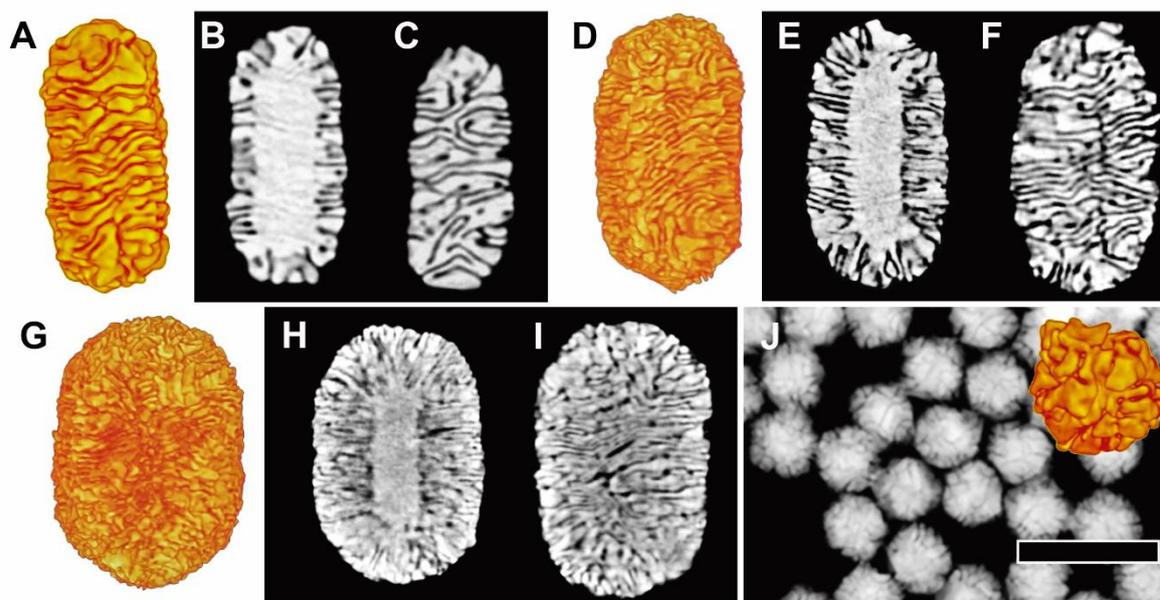


Figure 3. Effect of size and shape on chiral features. Gold nanorods of 165×73 nm (A–C), 210×112 nm (D–F) and 270×175 nm (G–I) grown in (*R*)-BINAMINE/surfactant mixtures were analyzed by HAADF-STEM. Tomography reconstructions (A,D,G, respectively) reveal their surface topography, whereas selected orthoslices show the growth of wrinkles from the gold nanorod seeds (B, E, H, respectively) and the internal structure of the wrinkles network (C, F, I, respectively). Reconstruction movies are provided as Supplementary Material (Movies S1-20). (J) Low magnification STEM image and tomography reconstruction (inset) of nanoparticles obtained by overgrowth of 30 nm gold nanospheres in an (*R*)-BINAMINE/surfactant mixture. Scale bar: 100 nm.

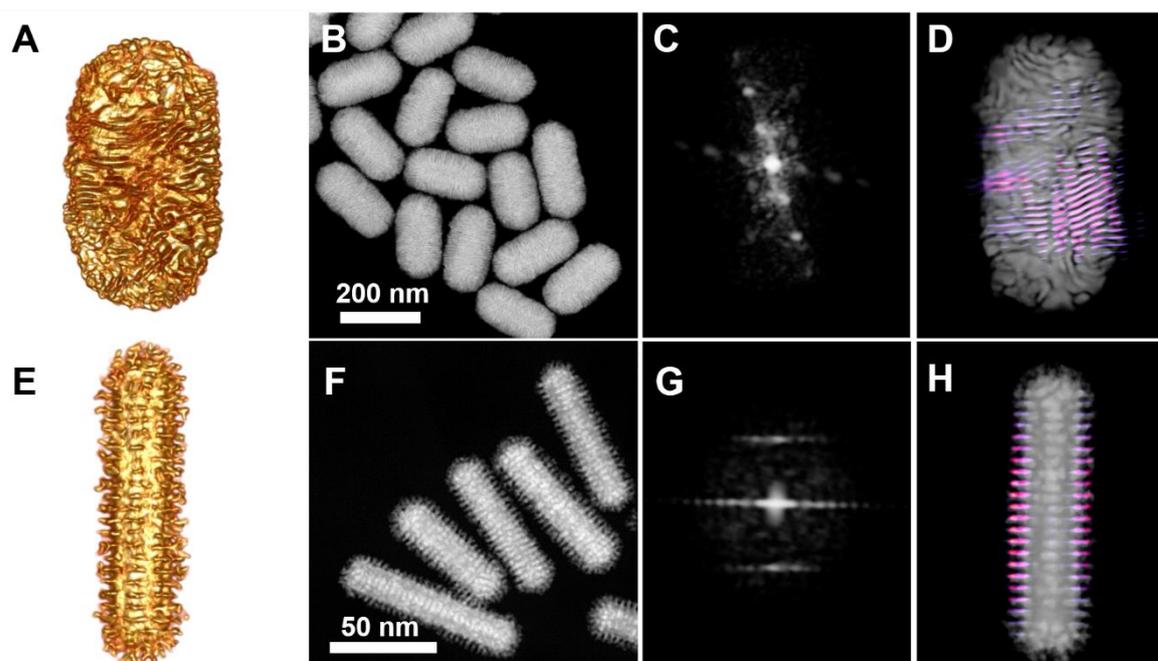


Figure 4. Qualitative analysis of chiral features. (A) Tomography reconstruction of a gold nanorod grown in (*R*)-BINAMINE/surfactant mixture (see also Movie S21). (B) Low resolution HAADF-STEM image of chiral gold nanorods obtained in the presence of (*R*)-BINAMINE. (C) Segmented 3D-FFT with the central and the periodic spots from which the inverse FFT was computed (see also Movie S8). (D) The inverse FFT (see also Movie S10) shows the areas of the particle with chiral features overlapped with the projection of the tomography, indicating a right handed angle. (E) Tomography reconstruction of an Au@Pt nanorod grown in (*R*)-BINOL/surfactant mixture (see also Movies S22). (F) HAADF-STEM image at low magnification of Au@Pt nanorods. (G) Segmented 3D-FFT with the central and the periodic spots from which the inverse FFT was computed (see also Movie S25). (H) The inverse FFT (see also Movie S27) shows the areas of the particle with chiral features overlapped with the projection of the tomography, indicating a right handed lower angle.

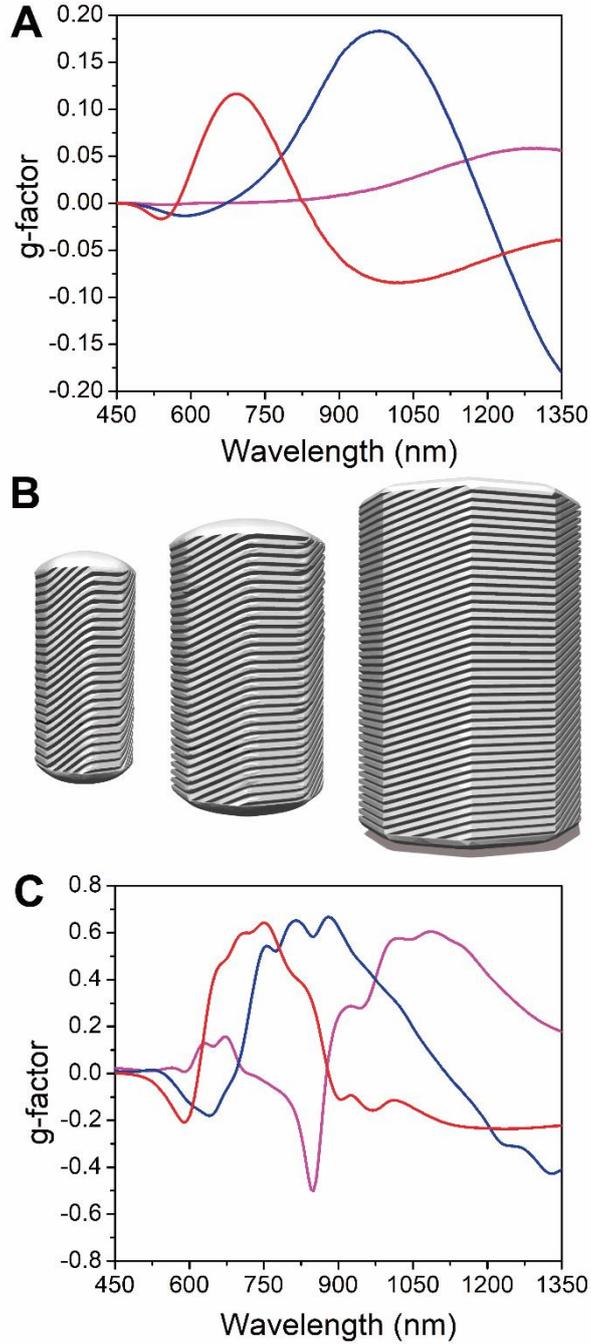


Figure 5. Effect of nanorod dimensions on the chiral plasmonic activity. (A) Spectral evolution of the anisotropy factor for chiral nanorods with increasing particle size: 165×73 nm (red), 210×112 nm (blue) and 270×175 nm (magenta). (B) Models of chiral gold nanorods used to simulate the chiral plasmonic properties (from left to right: 165×73 nm, 210×112 nm and 270×175 nm). (C) Calculated anisotropy factor spectra (from left to right in C: red, blue, and magenta).