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Interband Absorption Enhanced Optical Activity in Discrete Au@Ag Core-shell Nanocuboids: Probing Extended Helical Conformation of Chemisorbed Cysteine Molecules

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Abstract: Detailed understanding of the interaction between a chiral molecule and a noble metal surface is essential to rationalize and advance interfacial self-assembly of amino acids and metal-mediated anchoring of proteins. Here we demonstrate that an individual Au@Ag core-shell nanocuboid can serve as a plasmonic reporter of an extended helical network formed among chemisorbed cysteine molecules, through generating an interband absorption enhanced, Ag-surface-exclusive circular dichroism (CD) band in the UV region. The observed unusual and strong CD response in the hybrid Au@Ag-cysteine system can thus be used to probe, in a real-time manner, conformational evolution and structural rearrangement of biomolecules in general and also monitor the interfacial interaction between a metal surface and an adsorbed molecule, opening up the possibility of using Ag nanostructures as promising stereochemically attuned nanosensors.

Optical chirality and nonzero circular dichroism (CD) are present in a molecule if the molecular structure has neither a mirror plane nor an inversion center. In other words, the molecule acquires a sense of rotation and hence reacts differently to right- and left-handed circularly polarized lights.[1] One of the well-established methods, known as CD spectroscopy, is widely utilized to examine the efficiency of synthetic organic chemical reactions and determine enantiomer handedness, protein folding, and conformational changes of chiral molecules due to physical and chemical stimuli.[2] In particular, the molecular recognition capability in stereochemistry offers the possibility to design and realize "smart" systems with the ability of chiral discrimination.[3] Chiral detection of cysteine, a typical proteinogenic amino acid, has been intensively studied because of its critical role in many biological systems. For example, anomalous concentration of cysteine in blood is an important beacon of various diseases such as Alzheimer's disease, cardiovascular disease, liver damage, and skin lesions.[4] However, the CD signals of many biomolecules like cysteine are typically very weak, and thus a significant amount of materials at a relatively high concentration is required for producing a detectable signal, constituting a technical impediment in many practical aspects.

Subwavelength nanostructures made of noble metals (such as Au and Ag) support localized surface plasmons (LSPs) – the collective oscillation of conduction electrons at a metal-dielectric interface.[5a-5c] Upon resonant excitation of LSPs, the incident light energy can be squeezed into a nanoscale volume around a metal nanostructure, thereby largely enhancing the local field strength and consequently the light-matter interaction for a molecule, for instance, adsorbed on the surface of a metal nanostructure.[5d] The enhanced electromagnetic interaction serves as the basis for using LSPs-based nanosensors to locally detect nanoscale environmental changes, such as molecular-binding events, catalytic reactions, phase-changing processes, and hydrogen adsorption dynamics.[6a-6d] Note that recently the chiral plasmonic structures and chiral metamaterials have also been investigated for enhancing the optical activity and sensing of molecules.[6e-6g]

Besides supporting the LSPs, Au and Ag nanoparticles also have strong intrinsic interband absorption due to photo-excited interband transitions in the UV range (220 - 320 nm for Ag). The interband transition in a noble metal involves the promotion of an electron from an occupied *d*-level state to an empty state above the Fermi level of the metal, and the induced absorption is strongly determined by the joint density of *d* and *s* states of conduction electrons.[7a] Previous studies seldom reported the use of interband transitions because of their high energy levels located in the UV region, but recent research has ignited the interest in this intrinsic property of noble metals. For example, surfactants and capping molecules were observed to influence the intensity and linewidth of the interband absorption peaks of Au and Ag nanoparticles due to their spectral overlapping with the molecular absorption and this effect was successfully used for new biosensing applications.[7b] Moreover, the third harmonic generation from Au nanoparticles was strongly enhanced when the fundamental beam energy was approximately one third of the interband transition energy of Au.[7c] Considering significant matching of their resonance energies, the interband transitions of noble metals could also accelerate the electronic transitions of adhered chiral molecules and thus amplify the absorption difference of circularly polarized lights by the molecules.

Here we report for the first time, the observation of an unusual CD resonance at the interband transition region of discrete achiral Au@Ag core-shell nanocuboids (CSNCs) chemisorbed by chiral cysteine molecules. The new CD band of the hybrid system spectrally deviates from both the molecular electronic CD of pristine cysteine and the plasmon resonance bands of the Au@Ag CSNCs, and shows a 170-fold intensity enhancement compared to pure cysteine. In this work, comprehensive studies as functions of solution temperature, pH value and external ions, together with Raman spectroscopy and electromagnetic calculations, reveal that the formation of an extended helical network on the Ag surface through linking the amino nitrogen and carboxylate oxygen atoms of neighboring cysteine molecules by hydrogen bonding is responsible for the origin of the new UV CD band that is strongly amplified by the interband transition of Ag through Coulomb coupling and enhanced local fields around the Au@Ag CSNC.

Figure 1a depicts a typical TEM image of the as-prepared Au@Ag CSNCs. The inset shows the cysteine-coated CSNCs used in the CD experiment, demonstrating good dispersion and no aggregation. Figures 1b and 1c show the high-magnification TEM and STEM images of an individual Au@Ag/L-cysteine CSNC (~90 nm in length and ~ 60 nm in diameter), corroborating that the Au NR core (~50 nm in length and ~10 nm in diameter) is fully

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enwrapped with a uniform Ag shell, consistent with the elemental mappings of Ag and Au in Figures 1d and 1e. Note that the O and S elemental mappings in Figures 1f and 1g confirm a uniform coating of cysteine on the CSNC surface. Figure 1h depicts the Au and Ag crystal-lattice mappings profiled by the red dash line. The inset shows a Fast Fourier Transform image captured over a small area of the Au@Ag CSNC, and two clear sets of diffraction patterns are observed, indicating that both Au core and Ag shell are single crystals. The interplanar spacings measured for the core and shell regions are 0.210 nm and 0.232 nm, corresponding to Au (200) and Ag (111) crystal planes, respectively.

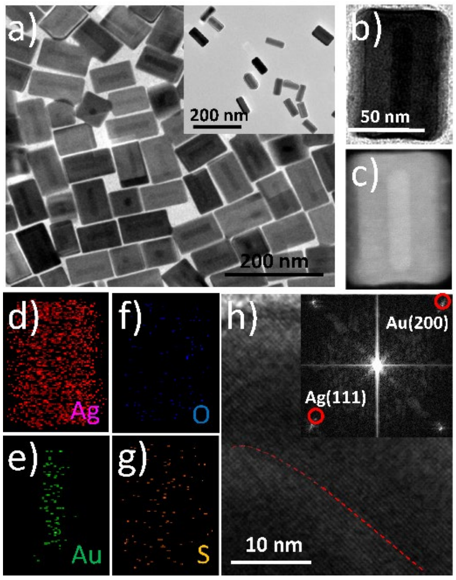

Figure 1. Morphology and composition characterizations of as-prepared Au@Ag CSNCs. a) Low-magnification TEM image of bare and L-cysteine coated Au@Ag CSNCs (inset). b) and c) High-magnification TEM and STEM images of an individual cysteine-capped Au@Ag CSNC. d-g) Elemental mappings of d) Au, e) Ag, f) O, and (g) S for the structure in b) and c). h) Au core and Ag shell crystal-lattice mappings profiled by the red dash line. The inset in h) is the FFT image captured over a small area of the Au@Ag CSNC.

Figure 2a shows the extinction spectra of as-prepared pristine L- and D-cysteine solutions, bare Au@Ag CSNCs, L- and D-cysteine-adsorbed Au@Ag CSNCs. It can be seen that the L- and D-cysteine molecules have the same absorption response peaked below 200 nm. The extinction spectrum of the CSNCs exhibits four well-defined plasmon bands, which are located at, from low to high energy, 620, 463, 422 and 346 nm, with the first two ascribed to the longitudinal and transverse dipolar modes, similar to the plasmon resonance bands of an Au nanorod,[8a] and the latter two to the octupolar and multipole modes, respectively.[8b] The mode assignment is consistent with the simulated charge distributions and electric near-field profiles shown in Figure S1. Upon the adsorption of cysteine, the four extinction bands of the CSNCs show a slight blue shift in peak position and a decrease in peak intensity, possibly due to the decrease in the local effective refractive index.

Figure 2b represents the measured CD spectra for the five samples studied in Figure 1a. As can be seen, the pure L- and D-cysteine show two mirror-symmetric bisignate CD resonances, manifesting their enantiomer correspondence, in the UV region close to the absorption band of cysteine where both peak position and spectral profile are similar to those of typical α-amino acids.[9a] In sharp contrast, the Au@Ag CSNCs colloid solution (10 nM) has no CD response, consistent with their achiral character. However, upon capping the achiral CSNCs (10 nM) with L-cysteine (1.35 μM), two bisignate (peak-dip) CD resonances emerge in the UV region, with the short-wavelength one (200 to 240 nm) being significantly weaker than the long-wavelength one (240 to 320 nm) in intensity. Since the second bisignate locates neither in the absorption band of the L-cysteine[4c,19c] nor in the typical plasmon bands of the CSNCs,[3b,9a,9b] here we name it a molecule-induced unusual CD and it could originate from conformational change of the chemisorbed cysteine molecules. Replacing L-cysteine with D-cysteine flips the spectral profile, demonstrating that the observed CD response indeed results from the differential absorption of the left- and right-handed circularly polarized lights by the hybrid system.

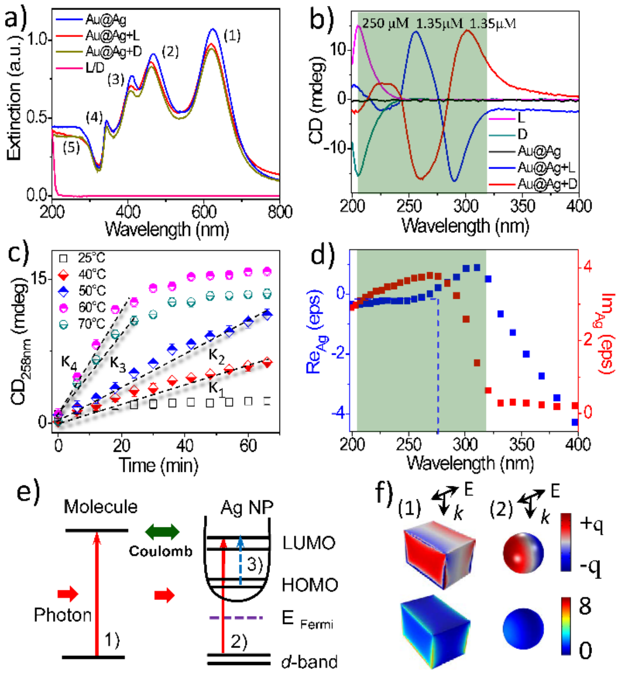

Figure 2. a) Extinction spectra of cysteine solution (7×10^{-4} M, pink curve), Au@Ag CSNCs (blue curve), and L- and D-cysteine adsorbed Au@Ag CSNCs (green and red curves). b) CD spectra of L-cysteine (pink curve, 250 μM), D-cysteine (green curve, 250 μM), bare Ag@Au CSNCs (black curve), and L- and D-cysteine coated Au@Ag CSNCs (1.35 μM, blue and red curves). The CD measurements were carried out after keeping the solutions for 24 h at 25 ºC. c) Time evolution of the CD intensity measured at 258 nm as a function of temperature for the L-cysteine capped Au@Ag CSNCs solution of 1.35 μM. A water bath was used to maintain the solution at varied temperature. d) The real and imaginary parts of the electric permittivity for bulk Ag. e) Quantum transitions in the cysteine-coated Au@Ag CSNC system. The solid vertical arrows represent the photoinduced transitions in cysteine and Ag, denoted by 1) and 2), respectively, with the green arrow showing their Coulomb coupling. Note that 2) represents an interband transition of Ag while 3) shows an intraband transition of Ag (*sp*-band). f) Simulated surface charge and near-field distributions at wavelength 300 nm for an Au@Ag CSNC (1) and Ag nanosphere of 20 nm diameter (2).

By defining an enhancement factor $EF_{CD} = CD_{\lambda,new}/CD_{\lambda,original}$, where $CD_{\lambda,new}$ and $CD_{\lambda,original}$ are the CD signals of pure cysteine and Au@Ag-cysteine complex at their respective spectral peaks, we estimate EF_{CD} to be ~170 for the new bisignate CD (~15.2 mdeg at 205 and 290 nm for the Au@Ag-D-cysteine of 1.35 μM and the D-cysteine complex of 250 μM, respectively). To further evaluate the absorption difference, we calculate the anisotropy or dissymmetry factor, g-factor,[9a] defined as $g = \Delta\alpha/\alpha$, where $\Delta\alpha$ and α are the molar CD and molar extinction, respectively. Using the measured extinction and CD signals at wavelength 290 nm, the g-factor for the hybrid system is determined to be 1.45×10^{-3}, three (two) times that of the Ag nanospheres(nanorods)/cysteine system (Figure S9 and S12). Control experiments show that the CD enhancement factor strongly depends on the composition and shape of the metallic nanostructures supporting the chiral molecules. For instance, cysteine-coated Au nanorods and nanospheres exhibit no detectable CD signal while cysteine-coated Ag nanospheres show a CD enhancement of 36 times (Figure S2). Such comparison indicates that the induced CD resonance is exclusive for Ag surfaces. This is probably due to the fact that Ag is more susceptible to environmental changes than Au,[9b] and therefore structural changes of chiral molecules could occur more easily on Ag.[9d] More surprisingly, by comparing with the electric permittivity of Ag in Figure 2d, we find that the unusual CD band is located exactly at the interband absorption region of Ag (shadowed area, 220 - 320 nm).

In general, it is believed that the surface plasmonic field of a metal nanoparticle can accelerate the electronic transition, and thus increase the absorption, of a molecule nearby, responsible for plasmon-enhanced molecular electronic CD because the enhanced local fields can amplify the absorption difference of circularly polarized photons.[9a,9b] Unfortunately, this mechanism cannot account for the observed CD resonance since our observations are distinctively different from previous theoretical and experimental studies in the following aspects. First, the signal magnitude of the induced CD (~170-fold enhancement) is significantly larger than the supramolecular UV CD observed in Ag$^+$/cysteine coordination polymers[4d,4e] or the plasmon-induced visible CD in chiral molecules capped Au nanostructures,[9e] both of which are comparable to their native molecular electronic CD. Second, the induced bisignate CD resonance occurs at the interband absorption region of Ag [region (5) in Figure 2a] rather than the conventional LSP bands of metal nanostructures [extinction peaks (1-4) in Figure 2a]. Moreover, the near-field enhancement factor of the CSNC at 300 nm is much smaller than that at its LSP bands (see Figure S1), indicating that the plasmon-enhanced optical activity is not the dominant role in the observed unusual CD resonance. Third, the induced CD is observed exclusively for Ag surfaces whereas the plasmon-induced CD is a generic effect for all plasmonic materials including both Ag and Au. These remarkable differences all indicate a different physicochemical mechanism responsible for the new UV CD band, rather than those previously reported plasmonic CDs located at visible range due to the far-field [7d] or near-field electromagnetic coupling.[7e]

Figure 2e indicates the Coulomb interaction induced coupling between cysteine and Ag due to energy matching of their molecular transition and interband transition, and the coupling efficiency depends on the local electric field strength. When the absorbing center of the hybrid Au@Ag-cysteine has different molar extinction coefficients for circularly polarized lights the extinction inequality results in unequal magnitudes of the left- and right-rotating electric field components of the incident light, thus giving rise to a differential absorbance quantified by the aforementioned dissymmetry factor. This picture seems to be able to explain the difference in dissymmetry factor observed for the Au@Ag CSNC and the Ag nanosphere because the former shows a much larger field enhancement factor than the latter (7.52 vs. 1.68). However, it cannot fully account for the observed Ag-exclusive CD resonance because Au also has interband transitions in the UV region. As mentioned earlier, here we propose that the unusual CD resonance arises from the formation of an extended helical network of neighboring cysteine molecules on the Ag surface through hydrogen bonding of their COO$^-$ and NH$_3^+$ groups, which has a new CD response at ~240 - 320 nm, spectrally matching the intrinsic interband absorption of Ag and thus being enhanced significantly. Indeed, Liu et al observed the formation of an extended helical network of cysteine molecules on the surface of photoreduced Ag nanoparticles.[9f] To verify our hypothesis, we carried out a series of sophisticated experiments, including temperature dependent molecular adsorption-desorption dynamics, pH-switched and ions-suppressed hydrogen bonding of COO$^-$ and NH$_3^+$, and surface-enhanced Raman spectroscopy (SERS). All our experiments together with full-wave electromagnetic simulations coherently support the above-proposed mechanism.

First, the temperature-dependent time-evolution of the observed CD indicates clear conformational changes of the chemisorbed cysteine molecules. At room temperature (25 °C), the CD signal intensity of the hybrid Au@Ag-L-cysteine system increases with reaction time, and reaches saturation after keeping the system for ~24 h (see Figure S3 in Supporting Information). As shown in Figure 2c, increasing the temperature from 25 °C to 60 °C shortens the time to reach thermodynamic equilibrium from ~24 h to 30 min, demonstrating an accelerated reaction rate for hydrogen bonding of COO$^-$ and NH$_3^+$ groups at high temperatures. Note that only the data points measured for the first 70 min are shown in Figure 2c in order to better visualize the intensity change at the onset of reaction, where the CD signal intensity of the system increases linearly with reaction time, following the well-known first-order adsorption kinetics.[6b,7a] From the linear fittings, the adsorption rate constant k is found to be 0.063, 0.168, 0.390, and 0.512 min^{-1} for 40, 50, 60 and 70 °C, respectively. At 60 and 70 °C, the adsorption rate constant becomes much smaller after ~30 min, mainly due to the adsorption saturation of cysteine on the surface of the CSNCs, i.e. reaching an adsorption-desorption dynamic equilibrium. Surprisingly, the CD intensity at 70 °C is persistently lower than that at 60 °C, possibly due to heat-mediated desorption of the cysteine molecules and consequent dissociation of COOH-NH$_2$. Note that increasing the temperature to 80 °C results in a much weaker CD signal as compared to 70 °C (results not shown). Note that the temperature dependence observed in our system distinctively differs from that for sub-3-nm Ag NPs coated with chiral supramolecular structures where both UV molecular CD and plasmon-induced CD bands diminished upon heating the solution due to heat-incurred disordering of the supramolecular structure.5 It also differs from the temperature-dependent and reversible plasmonic CD based on Au nanorod and DNA assembly and disassembly.[9g]

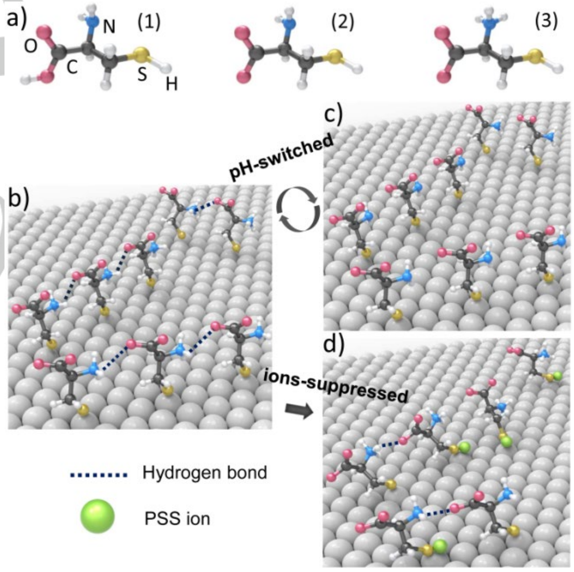

Figure 3. a1-3) Schematic representations of three possible charge states in a cysteine molecule: (1) neutral, (2) anionic and (3) zwitterionic. b-d) Formation of an extended helical network through hydrogen bonding of COO$^-$ and NH$_3^+$ in neighboring cysteine molecules b), high-pH-enabled dissociation of COOH-NH$_2$ c), and negative PSS ions modulated orientation of adsorbed cysteine molecules, leading to the formation of less helical networks d).

Second, the pH-controlled CD activity evidences the linking of COO$^-$ and NH$_3^+$ groups among cysteine molecules. In general, cysteine has three charge states as shown in Figure 3a, namely (a) neutral, (b) zwitterionic, and (c) anionic, among which the zwitterionic state favors forming an extended helical network on an Ag surface (Figure 3b). This can be confirmed by monitoring the CD signal of the hyrbid system with varied solution pH. Figure 4a shows that the induced CD signal drops dramatically with increasing pH, and becomes negligible at pH = 10. In contrast, the CD intensity remains unchanged in acidic environment (even at pH = 4, see the inset of Figure 4a). Considering the pKa values of

CO_2H (1.9), SH (8.4), and NH_3^+ (10.7), and the isoelectric point of cysteine (5.2),[10a] the CO_2H and NH_2 groups tend to deprotonate to CO_2^- and protonate to NH_3^+ at low pH, respectively, thereby facilitating the electrostatic interaction among zwitterionic cysteine molecules. This sensitive pH responsivity provides an additional degree of freedom to control the CD response of the hybrid system as schematically shown in Figures 3b and 3c. Figure 4b shows that the induced bisignate CD at pH = 7 disappears at pH = 10, but recovers when resetting the pH to 7. This "on-off" switching of the CD response can be cycled easily by concurrently setting the solution pH at 7 and 10 (see the inset of Figure 4b). Moreover, NMR and FT-IR spectra confirm the chemical environment and conformation change of cysteine molecules before and after absorbed on the surface of Au@Ag CSNC as well (Figure S7 and S8).

Third, the orientation modulation of the chemisorbed cysteine molecules by external negative ions suppresses the induced CD. In general, cysteine molecules vertically adhered on a surface of Ag are easier to form hydrogen bonding than those with random orientation. In other words, disturbing the molecular orientation on the Ag surface could decrease the induced CD signal by suppressing the formation of extended helical networks as shown in Figure 3d. To test this prediction, we added a certain amount of negatively charged polyelectrolyte (PSS) ions to the hybrid system and monitor the CD signal change as a function of PSS concentration. Note that the as-prepared Au@Ag CSNCs are positively charged due to the presence of CTAB surfactants, and therefore the PSS ions can easily attach on the Ag surface and, in the meanwhile, strongly disturb the molecular orientation of cysteine due to their electrostatic interaction. Consequently, occurrence of hydrogen bonding between COO^- and NH_3^+ groups is suppressed, resulting in the diminished CD as shown in Figure 4c. Specifically, the CD intensity decreases from 12.6 to 6.5 mdeg by increasing the PSS concentration from 0.20 to 0.40 g/L at a fixed amount. The inset shows that the maximum CD signal intensity at 258 nm monotonically decreases with PSS concentration while the extinction intensity of the complex at 615 nm shows little variation, confirming that the diminished CD does not come from the slight dilution of the complex solution.

Fourth, SERS measurements provide direct evidence of the proposed helical network conformation of cysteine molecules by detecting the molecular fingerprint of hydrogen bonding. Note that SERS was used to understand the interfacial interaction in metal-ligand systems, providing a cost-effective and robust technique for analyzing the interaction between metals and cysteine.[10b,10c] The SERS spectrum measured for blank Au@Ag CSNCs in Figure 4d exhibits no detectable peaks in the frequency above 500 cm^{-1}, demonstrating the cleanness of the sample. Interestingly, the spectra for the Au@Ag-L-cysteine complex measured after mixing them for 1 h and 24 h share several characteristic Raman peaks but also show several distinctively different bands. The strong Raman band at 233 cm^{-1} in both spectra can be attributed to Ag-S bond since the SH group of cysteine is chemically bonded to the Ag surface. The Raman band at 658 cm^{-1} is assigned to C-S stretching vibration. The spectrum measured after 1 h exhibits a characteristic peak at 511 cm^{-1}, ascribed to S-S bond, which cannot be found in the spectrum measured after 24 h because the formation of Ag-S bond. However, the latter spectrum shows two intense bands at 892 and 1390 cm^{-1}, assigned to C-COO^- stretching vibration and COO^- symmetric stretching vibration, respectively, indicating that the COOH group shortens the COO^--Ag distance and thus their Raman signals are significantly enhnaced by the plasmonic fields of the CSNC. The Raman peak at 1042 cm^{-1} is assigned to the stretching vibration of C-N bond, which is often weak in an ordinary Raman spectrum,[10d] and here its enhanced Raman intensity evidences the shortened distance between NH_3^+ and Ag. These distinct SERS enhancement and characteristic molecular vibrations strongly support the formation of helical networks between cysteine molecules through linking their COO^- and NH_3^+ groups.

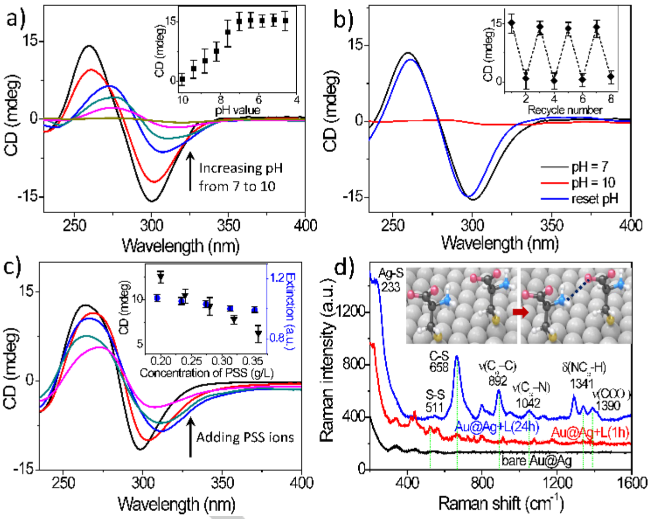

Figure 4. a) Measured CD spectra for the Au@Ag-L-cysteine complex with increasing the solution pH from 7 to 10. The inset shows the extracted maximal CD peak around 258 nm with decreasing the pH from 10 to 4. b) pH-switched CD "active" and "silence" of the complex. The inset shows the CD intensity at 258 nm by alternatively changing the pH from 7 to 10. c) Measured CD spectra for the complex with increasing the concentration of PSS from 0.20 to 0.40 g/L. The inset compares the CD intensity at 258 nm and the extinction intensity at 615 nm as a function of PSS concentration. d) SERS spectra of bare Au@Ag CSNCs (black curve) and the complex solution measured after mixing Au@Ag and cysteine for 1 h (red curve) and 24 h (blue curve). The concentrations of the Au@Ag CSNCs and cysteine are 10 nM and 1.35 μM, respectively.

Other control experiments were also carried out to further solidify our hypothesis and clarify some possibly ambiguous aspects. On the one hand, chloride ions were introduced to eliminate Ag^+ possibly existing in the hybrid Au@Ag-cysteine system, after which we observed no changes in either solution color or CD signal (Figure S4). On the other hand, a fresh Ag^+ solution mixed with L/D-cysteine well reproduces the CD spectra observed in previous studies (Figure S5) and the CD band at 360 nm related to the Ag^+…Ag^+ interaction was observed.[4b-4d] These results forcefully prove that the induced bisignate CD observed at the interband transition region of Ag in our experiment originates from the interfacial interaction of cysteine and Ag, which produces the helical networks with a new CD resonance amplified by Coulomb coupling (Figure S10). Moreover, our mechanism of generating optical activity can also be applied to other molecules (such as L/D- penicillamine) (Figure S11). Note that the mechanism proposed here differs from those previously reported ones in similar systems. e.g., Zhou et al. proposed that, the presence of chiral cysteine can induce atomic site defects in the CdTe surface to generate chiral responses.[10e] Tang's group demonstrated that the size-dependent CD responses caused by the quantum confinement effect can be observed if an optical coupling between cysteine molecules and semiconductor nanoparticles formed.[10f]

Finally, a semi-quantitative theoretical model is used to further understand the physical origin of the induced unusal CD. As concluded from our experiments, the interaction between the Au@Ag CSNC (or Ag nanosphere) and cysteine molecules leads to the formation of the new chiral conformation and the induced CD resonance. For simplicity without loss of generality, we model the molecular helical network of cysteine as a spiral molecule with two CD bands centered at ~230 and 275 nm. The chirality of the hybrid Au@Ag-spiral system can be expressed as $CD_M = Q_M^L - Q_M^R$, where Q_M^L and Q_M^R are the absorption of the system under left- and right-circularly polarized fields. Following the theoretical treatment described in SI,[10g] the chirality can be expressed as

$$CD_M = \frac{\omega \cdot \mathrm{Im}[\alpha_M] \cdot E_0^2}{|1-\bar{\alpha}\gamma|^2} 2\,\mathrm{Re}\left[(1+\bar{\alpha}^*)\frac{(1+\gamma)\Delta\alpha}{1-\bar{\alpha}\gamma}\right],$$

where α_M is the effective polarizability of the Au@Ag nanocuboid and γ is the electric susceptibility. $\bar{\alpha}$ and Δα are the averaged polarizability and the polarizability difference of the spiral molecule for the circularly polarized fields. From the above formula, it can be concluded that the CD of the hybrid system is induced by the spiral molecule (since it is proportional to Δα) and enhanced by the local field of the Au@Ag CSNC (since it is proportional to the $\mathrm{Im}[\alpha_M]$). Figure 5 shows the CD spectra obtained with the derived formula, and the results are consistent with our experimental results by reproducing the bisignate spectral profile and signal amplitude contrast.

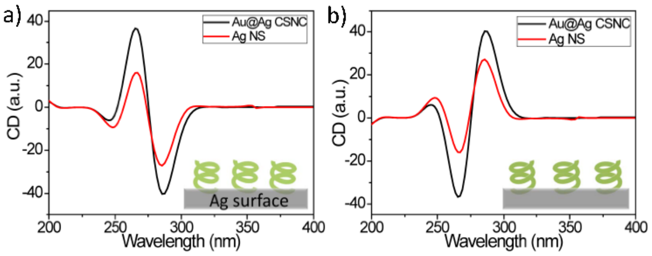

Figure 5. (a,b) Simulated CD spectra for an Au@Ag CSNC (black curves) and an Ag nanosphere (red curves) capped with vertically-aligned right-handed (a) or left-handed spiral molecules (b), respectively. The insets show the detailed models used in the simulations.

In conclusion, we report herein unusual optical activity induced in discrete archiral Au@Ag nanostructures capped with chiral cysteine molecules. Extensive experimental and theoretical investigations reveal that the induced CD is due to the formation of hydrogen-bonding-connected helical networks of chemisorbed molecules on the surface of Ag. This new CD resonance is further amplified through strong Coulomb coupling with the interband transition of Ag and enhanced by the local electric field in Au@Ag nanostructure (though the interband field enhancement is weaker compared with the intraband plasmonic enhancement). It can be switched on or off (prompted or suppressed) by controlling environmental conditions such as solution temperature, solution pH and external ions. These phenomena are beyond the scope of previously reported plasmon enhanced or induced chirality and open up fascinating opportunities for extending metal-nanostructures-enhanced CD spectroscopies to molecular structural recognition at low concentration in stereochemistry and chirality discrimination in biomedicine.

Acknowledgements

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Keywords: interband transition • optical activity • structural conformation • metal nanostructures • circular dichroism

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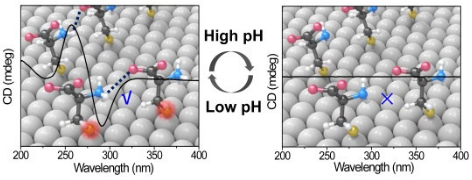

The discrete Au@Ag core-shell nanocuboids capped with cysteine molecules exhbit two bisignate circular dichroism (CD) resonances in the UV region, one corresponding to the molecular electronic CD of cysteine and the other induced unusual CD band. Comprehensive experimental and theoretical investigations reveal that the formation of extended helic networks among neighboring cysteine moelcules *via* hydrogen bonding of COO^- and NH_3^+ is the origin of the induced CD, which is dramatically amplified at the interband absorption of Ag due to Coulomb coupling and local electric field enhancement.

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