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In Situ Photoreduced Silver Nanoparticles on Cysteine: An Insight into the Origin of Chirality

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Chirality, one of the intriguing and inspiring phenomena in nature, was first observed in nanoscale materials in 2000 by Schaaff and Whetten by measuring intense optical activity in glutathione-protected gold nanoparticles (NPs).[1] A significant result toward this discovery was the controlled synthesis of a series of ligand-protected metal nanoparticle compounds (LMNPs) formed by a metal core protected with organic molecules.[2]Chiral LMNPs, such as gold and silver, are of considerable interest, because bulk Au and Ag are of face-centered cubic (fcc) structure and hence are achiral. Chiral NPs have led the way to broad applications in photonics, catalysis, drug delivery, biosensing, and many other fields.[3] Origin of chirality in chiral metal NPs is an interesting fundamental topic of research.[4]

Three possible mechanisms have been proposed to explain the chirality in LMNPs: 1) the intrinsically chiral metal core; 2) the dissymmetric field model; and 3) the chiral footprint model. Theoretical calculations suggest that the chirality can arise from an intrinsically chiral core, as well as from an achiral core placed in a chiral environment. Experimentally, ligand exchange on the LMNPs surface with chiral ligands often led to circular dichroism (CD) signals apart from the inherent CD response from the ligand itself. But the mechanism was not clear, because the metal-core structure being chiral or achiral was not known, moreover, another complication is that ligand exchange might result in alteration of the metal-core size and/or structure. Hence, chirality transferring from surfaces with symmetric or asymmetric ligands to the LMNPs is still not well understood. To date, an intriguing challenge for fundamental research on chiral LMNPs is to achieve full control of the metal-ions coordination process, the subsequent nucleation, and the particle growth at the nanoscale level throughout the synthesis process.[5]

Herein, we report that Ag^+ complexes with L- or D-isomers of cysteine (Ag^+–Cys) could be in situ photoreduced to form Ag NPs without the assistant of any other reducing agents or protecting ligands. The formation of cysteine-protected Ag NPs gives rise to an amazingly intense and consistent optical activity at the plasmonic wavelengths of Ag NPs (Figure 1). This photochemical method enables excellent spatial and temporal control for in situ observations, avoids the use of harmful strong reducing agents, can be carried out at room temperature, moreover, the light can be simply turned off at the end of the synthesis.

The photoreduction rate of $AgNO_3$ to elemental Ag in aqueous solution is very slow, but can be significantly increased by adding an organic catalyst.[6] This catalyzed photoreduction process has been successfully employed in the polymer-templated[7] and DNA-templated[8] synthesis of Ag NPs. Due to a range of functional groups (e.g., COOH, NH_2, and SH), zwitterionic amino acids are widely recognized as ideal candidates for reducing and/or modifying the NPs. A tripeptide has been designed to produce small Ag nanoplates, in which the amino acid might affect both the reduction and recognition processes and may act both as the reducing agents and protecting ligands.[9] However, few evidences have been presented on reduction of Ag^+ to Ag NPs by a single amino acid. In particular, it is known that cysteine has a certain reducing power[10] and also can act as protecting agent on NPs.[11] Because Ag^+ can form stable complexes with cysteine,[12] we reasoned that it would be possible to produce Ag NPs through photoreduction process under suitable conditions.

To test our hypothesis, Ag^+–Cys complexes of defined stoichiometry were first formed by mixing different amounts of $AgNO_3$ and L- or D-cysteine with final concentrations of 0.5 mM, which have been widely investigated by CD spec-

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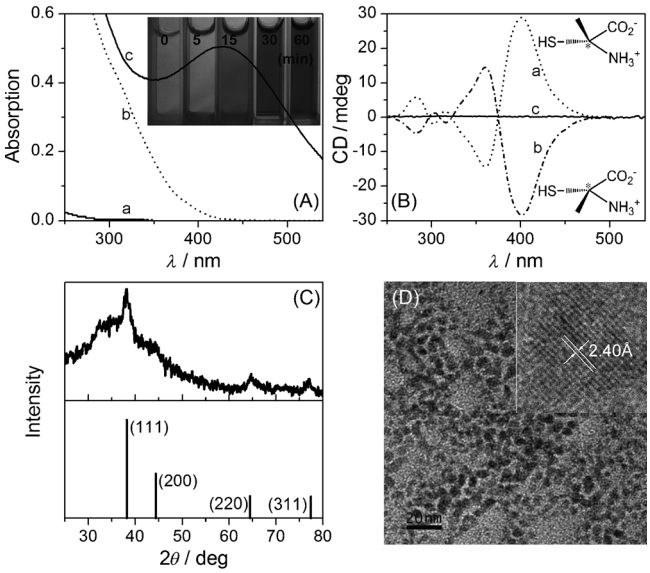

Figure 1. Characterizations on in situ photoreduction of Ag^+–Cys: A) UV/Vis absorption spectra of bare cysteine aqueous solution (a), Ag^+–Cys (b), and the photoreduced Ag NPs (c). The inserted photo shows the color changes of Ag^+–Cys solution with different exposure times; B) CD spectra of Ag NPs formed directly on the L-cysteine (a), D-cysteine (b), and racemic cysteine (c); C) XRD patterns of the as-prepared Ag NPs (top) and the well-defined fcc Ag (bottom); and D) TEM image of the photoreduced Ag NPs. The inset is a HRTEM image of a single particle. The conditions used in this system are as follows: [Cys] = 0.50 mM, [$AgNO_3$] = 0.55 mM, corresponding to $r = 1.1$ (r denotes the ratio of Ag^+ added per mole of cysteine), and $\lambda = 254$ nm UV light for 15 min exposure.

troscopy (data not shown).[12] It is known that Ag^+–Cys complexes have a 1:1 ratio of binding stoichiometry (denoted by r, i.e., the ratio of Ag ions added per mole of cysteine).[12] Preliminary observations showed that the UV exposure did not give useful information on the Ag NPs formation at $r < 1$ owing to the formation of Ag^+–Cys complexes (Figure S1 in the Supporting Information). Nevertheless, a little excess of [Ag^+] over [Cys], for example, $r = 1.1$, will activate the photoreduction process. Moreover, an interesting finding is that the photoreduction of Ag^+–Cys at $r < 1$ will occur by introducing a droplet of prephotoreduced Ag NPs at $r = 1.1$, indicating that once a metal atom, which acts as a nucleation center is formed, it acts as a catalyst for the reduction of the remaining metal ions present in the solution by autocatalysis. Our results indicate that cysteine can simultaneously act as complexing, nucleophilic, reducing, and protecting agents.

Upon mixing, the formation of Ag^+–Cys complexes at $r = 1.1$ was instantaneous, witnessed from both a dramatic increase in the UV absorbance (Figure 1A, curve b) and the significant CD signals of Ag^+–Cys complexes (Figure S1 in the Supporting Information). Exposing the Ag^+–Cys complexes to $\lambda = 254$ nm UV light for 15 min resulted in the appearance of a peak centered at approximately $\lambda = 420$ nm (Figure 1A, curve c), which is attributable to the surface plasmon resonance (SPR) of small Ag NPs forming.[8b,13] The onset of Ag NPs formation was accompanied by a color change from clear to vibrant deep yellow and then darkening to deep brown over a time period of one hour (the inset in Figure 1A), and the photoreduction process was considered complete in terms of no changes in the SPR peak intensity or shape after one hour of exposure. The XRD patterns of the as-prepared samples are all in agreement with the well-defined spectrum of fcc silver (Figure 1C), definitely demonstrating the formation of Ag nanocrystals. Both TEM and HRTEM images proved the formation of Ag NPs with diameters of about 5 nm after 15 min of UV light exposure (Figure 1D).

The most interesting is that the in situ photoreduction of Ag^+ bound to cysteine generated an intense CD signal around the SPR frequency of Ag NPs centered at about $\lambda = 405$ nm (Figure 1B, curve c), which is completely different from that of Ag^+–Cys complexes (Figure S1 in the Supporting Information)[12] and that of presynthesized large Ag NPs modified with cysteines[14]. When the exposure time increased corresponding to the increase in the size of Ag NPs, the CD peak at around $\lambda = 405$ nm presented redshift (Figure S2 in the Supporting Information). Moreover, under the same exposure time of 15 min, a larger r value corresponding to much larger Ag NPs made a larger redshift of the CD peaks at around $\lambda = 405$ nm (Figure S1B in the Supporting Information). Hence, the CD peak at about $\lambda = 405$ nm could be assigned to the coupling of Ag plasmon. The photoreduced Ag NPs by L- and D-cysteine generated two mirror symmetrical signals (Figure 1B, curves a and b), and reasonably the racemic cysteine-reduced and protected Ag NPs did not exhibit CD signals (Figure 1B, curve c). The bisignated CD peaks at about $\lambda = 405$ and 360 nm with the opposite sign and remarkably strong intensity might stand for the coupling of chiral signal of the protected ligands with the SPR of Ag NPs at both symmetric and antisymmetric hybrid modes.[15] The CD peak at $\lambda = 280$ nm was derived most likely from the chiral configuration of cysteine molecules on the surface of Ag NPs, because cysteine solely has a small CD peak at about $\lambda = 210$ nm. In addition, the coupling between the SPR of Ag NPs and chiral signal of the protected ligands is reduced,[15] because the difference in the wavelengths of the absorption peaks between cysteine ($\lambda < 220$ nm) and Ag NPs ($\lambda \approx 390$–500 nm) becomes large.

To explore the origin of chirality, we investigated the effects of pH, concentrations, and exposure times on the CD signals of in situ photoreduced Ag NPs on L-cysteine. Interestingly, this SPR-coupled CD signal can only appear under acidic conditions, and reaches the largest strength at pH of about 3.5. On the basis of the pK_a values (p$K_{a1,2,3}$ = 1.92 (CO_2H); 8.37 (SH); and 10.70 (NH_3^+)), and the isoelectric point (pI = 5.02) of cysteine,[16] the CO_2H groups are mostly deprotonated to CO_2^- at pH 3–5, whereas the deprotonation of SH are suppressed, and NH_2 is protonated to NH_3^+, maximizing the zwitterionic electrostatic interactions. This pH effects supported the zwitterionic nature for cysteines in the origin of chirality of the photoreduced Ag NPs. On the other hand, extreme acid conditions, for example, pH 2.0,

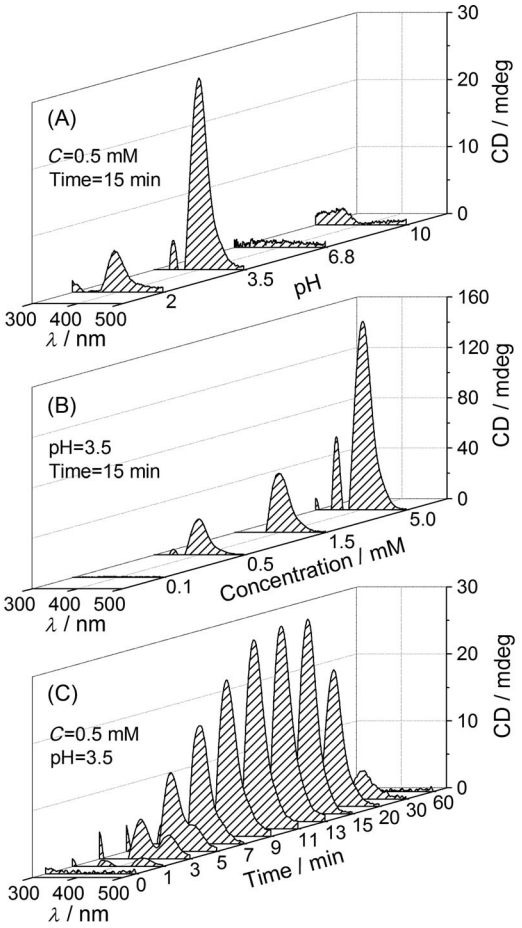

Figure 2. Effects of pH, concentrations, and exposure times on the SPR-coupled CD signals of the in situ photoreduced Ag NPs on L-cysteine.

significantly decreased the CD signal strength (Figure 2A), which might be caused by the suppression on dissociation of CO_2H groups. These results indicated that the deprotonation of CO_2H and the protonation of NH_2 both have important roles on the origin of chirality, which is consistent with the zwitterionic nature of cysteine.

The strengths of SPR-coupled CD signal have steady positive correlation with the concentrations (Figure 2B). This signal is too weak to be observed, when the system concentration is less than 0.1 mM, and increases with the system concentrations increasing. The CD intensity at about $\lambda =$ 405 nm is around 28.5 mdeg, when [Cys] = 0.5 mM, and it reaches 150 mdeg, when [Cys] = 5.0 mM. Theoretically, the CD intensity is proportional to sample concentration, however, tenfold increase in concentration of Ag^+–Cys system only makes fivefold increase in CD intensity. As the concentrations increase, the Ag^+ reduction became much easier, and the same exposure time would result in much larger Ag NPs, as demonstrated by TEM observations (Figure S3 in the Supporting Information), which might contribute to the disappearance of the CD signal. When [Cys] were larger than 5.0 mM, reaction mixture became turbid instead of bright yellow,[17] and the reduction process determined by exposure time became difficult to control. Nevertheless, when the [Cys] was 0.5 mM, and the pH was 3.5, the color of the photoreduced solution system was bright yellow (Figure 1A), and there is no large redshift in the SPR peak position of UV/Vis spectra within the exposure time of one hour, revealing that the in situ photoreduced Ag NPs did not aggregate. Hence, unless otherwise specified below, the [Cys] was 0.5 mM and the r value was 1.1. With the increase of exposure time, the CD signal first increased and became stable within 10 to 15 min (Figure 2C), and then the signal gradually weakened and finally disappeared. It appears that long exposure times allowed for the growth of small Ag NPs, which might increase the symmetry of the system. This weakens the chirality, which indicates a close relationship between the chirality and particle size.

X-ray-absorption fine-structure (XAFS) spectroscopy[18] demonstrated the existing of Ag–S bond instead of the Ag–O or Ag–N bonds in the photoreduction process (Figure 3A). FTIR spectral data also supported the formation

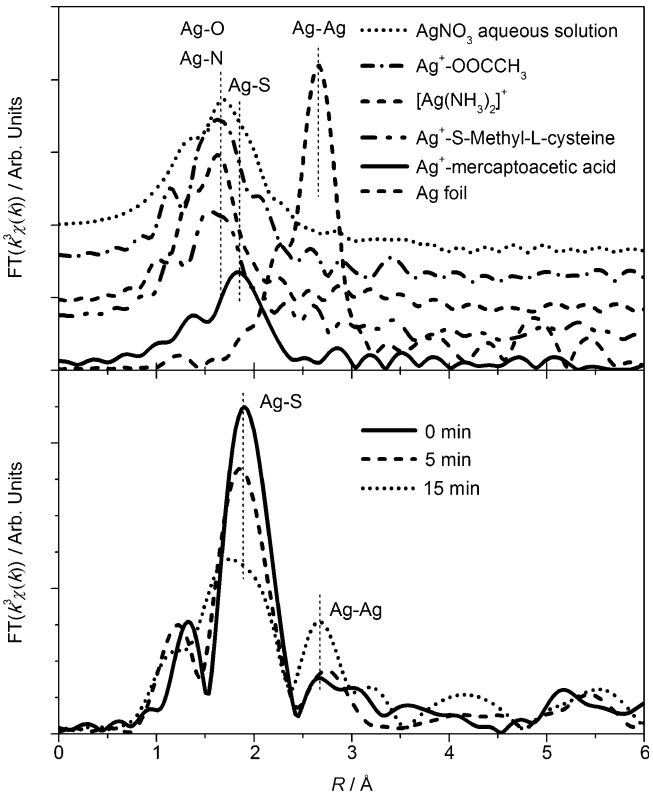

Figure 3. Formation of Ag NPs studied by in situ XAFS. Ag K-edge k^3-weighted EXAFS Fourier-transforms spectra of the A) control samples and B) the Ag^+–Cys system with different exposure time.

of Ag^+–S(R) bond in Ag^+–Cys solution, because the S–H stretching band of free Cys at $\tilde{\nu} = 2555\ cm^{-1}$ disappeared (Figure S4 in the Supporting Information). Recently, Shen et al.[12] proposed a chain-like polymeric structure with a -Ag^+-S(R)- repeat unit existing in the Ag^+–Cys solution (Figure 4A). Note that a double-stranded helical polymeric

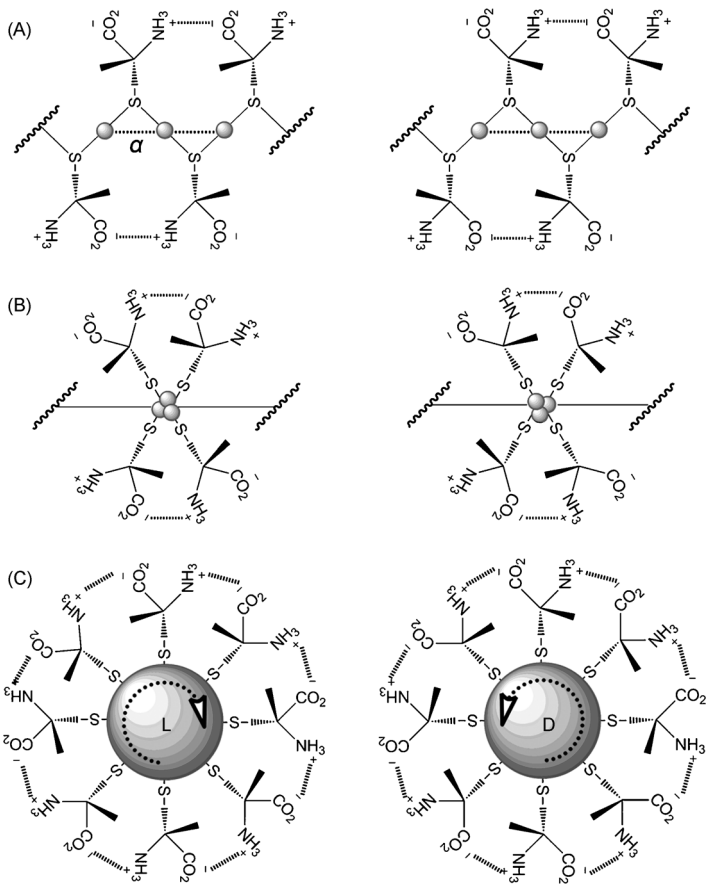

Figure 4. Hypothetical diagram of A) the electrostatic interaction and argentophilic attraction shown by dash line between adjacent ligands along the Ag^+–Cys polymeric backbone, in which α is the Ag-S-Ag angle, and the gray balls represent the Ag^+ or Ag NPs; B) the initial photoreduction of Ag^+ to Ag^0 as a nucleation center; and C) the chiral cysteine-protected Ag NPs. All left-hand side structures in figure refer to L-cysteine; right-hand side—to D-cysteine.

structure has been probed for Ag^+-D-penicillamine with zigzag chains of the -Ag^+-S(*R*)- repeat unit,[19] in which D-penicillamine is structurally similar to Cys. Moreover, the self-assembly of Ag^+–Cys into pure chiral helical nanobelts polymer[20] further evidenced a certain helicity of the Ag^+–Cys polymeric backbone in solution, which may attribute to the synergetic interplay of the electrostatic interaction among the R side chains and the $Ag^+\cdots Ag^+$ argentophilic attraction.[12,20] These two interactions should have key roles in the initial photoreduction of Ag^+ and in the origin of chirality. The electrostatic interaction at high pH would afford a larger Ag-S-Ag angle (α) than that at low pH (Figure 4A), because the electrostatic repulsion among the SR side chains now containing only CO_2^- negative charges would weaken the $Ag^+\cdots Ag^+$ argentophilic attraction. Extremely low pH may have similar effect as existing only NH_3^+ positive charges by suppressing the dissociation of CO_2H. Hence, it is more difficult to reduce Ag^+ to Ag^0 as a nucleation center at high pH or extreme low pH, which is consistent with the experimental results above.

To further investigate the intrinsic origin of chirality, instead of L-cysteine, its derivatives, including L-cysteine methyl ester (C–Cys), N-acetyl-L-cysteine (N–Cys), and S-methyl-L-cysteine (S–Cys) were explored in similar experiments (Figure S6 in the Supporting Information). Exposing the Ag^+-C-Cys system at $r=1.1$ to $\lambda=254$ nm, UV light resulted in the appearance of SPR extinction band centered at around $\lambda=425$ nm, indicating the formation of Ag NPs. And exposing the Ag^+-N-Cys system at $r=1.1$ to $\lambda=254$ nm, UV light resulted in the appearance of broad extinction from $\lambda=200$–500 nm, which has a shoulder peak at about $\lambda=420$ nm. HRTEM observations demonstrated the photoreduction of Ag^+ by C–Cys and N–Cys (Figure S7 in the Supporting Information), however, the reduced Ag by N–Cys showed an irregular shape, which might be contributed to the unusual absorption spectrum. Interestingly, no evidences on the photoreduction of Ag^+ by S–Cys was found from both the UV absorption spectrum (Figure S6A in the Supporting Information, curve c) and HRTEM (data not shown). In situ XAFS analysis clearly indicated that the photoreduction of Ag^+ occurs with the formation of Ag–Ag bonds during the exposure process, and shows the overall numbers of Ag–S bonds in the Ag^+–Cys system were decrease with the exposure time increase (Figure 3B). On the basis of these results, we may safely conclude that SH group of cysteine has greater tendency to reduce Ag^+ to Ag^0 in comparison to CO_2^- and NH_3^+ groups.[17] The oxidation site on cysteine may effectively remain at the sulfur atom, because of the presence of a lone pair of electron on S atom.[17] Above all, no SPR-coupled CD signal was observed from the UV radiation on Ag^+ complexes with C–Cys or N–Cys, implying the existence of a synergetic interplay between CO_2^- and NH_3^+ groups being responsible for the origin of chirality.

Generally, the observation of CD signals indicates either an inherently asymmetric chromophore or a symmetric chromophore in an asymmetric environment. In our case, the phenomena on the CD signal decrease along with the growth of Ag NPs (Figure 2C) might imply an achiral core of the Ag NPs with optical activity induced by a chiral adsorption pattern. The disordered aggregation will counteract the CD signal,[21] however, there is no significant aggregation of Ag NPs within the exposure time of one hour. Just recently, Zhu et al.[2a] commented that the observed chirality in $Au_n(SR)_m$ nanoparticle structures is resulted from a mixing of ligand orbitals with those of the surface gold atoms of the NPs, and therefore the chiral feature in $Au_n(SR)_m$ NPs is expected to become less prominent with increasing size. Interestingly, their prediction is consistent with our observations on in situ photoreduced Ag NPs on cysteine (Figure 2C). When the particles grow, the distribution and orientation of the surface atoms become more symmetrical. Another reason of the CD-signal decrease may be the decrease in cysteine concentration due to the consumption as reducing agents, which further supported the achiral core model. Recently, a large CD response of Ag NPs grown on chiral DNA-double stranded was observed at the

Ag NPs plasmon frequency.[22] One important similarity between this case and our system is that the metal NPs are formed and packed in low-symmetry chiral configurations, which might limit the aggregation of the NPs. The dissymmetric environment acts as a perturbing electrostatic field to break down the symmetry of the electronic states in the NPs and shows different molar extinction coefficients for the left- and right-polarized light. Hence, this inequality finally results in different magnitudes of the L- and R-rotating electric field components of light, giving rise to an optical activity corresponding to metal-based electronic transitions.[2a,3c,23]

Nanoscience is still in the discovery phase, and this is particularly true for chiral NPs. Only very few examples of well-defined optically active NPs have been synthesized.[24] In closing, it is worth speculating on the origin of chirality in in situ photoreduced Ag NPs on cysteine. At low pH, the Ag-S-Ag angle (α) became smaller, because of the $Ag^+\cdots Ag^+$ argentophilic attraction. Further, the UV radiation induced the electron transfer from sulfur to Ag^+ and resulted the formation of Ag^0 as a nucleation center, which can act as a catalyst for the reduction of the remaining metal ions. In the polymeric backbone with -Ag^+-S(*R*)- repeat units, $Ag_n{}^0$ gradually grows larger along with the increase in the number of Ag–Ag bonds and decreases in the number of the Ag–S bonds. In this process, the adsorbed cysteine molecules on Ag surface can only be arranged in one direction, because of the synergetic interplay between the CO_2^- and NH_3^+ groups, and finally resulted the origin of chirality of the cysteine-protected Ag NPs. Any change of either of the two groups to a neutral group will corrupt the synergetic interplay, break the balance of the ligand alignment, and induce the loss of the chirality. Reasonably, two isomers of cysteine resulted in two mirror symmetrical CD signals, indicating that chiral information and asymmetry at the molecular levels are transferred to the nanoscale particles. This understanding will shed light on comprehending chirality transcription from small molecules to nanoscale particles. Moreover, the SPR-coupled optical activity may pave the way for new types of "chirophotonic devices", and the use of this system for specific-target sensing by CD and surface-enhanced Raman spectroscopy is ongoing in our lab.

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Keywords: chirality · circular dichroism · cysteine · nanoparticles · surface-plasmon coupling

[1] T. G. Schaaff, R. L. Whetten, *J. Phys. Chem. B* **2000**, *104*, 2630–2641.
[2] a) M. Zhu, H. Qian, X. Meng, S. Jin, Z. Wu, R. Jin, *Nano Lett.* **2011**, *11*, 3963–3969; b) H. Yao, K. Miki, N. Nishida, A. Sasaki, K. Kimura, *J. Am. Chem. Soc.* **2005**, *127*, 15536–15543; c) Y. Zhou, Z. Zhu, W. Huang, W. Liu, S. Wu, X. Liu, Y. Gao, W. Zhang, Z. Tang, *Angew. Chem. Int. Ed. Angew. Chem. Int. Edit.* **2011**, *50*, 11456–11459; d) Y. Zhou, M. Yang, K. Sun, Z. Tang, N. A. Kotov, *J. Am. Chem. Soc.* **2010**, *132*, 6006–6013.
[3] a) C. Noguez, I. L. Garzon, *Chem. Soc. Rev.* **2009**, *38*, 757–771; b) A. O. Govorov, Y. K. Gun'ko, J. M. Slocik, V. A. Gerard, Z. Fan, R. R. Naik, *J. Mater. Chem.* **2011**, *21*, 16806–16818; c) A. Sánchez-Castillo, C. Noguez, I. L. Garzón, *J. Am. Chem. Soc.* **2010**, *132*, 1504–1505; d) Y. Li, Y. Zhou, H. Y. Wang, S. Perrett, Y. Zhao, Z. Tang, G. Nie, *Angew. Chem. Int. Ed. Angew. Chem. Int. Edit.* **2011**, *50*, 5860–5864.
[4] Y. Xia, Y. Zhou, Z. Tang, *Nanoscale* **2011**, *3*, 1374–1382.
[5] O. Pandoli, A. Massi, A. Cavazzini, G. P. Spada, D. Cui, *Analyst* **2011**, *136*, 3713–3719.
[6] H. Hada, Y. Yonezawa, A. Yoshida, A. Kurakake, *J. Phys. Chem.* **1976**, *80*, 2728–2731.
[7] B. L. Slaten, G. A. Gaddy, A. S. Korchev, J. L. McLain, E. S. Steigerwalt, G. Mills, *J. Phys. Chem., B* **2004**, *108*, 14485–14857.
[8] a) H. L. Liu, L. B. Yang, H. W. Ma, Z. M. Qi, J. H. Liu, *Chem. Commun.* **2011**, *47*, 9360–9362; b) L. Berti, A. Alessandrini, P. Facci, *J. Am. Chem. Soc.* **2005**, *127*, 11216–11217.
[9] J. Xie, J. Y. Lee, D. I. C. Wang, Y. P. Ting, *Acs Nano* **2007**, *1*, 429–439.
[10] E. C. Kendall, D. F. Loewen, *Biochem. J.* **1928**, *22*, 649–668.
[11] S. Mandal, A. Gole, N. Lala, R. Gonnade, V. Ganvir, M. Sastry, *Langmuir* **2001**, *17*, 6262–6268.
[12] J. S. Shen, D. H. Li, M. B. Zhang, J. Zhou, H. Zhang, Y. B. Jiang, *Langmuir* **2010**, *26*, 481–486.
[13] L. B. Yang, G. Y. Chen, J. Wang, T. T. Wang, M. Q. Li, J. H. Liu, *J. Mater. Chem.* **2009**, *19*, 6849–6856.
[14] T. Li, H. G. Park, H. S. Lee, S. H. Choi, *Nanotechnology* **2004**, *15*, S660–S663.
[15] Z. Li, Z. Zhu, W. Liu, Y. Zhou, B. Han, Y. Gao, Z. Tang, *J. Am. Chem. Soc.* **2012**, *134*, 3322–3325.
[16] I.-I. S. Lim, D. Mott, M. H. Engelhard, Y. Pan, S. Kamodia, J. Luo, P. N. Njoki, S. Q. Zhou, L. C. Wang, C. J. Zhong, *Anal. Chem.* **2009**, *81*, 689–698.
[17] Z. Khan, A. Talib, *Colloids Surf. B* **2010**, *76*, 164–169.
[18] T. Yao, Z. H. Sun, Y. Y. Li, Z. Y. Pan, H. Wei, Y. Xie, M. Nomura, Y. Niwa, W. S. Yan, Z. Y. Wu, Y. Jiang, Q. H. Liu, S. Q. Wei, *J. Am. Chem. Soc.* **2010**, *132*, 7696–7701.
[19] X. Jin, X. Xie, H. Qian, K. Tang, C. Liu, X. Wang, Q. Gong, *Chem. Commun.* **2002**, 600–601.
[20] C. Li, K. Deng, Z. Tang, L. Jiang, *J. Am. Chem. Soc.* **2010**, *132*, 8202–8209.
[21] Z. Zhu, W. Liu, Z. Li, B. Han, Y. Zhou, Y. Gao, Z. Tang, *Acs Nano* **2012**, *6*, 2326–2332.
[22] G. Shemer, O. Krichevski, G. Markovich, T. Molotsky, I. Lubitz, A. B. Kotlyar, *J. Am. Chem. Soc.* **2006**, *128*, 11006–11007.
[23] C. Gautier, T. Bürgi, *J. Am. Chem. Soc.* **2006**, *128*, 11079–11087.
[24] C. Gautier, T. Bürgi, *Chemphyschem* **2009**, *10*, 483–492.

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