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Continuously Tuning the Spectral Response of Chiral Plasmonic Patchy Particles through Galvanic Replacement Reaction

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Abstract: We demonstrate the continuous tuning of the circular dichroism spectra of chiral patchy particle structures fabricated by dynamic shadowing growth (DSG) using the galvanic replacement reaction (GRR), which is a wet chemical process where Au ions in solution are gradually replaced by Ag atoms in a support. It is found that the unpolarized and circular polarization optical responses generally shift to longer wavelengths as a function of reaction time. The red-shifts in the spectra are attributed to changes in the ambient refractive index, chiral patch morphology, and material composition. For reaction times less than 4 minutes, the circular dichroism spectra can be adjusted over a wide range of wavelengths in the visible and near-infrared region with only slight reductions in magnitude. Thus, the combination of dry (DSG) and wet (GRR) nanofabrication techniques offers a route to dynamically tune the spectral response of chiral plasmonic thin films.

Keywords: chiral plasmonics; dynamic shadowing growth; glancing angle deposition; colloid monolayers; wet chemistry

From ancient dichroic glass to medieval stained glass to modern theranostic tools, people have long employed the remarkable plasmonic properties of noble metal nanoparticles.[1] In spite of this extensive history, new developments continue to emerge from the fertile field of plasmonics. For example, metal nanoparticles that exhibit chirality (*i.e.*, lack reflective symmetry) have been the focus of many recent works and have garnered much attention.[2] This interest in chiral plasmonic nanoparticles and thin films has been incited by Pendry's proposal that negative refraction can be achieved for one handedness of circular polarization for strongly chiral films, even if both the permittivity and permeability values are positive over the region of interest.[3] In addition to negative refraction, chiral plasmonic materials have shown great promise for optical filtering and biosensing.[4-8] Much progress has also been made in the fabrication of chiral metal nanostructures, and many different methods have been described in the literature that meet this challenge.[2] These fabrication methods can be generally grouped into either wet chemistry techniques (*e.g.*, chiral molecule modification,[9] biomolecular self-assembly,[10] and gyroid block copolymer self-assembly[11]) and dry micro-/nanotechnology (*e.g.*, electron beam lithography,[12] photolithography,[4] Si etching,[13] and dynamic shadowing growth (DSG)[14, 15]). While different techniques have their own unique advantages and disadvantages, dry nanotechnology methods generally produce films with greater circular anisotropy.[12, 16] DSG, in particular, has demonstrated the ability to create strongly chiral films with high throughput.[17-20] However, wet chemistry and dry nanotechnology processes are not mutually exclusive, and their combination could allow for additional modification and optimization of the different chiral structures not achievable through a single process.

The galvanic replacement reaction (GRR) is an interesting wet chemical process that is a simple and efficient way to gradually replace Au ions in a solution with Ag atoms from a

support.[21] While the GRR for Au replacing Ag is the best known, GRRs are a broad class of reactions, and the mechanism behind these spontaneous reactions is always due to a difference in redox potentials. More specifically, the specific GRR for Au replacing Ag happens according to the following equation:[22]

$$3Ag(s) + HAuCl_4 \rightarrow Au(s) + 3AgCl(s) + HCl(aq), \quad (1)$$

where the standard reduction potential versus the standard hydrogen electrode is 0.22 V for the AgCl/Ag pair and 0.99 V for $AuCl_4$-/Au. This difference between the reduction potentials drives the oxidation of the template material (Ag) by the metal (Au) salt precursor. This single-step spontaneous electroless deposition process is a well-known method and has been comprehensively studied.[23] Sun and Xia have established that GRR proceeds through two different processes:[24] (1) the Ag template is dissolved as Au atoms deposit epitaxially on the surface of the template to form a seamless, hollow nanostructure with an outer boundary composed of Au/Ag alloy; (2) a dealloying process selectively removes Ag atoms from the alloyed walls, leaving a porous network of Au. Thus, the GRR offers a simple route to modify Ag nanostructures to variously create bimetallic Ag/Au structures, porous Ag/Au bimetallic structures, and porous pure Au nanostructures, where the different type of structure achieved depends on the reaction parameters (time, concentrations, etc.). This offers a potential method to tune the plasmonic properties of noble metal nanostructures by varying the material composition and morphology. Furthermore, such bimetallic structures can exhibit unique properties not found in single material nanostructures, including enhanced activity of plasmonic resonances.[25] From the discussion above, it is clear that chiral plasmonic nanostructures fabricated using dry nanotechnology methods could benefit from the application of the Au/Ag GRR, yet no such study has been performed. Therefore, we have applied the Au/Ag GRR (reaction equation 1) to

the chiral patchy particle structure fabricated using DSG, and monitored the optical response as a function of reaction time using transmission ellipsometry.[5] It is found that the unpolarized and circular polarization responses are generally red-shifted as a function of reaction time, which is a result of AgCl deposition. For reaction times less than 4 minutes, the circular dichroism spectra can be adjusted over a wide range of wavelengths in the visible and near-infrared region with only slight reductions in magnitude. Thus, GRR offers a route to dynamically tune the spectral response of chiral plasmonic thin films in the visible region.

The fabrication process for the Ag chiral patchy films begins by creating self-assembled colloid monolayers (SACMs) of polystyrene nanospheres (Polysciences, diameter of 500 nm) on glass and Si substrates. The SACMs are loaded into a vacuum deposition system such that their surface normal and the vapor incident direction form an oblique polar angle, $\theta = 86°$. Ag (Kurt J. Lesker, 99.999%) is then deposited in 30 nm increments at azimuthal angles, $\varphi = 0°$, 120°, and 240° sequentially, until a desired thickness of 120 nm at each φ is achieved. More detailed information regarding the fabrication of chiral patchy particles can be found in previous works.[14, 17] It is important to note that the quality of the obtained chiral patchy particles is directly related to the quality of the SACM used as a template. However, significant advances in SACM fabrication have been made, making colloidal self-assembly a large-scale, high throughput technique.[26] The SACM fabrication technique employed here creates consistently aligned arrays on the centimeter scale, which allows for the creation uniform chiral patchy particles over the entire film size (~1 cm^2). GRR is performed by first completely immersing each of the as-deposited Ag chiral patchy films into separate Eppendorf tubes containing 1 mL of 0.1 mM chloroaurate acid solution ($HAuCl_4.3H_2O$, 99.999%, Sigma-Aldrich). The chiral patchy particle substrates are immersed in solution for pre-determined times, corresponding with a total

immersion time of t = 1 s, 30 s, 1 min, 2 min, 3 min, 4 min, 5 min, 7 min, 10 min, 15 min, and 20 min, respectively. After removing from the test tubes at a specific time, each sample is rinsed thoroughly by DI water, dried in a N_2 stream, measured by ellipsometry, and then either re-immersed for further treatments and measurements or set aside for morphological characterization. The beam size diameter of the ellipsometer is ~2 mm and is smaller than the array size, so each ellipsometry measurement contains the optical responses of ~10^{10} chiral patchy particles.

The CD spectra for a chiral patchy particle film for different GRR times, t, at various increments over 20 minutes are shown in **Figure 1a**. It is important to note that the CD spectra are obtained through a Mueller matrix ellipsometry method that separates the linear and circular polarization contributions, as well as the birefringent from the dichroic contributions.[5] The chiral patchy particle film is a single domain structure, and therefore, the CD response is initially very strong, showing several resonances and convoluted bisignate features. As t proceeds, these features generally decrease in intensity and red-shift, and after t = 10 minutes, a significant reduction in intensity is observed. No significant changes are observed in the spectra over the t = 15 – 20 minute period. Notably, the negative peak that is initially around $\lambda \approx 700$ nm, Peak 1, red-shifts by more than 250 nm during the GRR process, and after only t = 4 minutes, it has already shifted to near λ = 900 nm (**Figure 1b**). Furthermore, the intensity of this peak does not significantly change over the range t = 0.5 – 4 minutes (**Figure 1c**), and over this same period, the peak shifts from $\lambda \approx 700 – 900$ nm. On the other hand, Peak 2 does not significantly change its spectral location over the GRR, hovering around $\lambda \approx 520$ nm, yet its intensity follows the same pattern as Peak 1 and does not significantly change over the range t = 0.5 – 4 minutes. These observations demonstrate that the GRR method offers a route to dynamically tune the CD

response of chiral plasmonic structures over a large portion of the visible and near-infrared region.

The behavior of the CD spectra during GRR is also echoed in the unpolarized transmittance spectra, as shown in **Figure 2a**. Initially several resonances can be observed as dips in the transmission spectra, and these transmission dips also generally flatten and red-shift as the GRR proceeds. Further, two significant dips appear around $\lambda \approx 700$ nm and $\lambda \approx 500$ nm at $t = 0$, and are labeled as Dip 1 and Dip 2 since they correspond with the aforementioned Peaks 1 and 2, respectively. In comparing the wavelength shifts of Dip 1 from the transmittance spectrum with Peak 1 from the CD spectrum (**Figure 2b**) as functions of t, it is found that the shifts are identical. This resonance generating Dip 1 is attributed to the localized surface plasmon resonances (LSPRs) of the noble metal nanostructures. Therefore, the shifts in the transmittances and corresponding CD spectra induced by the GRR acting on the plasmonic structures could arise from two different effects: an increase in nanostructure volume or a change in the refractive index of the material or ambient. It is important to note that the observed dips (extinction) in the transmittance spectra could have some contributions from scattering since the sizes of the patchy particles are on the order of the incident wavelengths. However, a recent investigation using finite-difference-time-domain simulations has determined that the extremely strong local circular dichroism in these patchy particles arises from the difference between the coupling of right and left-handed circular polarized light with the plasmonic modes of the chiral metal patches.[27] Thus, while some scattering may occur, the CD spectra of the pristine chiral patchy particles originate from plasmonic modes in the silver coating, and the energies of these modes change as the GRR proceeds.

In order to better understand the morphological changes in the Ag chiral patchy particles during the GRR, SEM images are taken at various stages during the reaction process. **Figure 3** shows the micrographs for t = 0, 1.5, 20 minutes. There appears to be a slight increase in porosity and surface roughness of the structures after t = 1.5 minutes. After t = 20 minutes, the patchy coating is significantly rougher and more porous, and some of the patches have been pulled off of the polystyrene beads. Additionally, new crystal structures appear on the surface of the film. Interestingly, these crystals interact strongly with the electron beam of the microscope, and change from well-defined cubic and rectangular structures to globular, amorphous structures after a few seconds of electron beam irradiation (**Figure 3d**). Image analysis software (ImageJ) can be employed to quantify the morphological changes observed in the SEM images, and it is found that the average area of the chiral patches, a_{avg}, increases as a function of GRR time. For t = 0, 1.5, and 20 minutes it was found that a_{avg} = 94 ± 7 nm^2, 101 ± 8 nm^2, and 130 ± 90 nm^2, respectively. Thus, the particle sizes increase with increasing GRR time, a factor that could contribute to the red-shifting of the CD and transmittance spectra.

Energy-dispersive X-ray spectroscopy (EDX) measurements are performed in order to confirm the composition of the patchy particles during the GRR process. Interestingly, the EDX spectra are virtually identical over the t = 0.5 - 20 minute time period, showing only the presence of Ag and Cl within the large background of C and Si (from the SACM substrates). Thus, X-ray diffraction (XRD) measurements are also used to determine the crystalline composition of the patchy particles. As expected, the chiral patchy particles show a polycrystalline Ag diffraction pattern at t = 0 (**Figure 4**). However, after t = 20 minutes, new peaks emerge that correspond with the diffraction pattern of AgCl. Thus, it is highly likely that the new crystals seen in the SEM images at t = 20 minutes (**Figure 3c**) are AgCl that are produced during the reaction. The

known reversible photochromic decomposition of AgCl could be related to the morphological changes seen in (**Figure 3d**). It is important to note that the XRD measurements are not able to detect the presence of Au in this case since the diffraction peaks of Au are completely overlapped by the peaks of Ag. It does appear that the GRR reaction occurs as described in **Equation 1** given the presence of AgCl in significant enough amounts to be detected by XRD. That is, Ag from the chiral patchy coatings is being consumed to create AgCl. However, it does not appear that the Au epitaxially replaces Ag within the patches during the GRR process, especially since EDX does not provide direct evidence for the presence of Au on the surface of the films. While it is not clear why Au does not deposit epitaxially in this case, it is suspected that the surface roughness of the deposited Ag and the presence of the polystyrene nanospheres might play a role in the abnormal behavior of the Au atoms in this structure.[28, 29] In any case, the deposition of AgCl on the chiral patches should contribute to the red-shifting of the CD and transmittance spectra by increasing the ambient refractive index surrounding the plasmonic nanostructures. The magnitude of this shift is related to the optical and morphological properties of both the plasmonic nanoparticle and adsorbing AgCl, in addition to the actual amount of AgCl deposited.

In conclusion, chiral patchy particle films have been modified by the Au/Ag galvanic replacement reaction. The reaction induces morphological changes in the Ag patchy coatings by increasing the surface roughness and particle size, creating additional pores, and depositing AgCl on the surfaces, and these changes modify the chiral LSPRs of the chiral patches. While Au or Au/Ag alloy are not detected in meaningful quantities, the GRR significantly modifies the CD spectra of the chiral patchy films in a very short time period. In general, the CD intensity decreases and the spectral features red-shift. Notably though, a negative peak shifts from $\lambda \approx$

700 – 900 nm over the reaction times t = 0.5 – 4 minutes, without a change in magnitude. Thus, as desired, the GRR method does dynamically modify the CD response of the chiral patchy particles over a wide range of wavelengths in the visible and near-infrared region. These results demonstrate that the combination of DSG for chiral structure fabrication, coupled with wet chemical methods, such as GRR, offers significant freedom and potential in the design of chiral plasmonic structures for specific applications.

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References:

1. S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. A. Requicha and H. A. Atwater, *Adv. Mater.*, 2001, **13**, 1501-1505.

2. V. K. Valev, J. J. Baumberg, C. Sibilia and T. Verbiest, *Adv. Mater.*, 2013, **25**, 2517-2534.

3. J. B. Pendry, *Science*, 2004, **306**, 1353-1355.

4. J. K. Gansel, M. Latzel, A. Frölich, J. Kaschke, M. Thiel and M. Wegener, *Appl. Phys. Lett.*, 2012, **100**, 101109.

5. G. K. Larsen and Y. Zhao, *Appl. Phys. Lett.*, 2014, **105**, 071109.

6. E. Hendry, T. Carpy, J. Johnston, M. Popland, R. Mikhaylovskiy, A. Lapthorn, S. Kelly, L. Barron, N. Gadegaard and M. Kadodwala, *Nat. Nanotechnol.*, 2010, **5**, 783-787.

7. W. Ma, H. Kuang, L. Xu, L. Ding, C. Xu, L. Wang and N. A. Kotov, *Nat. Commun.*, 2013, **4**.

8. J. K. Gansel, M. Thiel, M. S. Rill, M. Decker, K. Bade, V. Saile, G. von Freymann, S. Linden and M. Wegener, *Science*, 2009, **325**, 1513-1515.

9. A. O. Govorov, Z. Fan, P. Hernandez, J. M. Slocik and R. R. Naik, *Nano Lett.*, 2010, **10**, 1374-1382.

10. A. Kuzyk, R. Schreiber, Z. Fan, G. Pardatscher, E.-M. Roller, A. Hogele, F. C. Simmel, A. O. Govorov and T. Liedl, *Nature*, 2012, **483**, 311-314.

11. K. Hur, Y. Francescato, V. Giannini, S. A. Maier, R. G. Hennig and U. Wiesner, *Angew. Chem.*, 2011, **123**, 12191-12195.

12. C. Helgert, E. Pshenay-Severin, M. Falkner, C. Menzel, C. Rockstuhl, E. B. Kley, A. Tunnermann, F. Lederer and T. Pertsch, *Nano Lett.*, 2011, **11**, 4400-4404.

13. K. M. McPeak, C. D. van Engers, M. Blome, J. H. Park, S. Burger, M. A. Gosálvez, A. Faridi, Y. R. Ries, A. Sahu and D. J. Norris, *Nano Lett.*, 2014, **14**, 2934-2940.

14. G. Larsen, Y. He, W. Ingram, E. LaPaquette, J. Wang and Y. Zhao, *Nanoscale*, 2014, **6**, 9467-9476.

15. J. G. Gibbs, A. G. Mark, T.-C. Lee, S. Eslami, D. Schamel and P. Fischer, *Nanoscale*, 2014, **6**, 9457-9466.

16. A. G. Mark, J. G. Gibbs, T. C. Lee and P. Fischer, *Nat. Mater.*, 2013, **12**, 802-807.

17. G. Larsen, Y. He, W. Ingram and Y. Zhao, *Nano Lett.*, 2013, **13**, 6228–6232.

18. G. K. Larsen, Y. He, J. Wang and Y. Zhao, *Adv. Opt. Mater.*, 2014, **2**, 245-249.

19. Y. He, G. K. Larsen, W. Ingram and Y. Zhao, *Nano Lett.*, 2014, **14**, 1976-1981.

20. Y. He, G. Larsen, X. Li, W. Ingram, F. Chen and Y. Zhao, *Adv. Opt. Mater.*, 2015.

21. C. M. Cobley and Y. Xia, *Mater. Sci. Eng., R*, 2010, **70**, 44-62.

22. Y. Sun and Y. Xia, *Science*, 2002, **298**, 2176-2179.

23. C. Song, J. L. Abell, Y. He, S. H. Murph, Y. Cui and Y. Zhao, *J. Mater. Chem.*, 2012, **22**, 1150-1159.

24. Y. Sun and Y. Xia, *J. Am. Chem. Soc.*, 2004, **126**, 3892-3901.

25. M. B. Cortie and A. M. McDonagh, *Chem. Rev.*, 2011, **111**, 3713-3735.

26. P. Gao, J. He, S. Zhou, X. Yang, S. Li, J. Sheng, D. Wang, T. Yu, J. Ye and Y. Cui, *Nano Lett.*, 2015, **15**, 4591-4598.

27. Y. He, K. Lawrence, W. Ingram and Y. Zhao, *ACS Photonics*, 2015, **2**, 1246-1252.

28. C.-P. Chang, C.-C. Tseng, J.-L. Ou, W.-H. Hwu and M.-D. Ger, *Colloid Polym. Sci.*, 2010, **288**, 395-403.

29. W. Cai, W. Wang, L. Lu and T. Chen, *Colloid Polym. Sci.*, 2013, **291**, 2023-2029.

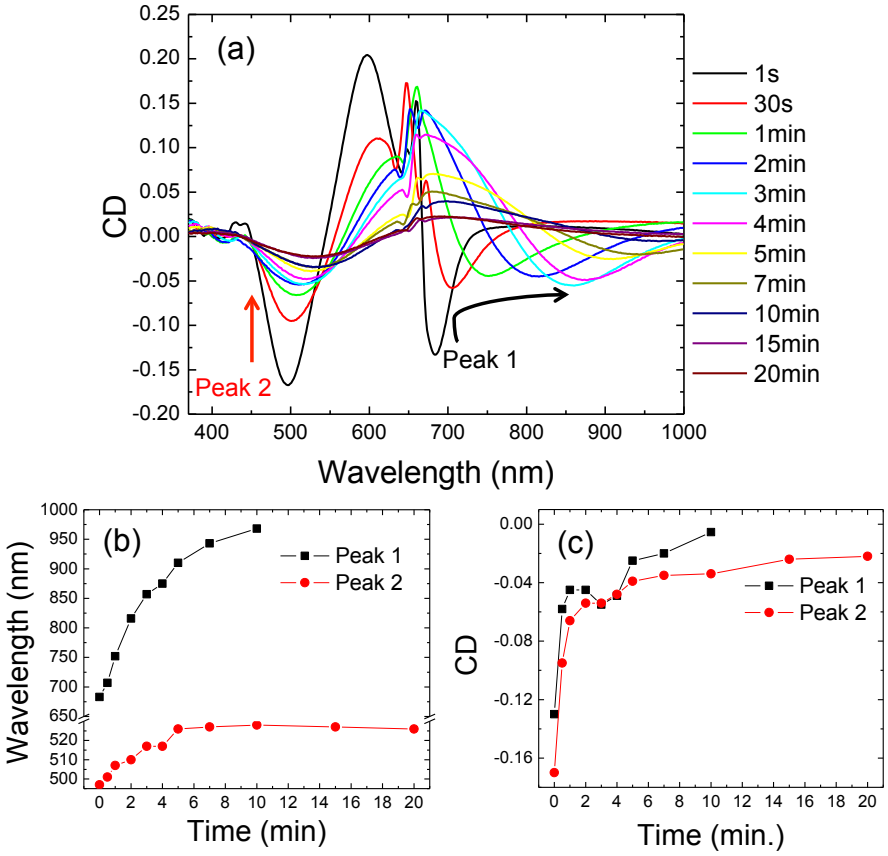

Figure 1. (a) CD spectra of the chiral patchy particles for various GRR reaction times, *t*. (b) wavelength and (c) CD intensity shifts of Peak 1 and Peak 2.

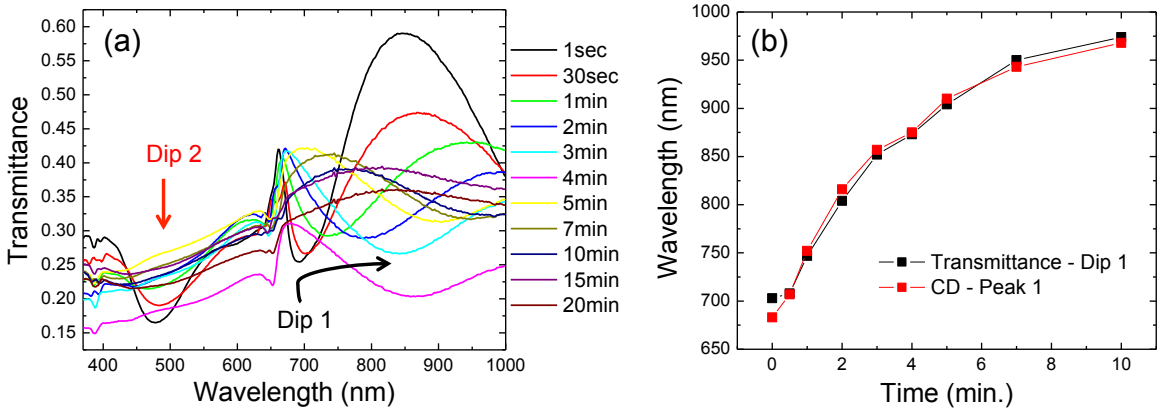

Figure 2. (a) Transmittance spectra for various GRR reaction times, *t*. (b) Comparison between the wavelength shifts of transmittance Dip 1 and CD Peak 1.

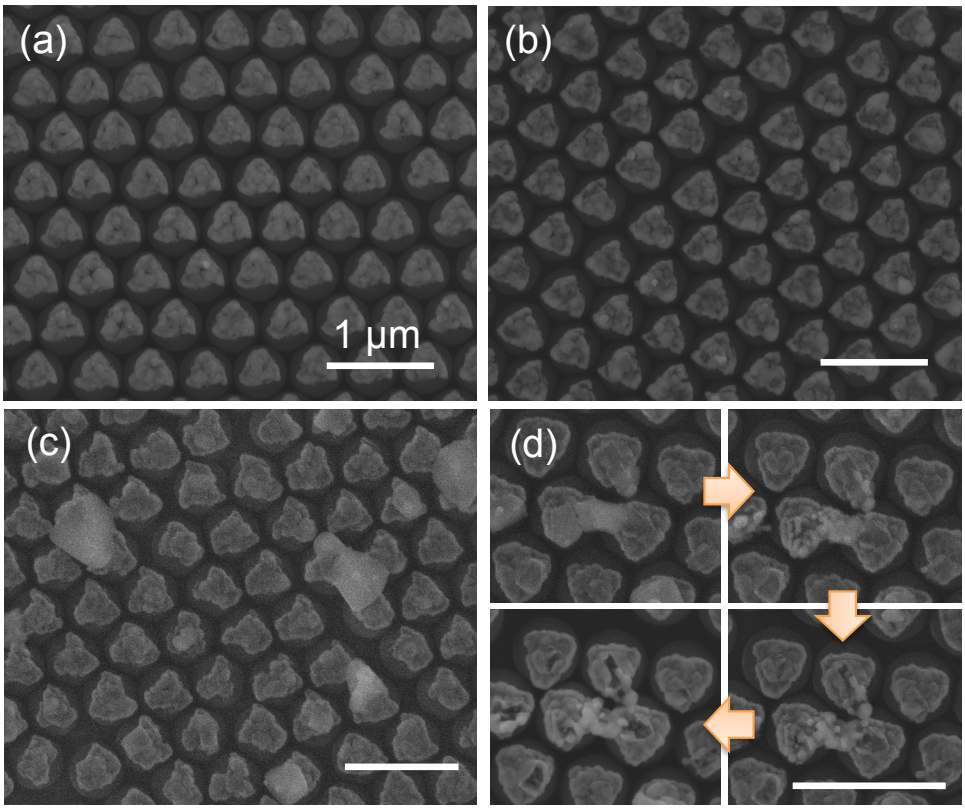

Figure 3. (a)-(c) SEM images of the chiral patchy particles at GRR times, t = 0, 1.5, and 20 minutes, respectively. (d) Sequential SEM images showing the effect of electron radiation on the surface crystals.

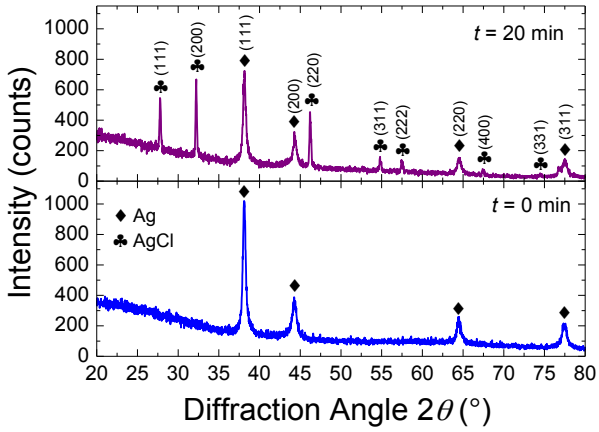

Figure 4. XRD patterns of the chiral patchy particle films at GRR reaction times $t = 0$ and $t = 20$ minutes. Peak attributions for Ag and AgCl are from card numbers 00-004-0783 and 00-31-1238, respectively.

TOC entry: We demonstrate the continuous tuning of the circular dichroism spectra of chiral patchy particle arrays using the galvanic replacement reaction.