Neat and Complete: Thiolate-Ligand Exchange on a Silver Molecular Nanoparticle

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S *Supporting Information*

ABSTRACT: Atomically precise thiolate-protected noble metal molecular nanoparticles are a promising class of model nanomaterials for catalysis, optoelectronics, and the bottom-up assembly of true molecular crystals. However, these applications have not fully materialized due to a lack of ligand exchange strategies that add functionality, but preserve the properties of these remarkable particles. Here we present a method for the rapid (<30 s) and complete thiolate-for-thiolate exchange of the highly sought after silver molecular nanoparticle $[Ag_{44}(SR)_{30}]^{-4}$. Only by using this method were we able to preserve the precise nature of the particles and simultaneously replace the native ligands with ligands containing a variety of functional groups. Crucially, as a result of our method we were able to process the particles into smooth thin films, paving the way for their integration into solution-processed devices.

Noble metal molecular nanoparticles (MMNPs),[1] or atomically discrete nanoclusters, possess a precise molecular formula characterizing the type and number of metal atoms in their core, ligands on their surface, and overall superatomic charge.[2−4] The discovery of these remarkably precise materials,[5] whose structure is absolutely determined[6−8] and feasible to model,[9−13] brought hope of a revolution in the understanding of nanoparticle catalysis,[14−16] optical and charge transport properties,[2,17,18] and even the creation of a new class of functional hybrid solids built from truly molecular nanoparticle crystals.[19] However, MMNPs are usually synthesized with capping ligands and solvents that are unsuitable for the end application. While ligand exchange strategies have become an essential postsynthetic modification tool for tuning the surface properties of *normal* NPs,[20−24] the situation is diametrically different in the case of MMNPs, where ligand exchange produces a heterogeneous ligand shell (i.e., an imprecise structure)[25−32] and even instability in the particle size.[33] The challenge is more urgent with Ag molecular NPs (AgMNPs), where no ligand exchange process, partial or complete, exists. Thus, without novel ligand exchange strategies suitable for MMNPs, this promising class of nanomaterials will continue to remain at the periphery of application space.

With this motivation in mind, we devised a novel unitary exchange process for the rapid and complete thiolate-for-thiolate ligand replacement in one of the most sought after

AgMNPs systems, the so-called intense broadly absorbing nanoparticle $[Ag_{44}(SR)_{30}]^{-4}$,[34] which finally extends the materials' utility to the realm of practical device processing.

Among all the fully resolved AgMNPs, $[Ag_{44}(SR)_{30}]^{-4}$ stands out[35] due to its remarkable multipeak broad band and large cross section absorptivity,[34] long-lived charge-separated excited state,[36] intriguing crystal structure,[37,38] and semiconducting nature.[39] All these properties have made the particle a potentially important material in light harvesting and optoelectronic devices, which require solution processing into morphologically smooth thin films. In its most stable form, up to a year at ambient conditions, $[Ag_{44}(SR)_{30}]^{-4}$ NPs are produced in highly basic aqueous solutions with ligands appended with hydrophilic electron-withdrawing nitro and carboxylate functional groups,[39] conditions that result in films of poor morphology. The exchange method described herein enables the transfer of $[Ag_{44}(SR)_{30}]^{-4}$ in high concentrations into volatile organic solvents resulting in a smooth solution-processed film and provides versatility to substitute the native ligands with ligands containing a variety of functional groups that device researchers would need in order to optimally design interparticle electronic coupling and interfacial charge transfer.

The MMNPs used in this study were synthesized using a modified version of our previously published method.[39] In a 20 mL vial, 5,5′-dithiobis(2-nitrobenzoic acid) (DTNBA) was reduced to 5-mercapto-2-nitrobenzoic acid (MNBA) with a fresh solution of sodium borohydride in water before the addition of the silver nitrate aqueous solution. The reaction was allowed to stir for ∼1 h during which the formation of the $[Ag_{44}(SR)_{30}]^{-4}$ NPs was complete. The as-synthesized NPs were purified by precipitation with the addition of methanol, and then the purified NPs were redispersed in a 1 M sodium hydroxide aqueous solution, where they are highly stable, with concentrations of 4.57 mg/mL. Further details of the synthetic protocol are available in the Supporting Information (SI). Ligand exchange was then performed by adding 1 mL of this solution to a solution of dichloromethane (DCM, 1 mL) and ethanol (1 mL) containing 0.013 mmol of the desired aryl thiol and 0.007 mmol of tetraphenylphosphonium bromide under vigorous stirring. In less than 30 s, the clear organic phase turned dark, as depicted in the schematic in Figure 1a, indicating the phase transfer while the aqueous phase turned clear yellow which is the color of free MNBA ligands. More
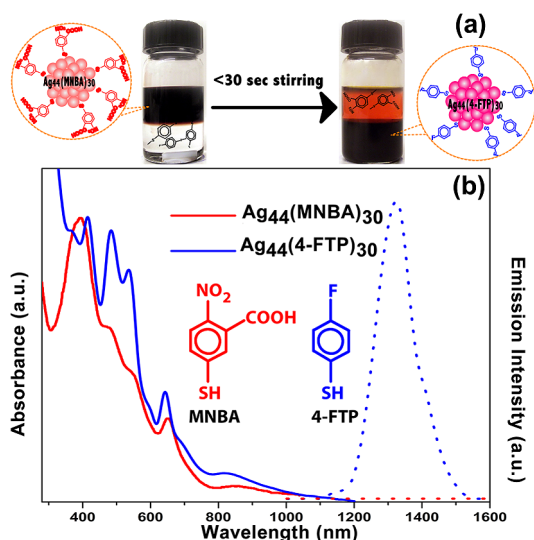
Figure 1. (a) Schematic of the ligand exchange procedure showing how the $[Ag_{44}(SR)_{30}]^{-4}$ NPs are transferred from water to DCM upon ligand exchange. (b) UV−Vis absorbance (solid curves) and emission (dashed) spectra of $[Ag_{44}(SR)_{30}]^{-4}$ NPs before (red) and after exchange (blue). The inset shows the molecular structure of the two ligands. The changes in the optical absorption spectra near the 400 nm region are due to the loss of the original ligand that contains an −NO$_2$ group, which absorbs at that wavelength.

than 94% (molar ratio) of the original NPs are exchanged through this process. The presence of ethanol in the organic phase is essential to accomplish the phase transfer of the NPs from water to DCM. The NPs in the organic phase are then decanted and purified by centrifugation after adding ethanol as a flocculent. Then, the NPs can be dispersed in acetone, DCM, or dichlorobenzene at various concentrations. This ligand exchange is the first rapid (<30 s) and complete exchange reported on MMNPs of Ag.

As a first example, the transfer was performed using 4-fluorothiophenol (4-FTP) in the organic phase. We chose this ligand for two practical reasons. First, 4-FTP seems to be a promising ligand for charge transport applications,[40] but the $[Ag_{44}(4\text{-}FTP)_{30}]^{-4}$ NPs were unstable for prolonged periods thus severely impacting their utility. Thus, we sought to overcome this limitation by "storing" the particle in a very stable form[39] that can be exchanged on demand. Another reason for choosing 4-FTP is that it contains a fluorine heteroatom that is chemically distinguishable from the original MNBA ligand, thus facilitating the investigation of the exchange process. UV−Vis optical absorption spectroscopy (Figure 1b) shows that $[Ag_{44}(SR)_{30}]^{-4}$ NPs retained all the optical features expected of the particle.[34,39] Notably as well, the emission spectrum of the exchanged MMNP in DCM shows a marked intensity enhancement over the original particle in water. The absence of the $[Ag_{44}(SR)_{30}]^{-4}$ NPs' emission in water may be attributed to dipolar interactions between water and the charge-transfer excited state of the NPs.[36,41]

Encouraged by the successful transfer of $[Ag_{44}(SR)_{30}]^{-4}$ to the organic phase, we investigated the composition of the exchanged particle. We performed negative mode ESI-MS to find the mass of the NPs after ligand exchange with 4-FTP. The ionization spectrum in Figure 2 shows the 4- peak along with the calculated isotopic pattern. The very good agreement between the two demonstrates that all the original MNBA
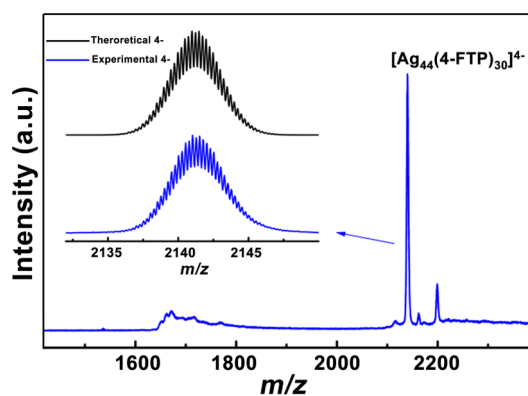
Figure 2. Negative mode ESI-MS of the NPs after exchange with 4-FTP thiols. Inset shows the expansion of the −4 charge state in comparison with the calculated isotopic pattern of $[Ag_{44}(SR)_{30}]^{-4}$.

ligands on the particles have been shed and replaced with 4-FTP. The full spectrum is shown in Figure S1 in the SI.

In an effort to further corroborate the total ligand exchange, we performed both XPS and CHN compositional analyses on the $[Ag_{44}(SR)_{30}]^{-4}$ NPs before and after exchange (Figures S2 and S3). After exchange, the clearly present nitrogen of the MNBA ligands is absent, while the fluorine peak, absent prior to the exchange, appears prominently. Furthermore, we performed ^{13}C NMR to monitor the distinguished signature of the carbonyl peak present in the original particles at ∼175 ppm (Figure S4). The peak was completely undetectable after the exchange, indicating the complete replacement of the native ligands by the incoming ones. Take together, ESI-MS and elemental analyses aided by ^{13}C NMR present robust evidence for the complete ligand replacement brought about by the ligand exchange strategy implemented in this work.

Remarkably, the ligand exchange rate for $[Ag_{44}(SR)_{30}]^{-4}$ is unlike anything observed in Au MMNPs systems. For instance, in one report on Au$_{25}$(SR)$_{18}$, it required at least 12 h during which an average of eight ligands were exchanged.[26] No thiol-for-thiol exchange has been reported for other AgMNPs systems for comparison. Such high exchange rates may be due in part to a *dissociative* process whereby the original ligands become detached from the NP prior to the attachment of the incoming ligands.[42] This mechanism is consistent with our observation when the ligand exchange experiment is conducted in the absence of thiol ligands in the organic (lower) phase. In this case NPs precipitate at the water−organic interface leaving behind free MNBA ligands in the aqueous (upper) phase (Figure S5).

The same postsynthetic ligand exchange procedure was extended to other aryl thiols, such as 4-nitrothiophenol (4-NTP) and 2-naphthalenethiol (2-NT), of high optical extinction coefficients and different electron withdrawing strengths in order to confirm the generality of the procedure reported here. Figure 3 shows the UV−Vis absorption spectra of the $[Ag_{44}(SR)_{30}]^{-4}$ NPs using the various ligands. The ligand exchanges were complete in all cases as confirmed by ESI-MS (see Figures S6 and S7 in the SI), pointing toward the versatility of the approach at appending the functionality of the NPs while preserving their molecular nature.

It should be also noted that exchange with nonaryl thiols causes a loss in the unique $[Ag_{44}(SR)_{30}]^{-4}$ optical features (Figure S8, SI) of the particle suggesting that the ligand's benzene ring plays an important role in the stability of the
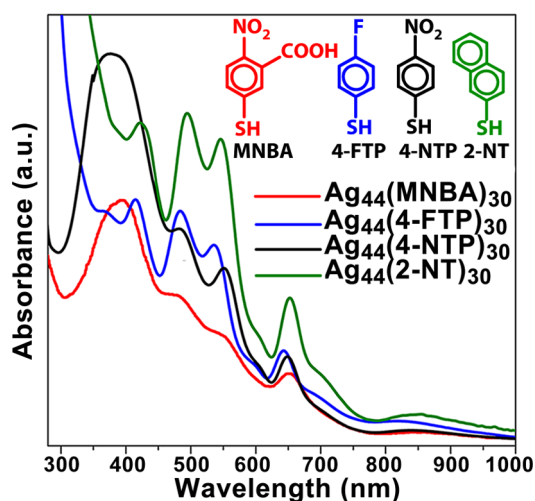
Figure 3. UV−Vis absorption spectra of $[Ag_{44}(SR)_{30}]^{-4}$ NPs before and after exchange with various ligands. The inset shows the molecular structures of the four ligands. The characteristic peak at ∼400 nm for of 4-NTP and MNBA is emanating from the ligand's absorption due to the −NO$_2$ group.

particle. We are currently investigating the size and purity of the nonaryl thiol exchanged particles.

Finally, an important outcome of our ligand exchange strategy is the transfer of $[Ag_{44}(SR)_{30}]^{-4}$ to solution conditions more appropriate for thin film processing, while basic aqueous solutions can still serve as useful particle storage media prior to processing. Thin films of particles spin-coated directly from an aqueous solution on silicon oxide substrates display a very rough surface topology (rms = 24 nm), as shown by AFM (Figure 4), compared to thin films made of ligand exchanged
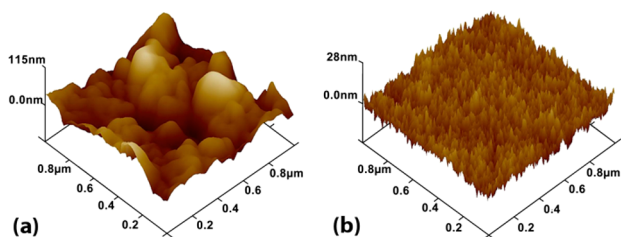
Figure 4. 3D AFM images of as-prepared $[Ag_{44}(SR)_{30}]^{-4}$ thin films before and after ligand exchange.

$[Ag_{44}(SR)_{30}]^{-4}$ MMNPs (rms = 0.2 nm), which present a smooth surface morphology as a prerequisite for any potential optoelectronic device applications of this particle.

In summary, we have demonstrated a rapid process for the total exchange of ligands on highly stable water-soluble $[Ag_{44}(SR)_{30}]^{-4}$ MMNPs to conditions suitable for solution processing of smooth thin films. The capability to tailor the terminal functionality[20] of molecular nature opens avenues for exploring solution-processed device applications of this promising class of nanoparticles.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and ESI-MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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