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Isotopic Exchange of Atomically Precise Nanoclusters with Materials of Varying Dimensions: From Nanoscale to Bulk

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silver nanoclusters (NCs) with materials of different dimensions, namely, NCs, plasmonic nanoparticles (NPs), and bulk metals, all made of silver. Isotopically pure ${}^{109}Ag_{25}(DMBT)_{18}^{-}$ and ${}^{107}Ag_{25}(DMBT)_{18}^{-}$ (DMBT is 2,4dimethyl benzene thiol) were reacted with Ag NPs of different sizes in the range of $\sim 2-11$ nm, protected with the same ligand. The exchange of ¹⁰⁷Ag/¹⁰⁹Ag atoms in the NC was monitored using electrospray ionization mass spectrometry. The reaction kinetics was analyzed by fitting the temporal evolution of the reactant concentration to a kinetic model. The reaction timescales of NC-NP reactions were significantly longer compared to those of the NC-NC exchange process under similar conditions. Differences



between NC-NC exchange and NC-NP exchange highlighted the importance of the structure in controlling the reaction. Moreover, isotopic exchanges of the NC were also studied with the bulk metal to obtain a complete understanding of how the kinetics of atom transfer varies upon changing the size of the reacting partner from nanoscale to bulk.

1. INTRODUCTION

Atomically precise nanoclusters (NCs) are a class of nanomaterials that are gaining importance due to their precise structures and unique properties.¹⁻¹² These NCs are composed of a metal core capped by ligand monolayers. One of the growing areas of research is exploring the chemical reactions of these NCs.¹³ Ligand exchange^{14–18} and metal exchange^{17,19–21} reactions of NCs have been explored by various research groups. Intercluster reactions have established that NCs can react just as molecules.^{13,22,23} Au₂₅(SR)₁₈⁻ and Ag44(SR)30⁴⁻ (SR is a thiolate ligand) react spontaneously to form alloy NCs as the product.²² Similar reactions were also observed between $Au_{25}(SR)_{18}^{-}$ and $Ag_{25}(SR)_{18}^{-,23,24}$ Inter-cluster reactions were also used to create bimetallic^{22,23,25} and trimetallic NCs.²⁶ Literature studies suggest that a possible route of such reactions is through the exchange of metal or metal-ligand fragments.²² Monolayers of ligands, protecting the surface of the NCs, are dynamic,²⁷ and the metal-ligand interface plays a decisive role in controlling such reactions of NCs.²⁸ Zhang et al. further showed that collisions between NCs are essential for such reactions to occur.²⁹ Li et al. also demonstrated intramolecular metal-exchange pathways in NCs.³⁰ However, a complete understanding of the mechanism of reactions of NCs is still elusive.

Recent studies revealed that there can also be specific interactions between NCs and nanoparticles (NPs). Ag44(SR)30⁴⁻ NCs interact with gold nanorods and form shells of NCs surrounding the nanorods.³¹ However, the

possibilities of atomic exchange have remained unexplored in this case. In another report, Bose et al. reported the formation of superlattices by the reaction of $Au_{25}(SR)_{18}^{-}$ with AgNPs due to the formation of uniformly sized alloy NPs by atom transfer between NCs and NPs.³² Kazan et al. showed that doping in NCs can occur by a reaction with metal surfaces.³³ From such studies, it is clear that NCs behave differently in the case of NC-NC, NC-NP, or NC-bulk surface reactions, and in each case, the reactions are guided by specific driving forces. However, further research in this area is required to address how the mechanism, kinetics, and dynamics are affected during reactions of NCs with particles of different size regimes.

Isotopic exchange reactions have been widely used to understand dynamics in the structures of proteins and polymers.^{34–37} Similarly, isotopic exchange in NCs also resolved their structural dynamics.^{38,39} Two $Ag_{25}(DMBT)_{18}$ NCs, prepared with isotopically pure ¹⁰⁷Ag and ¹⁰⁹Ag, respectively, reacted to produce isotopically mixed $Ag_{25}(DMBT)_{18}^{-.40}$ The isotopic exchange was similar to the exchanges observed in H₂O and D₂O, which revealed that NCs indeed behave as simple molecules. Such isotopic exchanges in

Received: March 13, 2021 **Revised:** July 8, 2021 Published: July 19, 2021





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Figure 1. (A) Schematic showing NPs of increasing sizes, (B,C) ESI MS of (a) parent isotopic NCs, ${}^{107}Ag_{25}(DMBT)_{18}^{-}$ and ${}^{109}Ag_{25}(DMBT)_{18}^{-}$, respectively, and products formed by the reaction of the isotopic NCs with (b) ~11, (c) ~4, (d) ~2 nm AgNPs, and (e) NC (made from naturally abundant Ag) at 1:5 molar ratio in each case. (D) Plot showing the extent of isotopic exchange (%) as a function of the ratio of the concentration of NPs (C_{NP}) and concentration of isotopic NCs (C_{NC}°) used in the NC–NP and NC–NC reactions.

NCs were driven by their entropy of mixing and were distinctly different compared to bimetallic intercluster atomic exchanges of different metals, which are mainly driven by enthalpy.²² However, the isotopic exchange in NCs upon reaction with classical NPs and bulk metals was not explored earlier. NPs exhibit different sizes, facets, stability, and surface area. Similarly, bulk metals also offer different interfaces for the reaction. The isotopic exchange in each of these cases is expected to show different behaviors. A complete study of the isotopic exchange of NCs with materials of different sizes will provide further insights into how the spontaneous atom exchange of NCs varies with the size of the reacting material.

In this work, we studied the isotopic metal atom exchange kinetics of NCs upon reaction with NPs of different sizes and demonstrated how the kinetics of reactions change with an increase in the size of the reacting particles. We used isotopically pure ${}^{107}Ag_{25}(DMBT)_{18}^{-109}Ag_{25}(DMBT)_{18}^{-109}$ (DMBT is 2,4-dimethyl benzene thiol) and Ag NPs protected by DMBT (AgNPs@DMBT) in the size range of ~2-11 nm, made from isotopically mixed (natural) Ag, for our reaction. The isotopic exchange was studied using high-resolution electrospray ionization mass spectrometry (ESI MS). We further explored the isotopic exchange in NCs by the reaction with Ag foil and Ag powder to understand how the exchange kinetics is affected upon reaction with bulk materials as well. The exchange was also studied after forming a self-assembled monolayer of DMBT ligands on the Ag foil, which also highlighted the role of the protecting ligands or the ligandmetal interface in controlling the atom transfer process.

2. EXPERIMENTAL METHODS

2.1. Materials. Silver nitrate (made of naturally abundant Ag) was purchased from RANKEM, India. 2,4-DMBT, tetraphenyl phosphonium bromide (PPh₄Br), and sodium borohydride (NaBH₄) were purchased from Sigma-Aldrich. Ag foils (>98% purity) were obtained from the local market and Ag powder of size ~2–3.5 μ m was obtained from Sigma-Aldrich. The solvents used were of high-performance liquid chromatography grade. Isotopically pure ¹⁰⁷Ag (98%) and ¹⁰⁹Ag (98%) foils were purchased from Cambridge Isotope Laboratories, Inc.

2.2. Synthesis of ¹⁰⁷Ag₂₅(DMBT)₁₈⁻ and ¹⁰⁹Ag₂₅(DMBT)₁₈⁻. Isotopically pure ¹⁰⁷Ag₂₅(DMBT)₁₈⁻ and ¹⁰⁹Ag₂₅(DMBT)₁₈⁻ NCs were synthesized using isotopically pure ¹⁰⁷AgNO₃ and ¹⁰⁹AgNO₃ salts and following the previously established synthetic protocols.^{40,41} Details of synthesis are mentioned in the Supporting Information, and ESI MS of the NCs is presented in Figure S1.

2.3. Synthesis of AgNPs. DMBT-protected AgNPs (referred to as AgNPs@DMBT) were synthesized by modifying the conventional protocols known for the synthesis of AgNPs.^{42,43} In a typical synthesis, 25 mg of AgNO₃ (commercially available, made from naturally abundant Ag) was dissolved in 0.5 mL of water, and 58 μ L of 2,4-DMBT in 10 mL of MeOH was added to it. Subsequently, Ag was reduced to its zero-valent state by slowly adding a freshly prepared NaBH₄ solution in 8 mL of ice-cold water. Two sets of syntheses were carried out by using different quantities of NaBH₄ (35 and 25 mg) to alter the size of the resulting NPs.

The reaction mixture was stirred for about 12 h at room temperature. The as-synthesized particles were first precipitated and then repeatedly washed with methanol. Finally, the AgNPs@DMBT were obtained as dark brown precipitates. These NPs were soluble in dichloromethane (DCM) and further characterized by using UV-vis and high-resolution transmission electron microscopy (HRTEM) (Figure S2A,B). The plasmonic nature of the particles was reflected in their UV-vis spectra. A particle size distribution of 1.8 ± 0.5 and 3.9 ± 1.2 nm was observed in the HRTEM images of the NPs synthesized using 35 and 25 mg of NaBH₄, respectively. Another synthesis was performed by slightly altering the precursor quantities with 50 mg of AgNO₃, 10 µL of 2,4-DMBT, and 25 mg of NaBH₄. AgNPs@DMBT of slightly larger size were formed in this case, which showed a reduced solubility in DCM. Therefore, they were dispersed in DCM and subsequently characterized using UV-vis and HRTEM (Figure S2C). These AgNPs showed a particle size distribution of 11.2 \pm 3.1 nm. The AgNPs@DMBT were stable for weeks when stored in a refrigerator under dark conditions. The sizes of the particles refer to the metal core diameter observed in HRTEM images. The binding of the DMBT ligands on the surface of the AgNPs was confirmed from Raman spectroscopic studies, as shown in Figure S3. Upon functionalization of the AgNPs, the S-H bond of DMBT was replaced by an Ag-S bond, which was proved by the absence of the S-H stretching peak.

2.4. Reaction between NCs and AgNPs. For carrying out the reactions of the NCs with AgNPs, first, stock solutions of 1 mg/mL were prepared for all the particles. Then, $20 \ \mu$ L of the stock NC solution was mixed with 20, 40, 60, and 100 μ L of the stock NP solution, and the reaction mixture was appropriately diluted with DCM, keeping the total volume as 5 mL. This allowed reactions to occur at different NC/NP concentrations (i.e., 1:1, 1:2, 1:3, and 1:5, respectively in w/v). A similar procedure was followed for the reaction with AgNPs of the three different sizes.

2.5. Preparation of Monolayer-Protected Foils. Ag foils were first washed with soap water and then cleaned with methanol to remove the surface contaminants. The Ag surface was further cleaned with acetic acid and again with methanol. The cleaned Ag foils were then dried by purging with N₂ gas. Ag foils of size 1 cm \times 1 cm were used in our experiments. For preparing the monolayers on the foils, the cleaned Ag foils were soaked in a methanolic solution of the thiol (1 mM). It was kept undisturbed overnight, and then, the excess thiol was washed using methanol. The cleaned monolayer-protected foils were then dried under N₂ gas.

2.6. Reaction with Bare and Monolayer-Protected Foils. 20 μ L of the stock (1 mg/mL) NC solution was diluted with DCM to a final volume of 5 mL. Bare and monolayer-protected foils were then immersed in this NC solution, and the reaction was monitored with time.

2.7. Reaction with Ag Powder. From the stock NC solution (1 mg/mL), 20 μ L of the sample was taken out and diluted in DCM to a total volume of 5 mL. To this solution, Ag powder of desired mass was added, and the reaction was monitored with time.

3. RESULTS AND DISCUSSION

3.1. Reaction of Isotopic NCs with Plasmonic NPs. To investigate the interparticle isotopic exchange between sub-nanometer-sized NCs and classical plasmonic nanomaterials,

we chose $Ag_{25}(DMBT)_{18}^{-}$ and AgNPs@DMBT with increasing size as our systems of study (Figure 1A). Metallic NPs show different facets and distribution of capping ligands on the NP surface compared to NCs. Moreover, as conventional NPs are larger compared to atomically precise NCs, they are expected to exhibit more stability due to their reduced surface area. All such factors may significantly alter the dynamics and kinetics of exchange compared to intercluster isotopic exchanges.

We present the essential characterization data of the materials used, although briefly and that too in the Supporting Information. We prepared isotopically pure ${}^{107}Ag_{25}(DMBT)_{18}$ and ${}^{109}Ag_{25}(DMBT)_{18}^{-1}$. The ESI MS data of the samples confirm the purity of ${}^{107}Ag_{25}(DMBT)_{18}^{-1}$ (Figure 1Ba) and ¹⁰⁹Ag₂₅(DMBT)₁₈⁻ (Figure 1Ca), which show peaks centered at m/z 5142 and m/z 5192, respectively Full-range mass spectra of the systems are presented in the Supporting Information (Figure S1). The AgNPs@DMBT were made from naturally abundant Ag, which contained ¹⁰⁷Ag and ¹⁰⁹Ag in the ratio 51.8:48.2. Three AgNPs@DMBT systems of average sizes, 1.8 ± 0.5 , 3.9 ± 1.2 , and 11.2 ± 3.1 nm, were used in our study. TEM images of the AgNPs and particle size distribution from TEM are presented in Figure S2. These are referred to as ~2, ~4, and ~11 nm AgNPs, respectively, in the subsequent text. The optical absorption spectra of the AgNPs are also presented in Figure S2, which showed that the particles are plasmonic in nature. The synthetic protocol and characterization of the NCs and the NPs were discussed in the Experimental Methods. Note that Ag NPs of lower sizes exhibiting plasmonic behavior have also been reported earlier.44 The surface plasmonic nature of the ~ 2 nm AgNPs also supported that the sample did not contain any significant contribution from NCs. Isotopically pure NCs $[{}^{107}Ag_{25}(DMBT)_{18}^{-}/{}^{109}Ag_{25}(DMBT)_{18}^{-}]$ were mixed with AgNPs@DMBT at varying NC: NP concentrations (w/v). We monitored the isotopic exchange in the NC by using ESI MS. Time-dependent ESI MS was performed on the reaction of ${}^{107}Ag_{25}(DMBT)_{18}^{-}/{}^{109}Ag_{25}(DMBT)_{18}^{-}$ with different AgNPs@DMBT NPs: ~2 (Figure S4), ~4 (Figure S5), and \sim 11 nm (Figure S6) at NC/NP mixing ratios of 1:1, 1:2, 1:3, and 1:5, respectively, in each case. Mixing ratios are given in terms of w/v concentration of the particles. Upon mixing the solutions of 107 Ag₂₅(DMBT)₁₈⁻ and AgNPs@DMBT, isotopic exchange of 107 Ag with 109 Ag occurred in the NCs. Due to the exchange of ¹⁰⁷Ag with ¹⁰⁹Ag, the parent peak distribution of $^{107}\text{Ag}_{25}(\text{DMBT})_{18}^{-}$ (m/z 5142) broadened gradually and shifted to a higher mass with the progress of the reaction and finally attained an equilibrium state after about 1 h (Figures S4-S6, panel a in each case). Similar results were also obtained when ¹⁰⁹Ag₂₅(DMBT)₁₈⁻ was reacted with AgNPs@ DMBT of different sizes (Figures S4-S6, panel b in each case). In this case, the parent peak for ${}^{109}Ag_{25}(DMBT)_{18}$ (m/z 5192) broadened and shifted to lower mass, with the progress of the reaction due to the exchange of ¹⁰⁹Ag with ¹⁰⁷Ag atoms.

We attempted to quantify the effect of size of AgNPs on the extent of interparticle isotopic exchange. A schematic showing AgNPs@DMBT of increasing size is presented in Figure 1A. We found that the extent of isotopic exchange (%) increased with an increase in the concentration of AgNPs (NC/NP concentration from 1:1 to 1:5) in the solution for each size of the NPs (Figure S7). Corresponding UV–vis spectra of the NC–NP mixtures, equilibrated after ~1 h of reaction, are presented in Figure S8. For the reaction with ~2 and ~4 nm



Figure 2. Abundance of the parent isotope (%) in NC as a function of reaction time (min) during the reaction with (A) ~ 2 , (B) ~ 4 , and (C) ~ 11 nm AgNPs at different NC/NP concentrations. The curves are fitted with a biexponential function. The average of three kinetic measurements is plotted, and the uncertainty is indicated by error bars at each point.

AgNPs at lower concentrations, that is, a NC/NP ratio of 1:1 or 1:2, the UV–vis spectra of the mixture resembled those of the NC with slight changes in the peak position, suggesting interaction between the particles. At higher NP concentrations, that is, a NC/NP ratio of 1:3 or 1:5, the plasmonic peaks of the NPs became prominent, which also showed minor shifts in peak positions and width, indicating slight changes in the size distribution of the plasmonic particles due to isotopic exchanges. In the reaction of the NC with ~11 nm AgNPs, the spectra resembled a mixture of NC and NP with dominant NC features at all NC/NP concentrations due to the lesser extent of isotopic exchange.

For comparison with the isotopic exchange in sub-nanometer-sized NCs under identical conditions, we also carried out reactions of $^{107}\mathrm{Ag}_{25}(\mathrm{DMBT})_{18}^{-}/^{109}\mathrm{Ag}_{25}(\mathrm{DMBT})_{18}^{-}$ with Ag₂₅(DMBT)₁₈⁻ synthesized from naturally abundant Ag (NC-NC reaction). The isotopic exchange in this case was rapid and stoichiometric in nature, and the system equilibrated instantaneously (Figure S9), as observed earlier.⁴⁰ Though the size of the NC $(1.9 \pm 0.5 \text{ nm})$ (Figure S10) was comparable to the size of the \sim 2 nm plasmonic NPs and both were protected by the same monolayer of ligands, the drastic difference in their reactivity highlighted how the precision in the structure of the particles controlled the reaction. Isotopic exchange in the case of the NC-NC reaction was highly facile, in comparison to the reaction of the NC with plasmonic NPs of similar size. This suggests that the exchange between identical metalligand fragments that constitutes the aspicule structure⁴⁷ of the NCs is a major reason behind the fast reaction in the case of the NC-NC reaction. The final exchanged states (after ~ 1 h of reaction) for 1:5 molar ratio in the case of all the NC-NP (~2, ~4, and ~11 nm) and NC-NC reactions are presented in Figure 1B,C. This revealed that the isotopic exchange in the NCs increased with a decrease in the size of the reacting particles and the extent of exchange was maximum in the case of the NC-NC reaction. This was true for all molar ratios of mixing, as evident from Figure 1D, which showed isotopic exchange (%) in the final product NC as a function of the NP/ NC concentrations (w/v) for all the reactions. However, it is to be noted that the number of particles per milliliter (details are presented in the Supporting Information) will be significantly different in identical w/v concentrations of NCs and NPs. The number of particles per milliliter is higher for NCs compared to the larger NPs with equivalent amounts of Ag in them. Therefore, the higher probability of interaction in the case of the NC-NC reaction also contributes to the higher

extent of exchange. Here, the isotopic exchange (%) was calculated from the m/z values and isotopic distribution of the peaks of the NCs after completion of the reaction. Further details of this calculation are presented in the Supporting Information. It is to be noted that the AgNPs were made from naturally abundant Ag, where both ¹⁰⁷Ag and ¹⁰⁹Ag atoms were present. Although only exchanges of the type 107-109 were detectable in ESI MS, it is obvious that there were also exchanges between similar isotopes (107-107) and (109-109) as well. Also, as the ratio of 107Ag/109Ag in the parent AgNPs was nearly 1, both the isotopic atoms had an equal probability of exchange at least in the initial stages of the reaction. However, using only one of the reactants as isotopically pure $[Ag_{25}(DMBT)_{18}^{-}]$ in this case] was sufficient to understand the kinetics of the reaction. Moreover, by analyzing the final reaction products using TEM, we confirmed that both NCs and NPs were present in the mixture after attaining the thermodynamic equilibrium (Figure S11).

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To obtain further insights into the kinetics of this isotopic exchange, that is, the timescales and rates of isotopic atom transfer during NC-NP reactions, we monitored the decrease in the abundance (%) of the parent isotope in the NCs as a function of time of reaction. Here, the abundance (%) of the parent isotope in the NCs refers to the abundance of ¹⁰⁷Ag or ¹⁰⁹Ag when the reaction was performed with $^{107}Ag_{25}(DMBT)_{18}^{-}$ or $^{109}Ag_{25}(DMBT)_{18}^{-}$, respectively. As both cases gave similar results, we considered an average of these two cases in calculating the abundances in Figure 2. The abundance of the parent isotope in the NCs (%) versus the time (min) of reaction is shown in Figure 2A–C, for ~ 2 , ~ 4 , and ~11 nm AgNPs, respectively. In each of these cases, the kinetics was monitored for four different NC/NP mixing ratios, that is, 1:1, 1:2, 1:3, and 1:5, respectively. The abundance of the parent isotope was assumed to be 100% at zero reaction time, and this theoretical data point was included in all cases. In each case, the abundance of the parent isotope (%) [Y(t)] was fitted to a biexponential function of the form, $Y(t) = A_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$. Here, τ_1 and τ_2 are the two timescales of the reaction and A_1 and A_2 are proportionality factors to the contribution of each timescale. A_0 denotes the value of Y(t) when the reaction attains equilibrium. The average reaction time, τ , was determined by integrating Y(t)over time. Further details of the fitting are presented in the Supporting Information. The values of τ_1 and τ_2 and the calculation of τ are presented in Table S1. The two timescales differed by approximately 1 order of magnitude. The faster

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Figure 3. Average timescales (τ) of the isotopic exchange reaction of the NC with AgNPs of different sizes and at different NC/NP mixing ratios.



Figure 4. (A) Abundance of the parent isotope (%) in the NC as a function of reaction time (h) during the reaction with bare and monolayerprotected Ag foils. A schematic showing the reaction of the NCs with a foil is presented as an inset. (B) ESI MS of (a) $^{107}Ag_{25}(DMBT)_{18}^{-}$ and product taken after 48 h of the reaction of $^{107}Ag_{25}(DMBT)_{18}^{-}$ with (b) bare and (c) DMBT-protected Ag foils.

reaction component, that is, the shorter timescale of the reaction, possibly corresponds to the exchange of the surface atoms, whereas the slower reaction component, that is, of the longer timescale, corresponds to the diffusion of exchanged atoms into the core to attain an equilibrium state, as observed earlier in the case of intercluster isotopic exchanges.³⁸ The variation in τ with different NC/NP mixing ratios for the three different sizes of AgNPs@DMBT is presented in Figure 3. For a particular size of AgNP, τ decreased, that is, the rate increased with the increase in the concentration of the AgNPs in the solution, that is, from the NC/NP mixing ratio of 1:1 to 1:5. Thus, a higher concentration of AgNPs favored higher exchange rates and transferred more atoms to the NCs, resulting in a greater isotopic exchange (%), as observed in Figure 1D. Also, the reaction timescale or rate showed a dependence on the size of the AgNPs, as presented in Figure 3. Generally, τ increased or rate decreased as we increased the particle size. However, this correlation decreased with an increase in the concentration of the NPs (NP/NC ratio) in the solution. This might be attributed to the fact that at a higher NP concentration, a higher number of collisions occurred between the NCs and the NPs, which dominated over other factors such as size or surface area of the NPs in controlling the timescales of the reactions.

3.2. Reaction of Isotopic NCs with Bulk Silver Foils. From the above experiments, it was clear how the isotopic exchange of NCs with NPs differed compared to an intercluster isotopic exchange. We further attempted to understand how bulk metal also transfers atoms to the NCs. We investigated the isotopic exchange in the NCs upon reaction with bare and monolayer-protected Ag foils. Here also, the NC used was isotopically pure $[^{107}Ag_{25}(DMBT)_{18}^{-}/^{109}Ag_{25}(DMBT)_{18}^{-}]$ and the Ag foils were composed of naturally abundant Ag. The methods used for cleaning the metal surface and preparation of the monolayers on the foils were discussed in the Experimental Methods. The NC concentration was kept the same as that used in the case of reactions with AgNPs. An Ag foil $(1 \text{ cm} \times 1)$ cm) was immersed in the NC solution, and the reaction was monitored for about 48 h. ESI MS was performed by taking out small fractions of the solution at different time intervals. No external stirring was applied to avoid the effect of any mechanical perturbations on the isotopic exchange process. Time-dependent ESI MS revealed that exchange in the NCs was drastically less when reacted with bare Ag foil (Figure S12). The peaks for the parent NC ions were almost unshifted and exhibited only slight broadening in the isotopic distribution with time. In contrast, when the Ag foil was protected by a monolayer of 2,4-DMBT ligands (Ag foil@ DMBT), significant exchange was observed (Figure S13). Similar behavior was observed using both ¹⁰⁷Ag₂₅(DMBT)₁₈ and ${}^{109}\text{Ag}_{25}(\text{DMBT})_{18}^{-}$ as the isotopically labeled NCs. The abundance of parent isotope (%) is presented as a function of reaction time in Figure 4A. This revealed that there was negligible change in the abundance of the parent NCs upon reaction with the bare Ag foil. However, upon reaction with Ag foil@DMBT, the abundance of the parent isotope of the NCs decreased significantly with the reaction time. The exchange was initially fast, and hence, the abundance decreased sharply in the initial 3 h of the reaction. The reaction then slowed down, and the abundance of the parent NCs decreased gradually to about 75% after 48 h. The isotopic exchange kinetics in the case of the reaction with Ag foil@DMBT also followed a biexponential fitting with two timescales of 1.78 and 18.17 h for the shorter and longer reaction component, respectively. ESI MS showing product NCs after 48 h when $^{107}\!Ag_{25}(DMBT)_{18}^{-}$ was used for the reaction with bare and monolayer-protected foils is presented in Figure 4B. A similar exchange was also observed during the reaction with ¹⁰⁹Ag₂₅(DMBT)₁₈⁻ (Figures S12 and S13). From our study, it is clear that the preadsorbed thiols on the Ag foils accelerated the reaction. A similar observation was also reported by Bürgi and co-workers where doping of Au NCs was observed by the reaction with Ag foils.³

3.3. Reaction of Isotopic NCs with Bulk Ag Powder. We further investigated the reaction of the NCs with bulk Ag powder. From the previous experiments, we know that the bare Ag foil exhibited negligible reactivity. However, we know that the reactivity increases with an increase in the surface area. To explore the role of the surface area of the bulk metal on the isotopic exchange process, we performed a reaction of the NCs $[^{107}Ag_{25}(DMBT)_{18}^{-}/^{109}Ag_{25}(DMBT)_{18}^{-}]$ with bare Ag powder. First, we performed a reaction with about 80 mg of Ag powder, which was almost equivalent to the mass of $1 \text{ cm} \times 1$ cm bare Ag foil of ~0.1 mm thickness. Time-dependent ESI MS (Figure S14A) revealed that the reaction of the NCs with Ag powder was somewhat favored. While in the case of the bare Ag foil, the exchange was negligible even after 48 h, whereas a significant extent of exchange was observed within 2 h of the reaction with the Ag powder. Upon reducing the quantity of the Ag powder to 40 and 20 mg, the isotopic exchange decreased (Figure S14B,C). The decrease in the abundance of the parent isotope in the NCs (%) was studied similarly as a function of reaction time to obtain greater insights into the kinetics of the reaction. This is presented in Figure 5. The reaction was not monitored beyond 2 h as the intensity of the NCs in ESI MS started to decrease, which might be attributed to a certain extent of degradation of the NCs in the presence of Ag powder. It can be seen from Figure 5 that for the first 5 min, there was no change in the abundance of the isotope, suggesting a very slow initial reaction rate, and then, the reaction progressed gradually. Thus, it is clear that initially, a certain period of time was required for the activation of the bare surface of the Ag powder, and this activation might have occurred due to the adsorption of NCs on the surface or the deposition of Ag-thiolates, resulting from the decomposition of the NCs. We also monitored the reaction using UV-vis studies (Figure S15), which also showed that there was a certain extent of degradation of the NCs in the presence of the Ag powder and this degradation also increased with an increase in the amount of Ag powder. However, the kinetics of reactions could not be fitted with mono-, bi-, or triexponential



Figure 5. Abundance of parent isotope (%) of the isotopic NC as a function of time (min) during the reaction with various quantities of Ag powder, with a fixed quantity of the NC. A scheme of this reaction is presented as an inset. The average of three kinetic measurements is plotted, and the uncertainty is indicated by error bars at each point.

functions, suggesting even complex steps involved in the case of the isotopic exchange reaction of NC with bulk Ag powder, which might arise due to the degradation of the NCs or the possibility of oxygen adsorption on the surface of the Ag powder.

It is evident that in the case of the above reactions with AgNPs, bulk foil, or powder, there will be changes in their isotopic composition as well, as atoms from the NCs will also be transferred to them. These changes may occur through the deposition of isotopically enriched metal or metal thiolates coming from the NCs. Although isotopic exchanges are mainly driven by the entropy of mixing, in these reactions, there could also be some enthalpy effects depending on the exchanges occurring on the AgNPs or bulk Ag counterparts. The enthalpy effects could arise from possible ligand exchanges, slight changes in the size and morphology of the AgNPs, or possible changes in the surface of the Ag foil or Ag powder upon reaction with the NCs. However, this aspect could not be investigated in the current study as AgNPs are beyond the mass range of the present instrument. MS in the megadalton range with adequate resolution should be able to detect this.⁴⁸⁻⁵⁰ Moreover, using isotopically enriched DMBT ligands will also help to resolve the extent of ligand exchanges in these reactions, which are areas for future study. Future investigations will also involve studying the effect of shape of the materials on such exchange reactions. The state of the surface of the reacted foil and Ag powder might also be of potential interest for further studies. The isotopic composition of the surface of the bulk Ag foil or Ag powder might also get altered upon reaction with the NCs.

4. CONCLUSIONS

By using isotopic exchange reactions, we presented a complete study on how the dynamics of the spontaneous atom transfer process in atomically precise NCs vary upon reaction with materials of different sizes. Isotopically pure NCs, $^{107}Ag_{25}(DMBT)_{18}$ and $^{109}Ag_{25}(DMBT)_{18}$, were used in our study. Upon increasing the size of the reacting partner from the NC to the NP regime, protected with the same ligand, the exchange process was found to slow down. The exchange rates further decreased upon reacting with materials in the bulk such as a metal foil and micron-scale metal powder. By monitoring the time-dependent changes of the isotopic abundance of the reacting NCs, we analyzed the kinetics of the process and

determined the different timescales involved in such reactions. The isotopic exchanges are mainly brought about by the entropy of mixing. Our studies demonstrate the spontaneity of atom transfer when NCs are brought in contact with NPs and bulk metals. This method may emerge as a simple procedure to alter the isotopic composition of metal surfaces.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c02264.

Instrumentation; experimental methods of the synthesis of NCs; biexponential fitting of the reaction kinetics; ESI MS of pure $^{107}Ag_{25}(DMBT)_{18}$ and $^{109}Ag_{25}(DMBT)_{18}$ NCs; time-dependent and concentration-dependent ESI MS of reaction of isotopic NCs with Ag NPs of different sizes, bare and monolayer-protected Ag foils, and bulk Ag powder; and TEM and optical absorption spectra for the characterization of the parent NCs and NPs as well as their reaction products (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

P.C. and A.N. thank IIT Madras for providing their postdoctoral fellowships. P.B., J.R., and B.M. thank IIT Madras for their doctoral research fellowships. A.C. thanks CSIR for her doctoral research fellowship. We thank the Department of Science and Technology, Government of India, for supporting our research programme.

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