

# Temporal Fluctuations in Interparticle Interactions Drive the Formation of Transiently Stable Nanoparticle Precipitates

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## ABSTRACT

The pH dependent temporal fluctuations in the strength of electrostatic interactions is explored to unveil a transient self-assembly response in plasmonic nanoparticles. The assembly process was triggered by the electrostatic attraction between positively-charged gold nanoparticles (AuNPs) and an aggregating agent, ethylenediaminetetraacetic acid (EDTA). The autonomous changes in the pH and ionic strength of the solution, under the influence of atmospheric CO<sub>2</sub>, weaken the aggregating ability of EDTA and initiate the complete disassembly of [+] AuNP - EDTA precipitates. The use of a non-destructive mode of autonomous disassembly helped in achieving some of the desirable feats in the field of transient self-assembly like easy removal of waste, formation of a transiently stable precipitate state and negligible dampness in redispersion. The chemical strategy adopted in the present work, to introduce transientness, can act as a generic tool in creating the next generation of complex matter.

## INTRODUCTION

Living systems have an extraordinary ability of creating and sustaining life by using highly reconfigurable and adaptive structures (active assemblies).<sup>1,2</sup> These assemblies are transient in

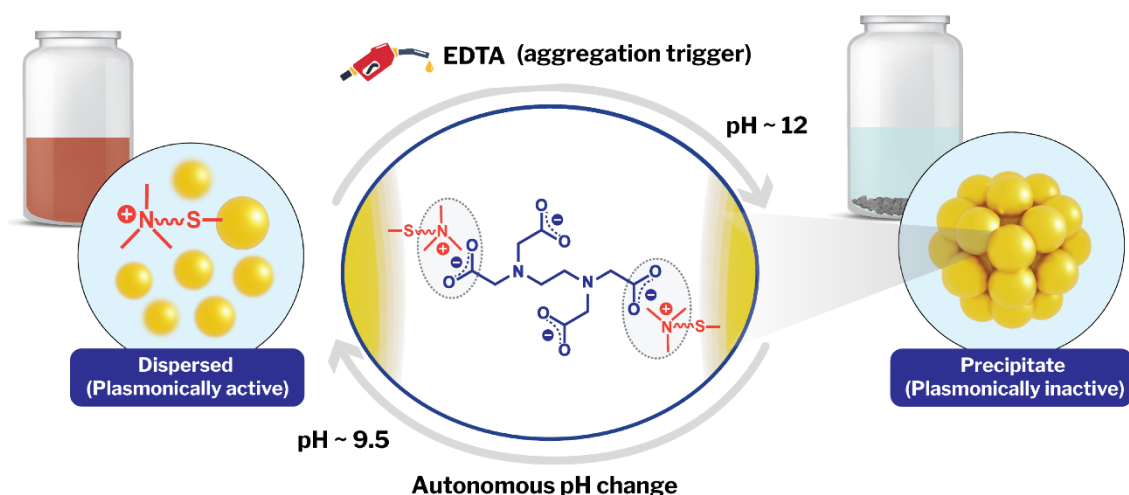
nature, and are crucial for driving various cellular functions including those of microtubules and actin filaments.<sup>3</sup> Such structures have inspired researchers to develop artificial systems with similar levels of re-configurability.<sup>4–13</sup> A key strategic challenge in the construction of such active assemblies is the ability to introduce autonomous fluctuations in the strength of interparticle interactions.<sup>2,4–10,12,13</sup> A typical transient self-assembly process starts with an assembly step triggered by an external force, followed by an autonomously driven disassembly step. One of the initial pioneering works in this direction was performed by Grzybowski and co-workers, where light was used as a trigger for the transient assembly of gold nanoparticles (AuNPs).<sup>14</sup> Light is a ‘neat’ trigger as it inflicts minimal chemical modification, resulting in ‘zero waste generation’. Inspired by this, light was extensively used as a trigger to impart temporal response to many molecular and nanoparticle systems, thereby pushing the field of self-assembly beyond the static domain.<sup>14–17</sup>

Another approach of creating active assemblies utilize chemicals to trigger a self-assembly response.<sup>2,5,7–9,18,19</sup> In this direction, van Esch and co-workers have elegantly demonstrated the use of triggered esterification and autonomous de-esterification reactions to drive the formation of transiently stable structures.<sup>20–22</sup> Subsequently, similar design principles were extended to other chemical triggers like carbodiimide derivatives for the transient formation of anhydride based gels, and aggregates.<sup>23,24</sup> Recently the groups of Hermans and George have, independently, used redox triggers to design a transient self-assembly response in various molecular systems.<sup>25–28</sup> In another set of transient self-assembly, Prins and co-workers developed a strategy where adenosine triphosphate (ATP) acted as a template to drive the transient self-assembly of a cationic surfactant into vesicles.<sup>29</sup> Furthermore, George and co-workers have used ATP to drive chiral supramolecular polymerization of different amphiphilic molecules, and mimic transient self-assembly of biological molecules.<sup>30–32</sup> In another original approach, Walther and co-workers developed a general protocol to drive a transient self-

assembly response by using two antagonistic signals; a fast promoter and a dormant deactivator.<sup>33</sup> Here, the promoter induces the speedy self-assembly process, while the dormant deactivator, triggers the disassembly process in a sluggish fashion.<sup>10,11,34</sup> Despite the rapid advances made in this area, a transient self-assembly process is often encountered with the challenge of dampness (loss of property) during subsequent self-assembly cycles.<sup>5,8,29</sup> Additionally, with NPs as building blocks, even the ideal and '*sought-after*' response of transiently switching between dispersed and precipitated stages is not trivial. It should be noted that, such a response has been demonstrated with the help of light as a trigger.<sup>14,35,36</sup> A possible reason for this discrepancy is the '*zero formation*' of waste during light-triggered transient self-assembly process. Whereas, during a chemically triggered self-assembly process, the deactivation step necessitates a chemical breakdown of the activated monomer, resulting in the generation of waste.<sup>5,8</sup> Therefore, one of the current challenges in the field is to develop strategies that will produce minimum or easily removable waste during the process of triggered transient self-assembly. A way out is to drive the triggered assembly process to a transiently stable precipitated stage, which in turn can pave the way for the easy removal of waste from the system. In this direction we aim to design a protocol where NPs could, transiently, precipitate out from the solution, resulting in an easy separation of waste and improved redispersion response.<sup>27-29</sup> Furthermore, realizing such transiently stable precipitates with plasmonic NPs can open up the possibility of coupling distinct functions to dynamic NP systems.<sup>37-39</sup>

The present work exploits temporal fluctuations in electrostatic interactions to drive a chemically triggered self-assembly of plasmonic NPs, ultimately resulting in the formation of a transiently stable precipitate state (Scheme 1). Here, the assembly process was triggered by the electrostatic attraction between positively charged AuNPs and a negatively charged aggregating trigger (EDTA). The disassembly occurred due to the autonomous changes in the

pH and ionic strength of the solution, under the influence of atmospheric CO<sub>2</sub>. This is in contrast with most of the reported transient self-assembly systems, where a chemical degradation of the activated monomers is essential to drive the disassembly process.<sup>5,7,9,13</sup> Whereas, our strategy of non-destructive disassembly allowed the minimal accumulation of waste as well as a transient switching between completely precipitated and redispersed stages of plasmonic NPs. This paved the way for the easy removal of waste generated, leading to the complete reversibility in transient self-assembly cycles with negligible dampness in redispersion.



**Scheme 1.** A transient switching between completely precipitated and redispersed stages of plasmonic NPs was achieved by exploring the pH dependent temporal fluctuations of electrostatic interactions

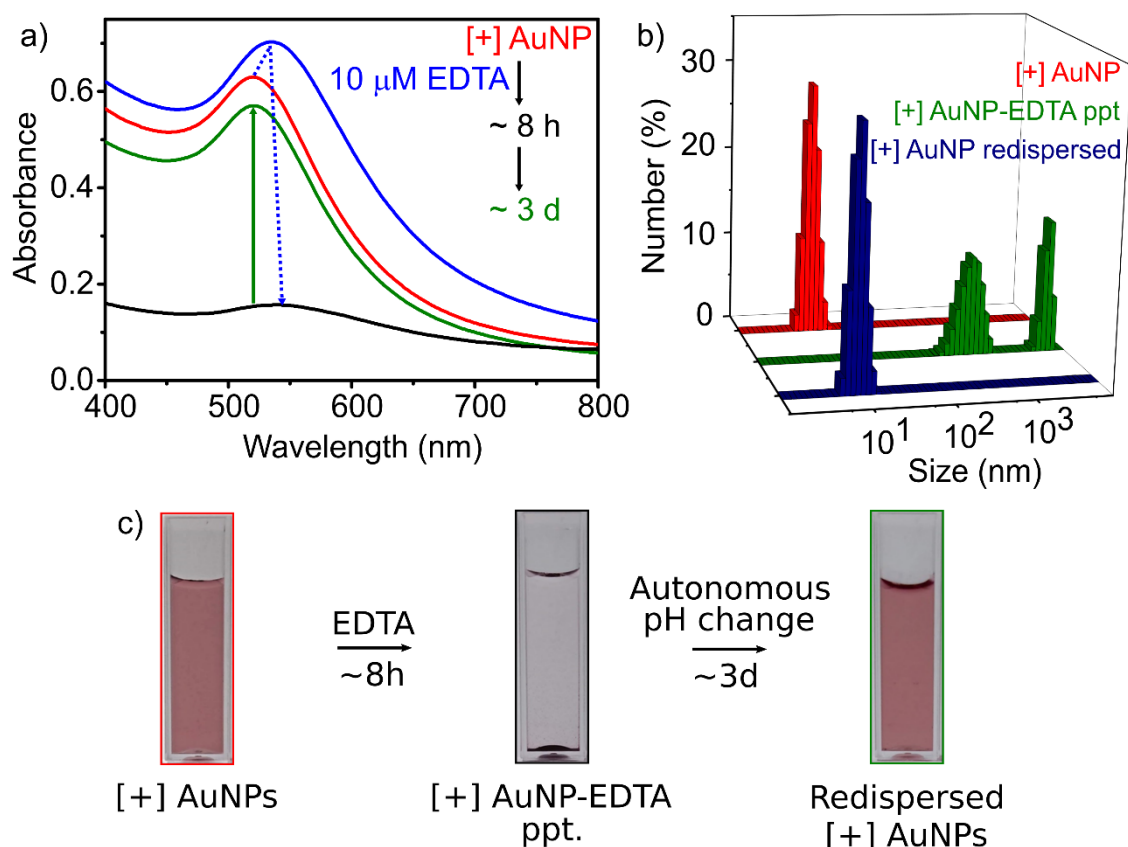
## RESULTS AND DISCUSSION

### Transient Self-Assembly

We aimed to explore the pH dependent fluctuations in the electrostatic interaction between quaternary ammonium and carboxylate groups. For this, AuNPs ( $5.5 \pm 0.8$  nm) functionalized with 11-mercaptoundecyl-N,N,N-trimethyl-ammonium chloride ligands ([+])<sup>40,41</sup> and EDTA were used as the building block and aggregating trigger, respectively (Figures S1 & S2 in the Supporting Information). Addition of 10  $\mu$ M EDTA to 60  $\mu$ M [+] AuNPs (in terms of Au

atoms) resulted in an immediate bathochromic shift of ~15 nm, confirming the plasmon coupling and aggregation of [+] AuNPs (blue curve in Figure 1a). The aggregates gradually precipitated from the solution, and ultimately settled at the bottom of the cuvette in ~8 h (black curve in Figures 1a & c). It should be noted that EDTA can efficiently precipitate [+] AuNPs from the solution only at high pH values (pH ~12). Whereas, no noticeable aggregation of [+] AuNPs was observed at lower pH values (pH ~9.5), even after ~2 days. This differential aggregation response is possibly because of the electrostatic repulsions between quaternary ammonium groups on [+] AuNPs and protonated amines on EDTA at lower pH values (see Section 3 in Supporting Information for details, Figures S3-S5).<sup>42</sup> Having established that aggregation and stability of [+] AuNP – EDTA precipitates depend on the pH of the solution, autonomous ways of acidifying the solution were explored to efficiently release [+] AuNPs from the precipitates (Scheme 1 and Figure 1a). In this pursuit, a disassembly experiment performed in an open vial resulted in the complete redispersal of [+] AuNPs in ~3 days (green curve in Figure 1a). This autonomous redispersal of [+] AuNPs was accompanied with a decrease in the pH of the solution from ~12 to ~9.5, thereby confirming the decisive role of pH in breaking the [+] AuNP - EDTA precipitates. The transient switching between plasmonically active and inactive NP states was apparent from the changes in the optical photographs of the solution as well (Figure 1c). The UV-Vis changes associated with the *triggered* aggregation and *autonomous* disassembly were well complemented with Dynamic Light Scattering (DLS) studies as well (Figure 1b). Interestingly, there was no persistence of aggregates in the solution, indicating a complete redispersal of [+] AuNPs from the precipitates (blue bar in Figure 1b). The generality of our approach was proved by demonstrating similar transient self-assembly processes in plasmonic NPs of varying size (~11 nm AuNP) and core (~5 nm [+] AgNP; Figure S6). To the best of our knowledge, such a response of transient switching between plasmonically active and inactive stages in NPs, by chemical triggers, is scarce in the literature.

In support of this, Boekhoven and co-workers have recently witnessed the propensity of AuNP precipitates to fall into a kinetically trapped state and become incapable of showing any transientness.<sup>38</sup>

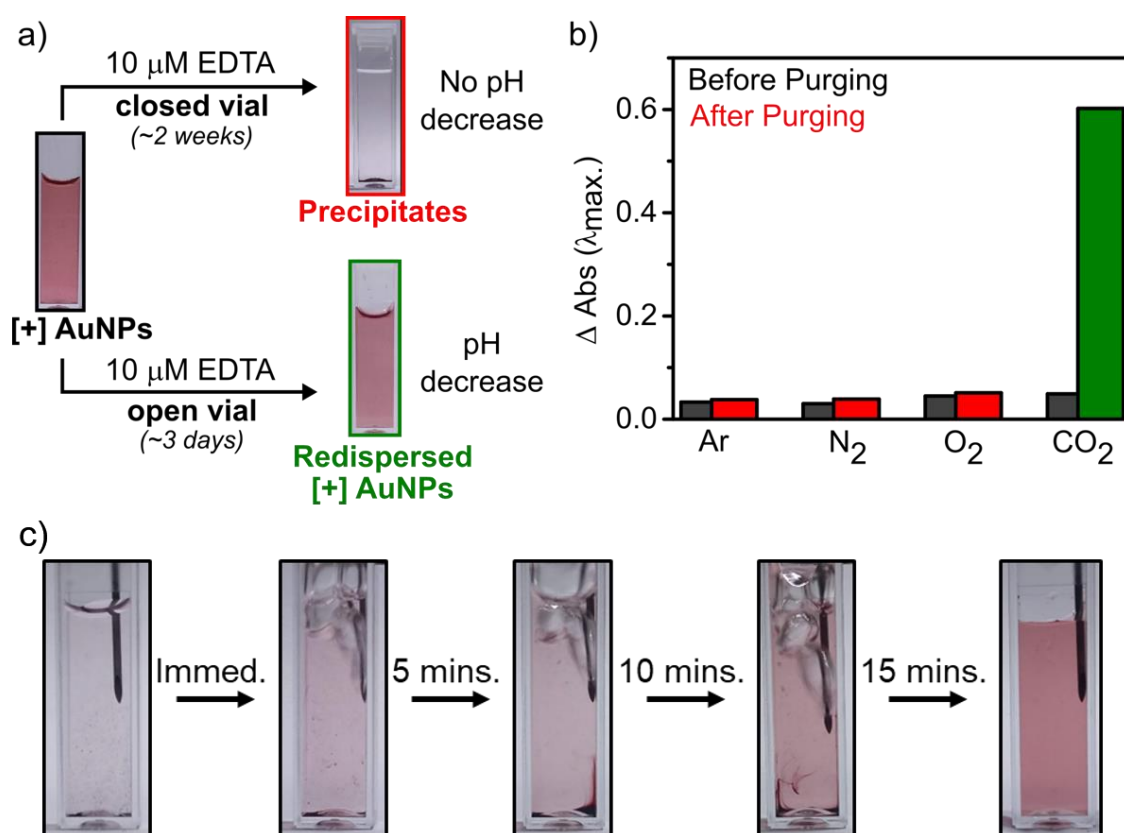


**Figure 1.** Transient self-assembly of plasmonic [+] AuNPs. (a) Variation in the absorption of [+] AuNPs in the presence of 10  $\mu\text{M}$  EDTA. (b) DLS plots confirming the assembly-disassembly processes. (c) Optical photographs of dispersed [+] AuNP, sedimented [+] AuNP - EDTA precipitates and completely re-dispersed [+] AuNPs, during a single cycle of transient self-assembly.

### Mechanism of Transient Self-Assembly

In order to elucidate the mechanism of transientness, we first tested the necessity of an open vial for the autonomous redispersion of [+] AuNPs. The pH of the solution remained unchanged ( $\sim 12$ ) and no signs of NP redispersion was observed even after  $\sim 2$  weeks, when [+] AuNP – EDTA precipitates were incubated in a closed vial (Figure 2a). Upon performing similar

experiments in an open vial, the solution pH lowered to  $\sim 9.5$  and the precipitates redispersed within  $\sim 3$  days (Figure 2a). This indicates the necessity of components from the atmosphere



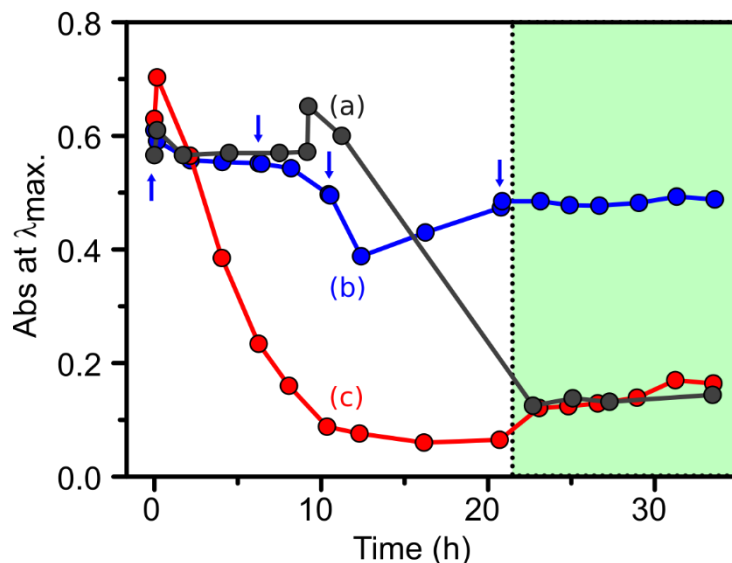
**Figure 2.** Mechanism of transient self-assembly. (a) Optical photographs showing the necessity of open vial for the autonomous redispersion of [+] AuNPs from the precipitates. (b) Bar diagram showing the effect of bubbling of different atmospheric gases (for 1h) on the absorbance of solution containing [+] AuNP - EDTA precipitates. (c) Optical photographs clearly showing the redispersion of [+] AuNPs, upon purging a solution of [+] AuNP - EDTA precipitates with CO<sub>2</sub> for  $\sim 15$  min.

for triggering the disassembly step. Accordingly, the response of [+] AuNP - EDTA precipitates to different atmospheric gases was systematically studied. Within  $\sim 15$  mins of purging, CO<sub>2</sub> disrupted the [+] AuNP - EDTA precipitates and completely redispersed the plasmonic NPs (Figures 2b & c). On the contrary, other major atmosphere gases like N<sub>2</sub>, O<sub>2</sub>, and Ar failed to disassemble the precipitates even after  $\sim 1$  h of continuous purging (Figure 2b). The exclusivity of CO<sub>2</sub> to disassemble [+] AuNP - EDTA precipitates can be understood from its ability to acidify an aqueous solution by forming carbonic acid (H<sub>2</sub>CO<sub>3</sub>).<sup>43,44</sup> Under such

acidic conditions, the amine groups on EDTA gets protonated and loose its ability to glue the [+] AuNPs together in the precipitate, leading to the complete disassembly of plasmonic NPs.

In another finding, contrasting outcomes were witnessed when [+] AuNP was exposed to the same amount of chemical trigger in two different pathways. Specifically, we compared the responses of [+] AuNPs when 10  $\mu$ M EDTA was added in single and multiple batches (4 x 2.5  $\mu$ M). As shown before, the addition of 10  $\mu$ M EDTA at once resulted in the instantaneous decrease of the absorption intensity, followed by the complete precipitation of [+] AuNPs – *the assembling pathway* (red curve in Figure 3). In contrary, [+] AuNPs retained their colloidal stability (*non-assembling pathway*) when the same amount of EDTA was added in four aliquots (blue curve in Figure 3). This intriguing observation can be rationalized by understanding the differential responses of precipitated and un-aggregated AuNPs towards the changes introduced by atmospheric CO<sub>2</sub>. Under the action of atmospheric CO<sub>2</sub>, EDTA consistently loses its aggregating ability because of the decrease in pH as well as an increase in the ionic strength of the solution (*vide infra*). As a result, the addition of the trigger in batches allows CO<sub>2</sub> to suppress the bridging ability of EDTA. The necessity of atmospheric CO<sub>2</sub> for installing the observed aggregation dependence on method of trigger addition (single vs multiple) was validated by adding multiple aliquots of EDTA (4 x 2.5  $\mu$ M) to [+] AuNPs in a closed vial. Interestingly, the [+] AuNPs uniformly precipitated out of the solution similar to the response seen during the single addition experiment (curve grey in Figure 3). This once again confirm the necessity of atmospheric CO<sub>2</sub> in installing transientness to the present system.



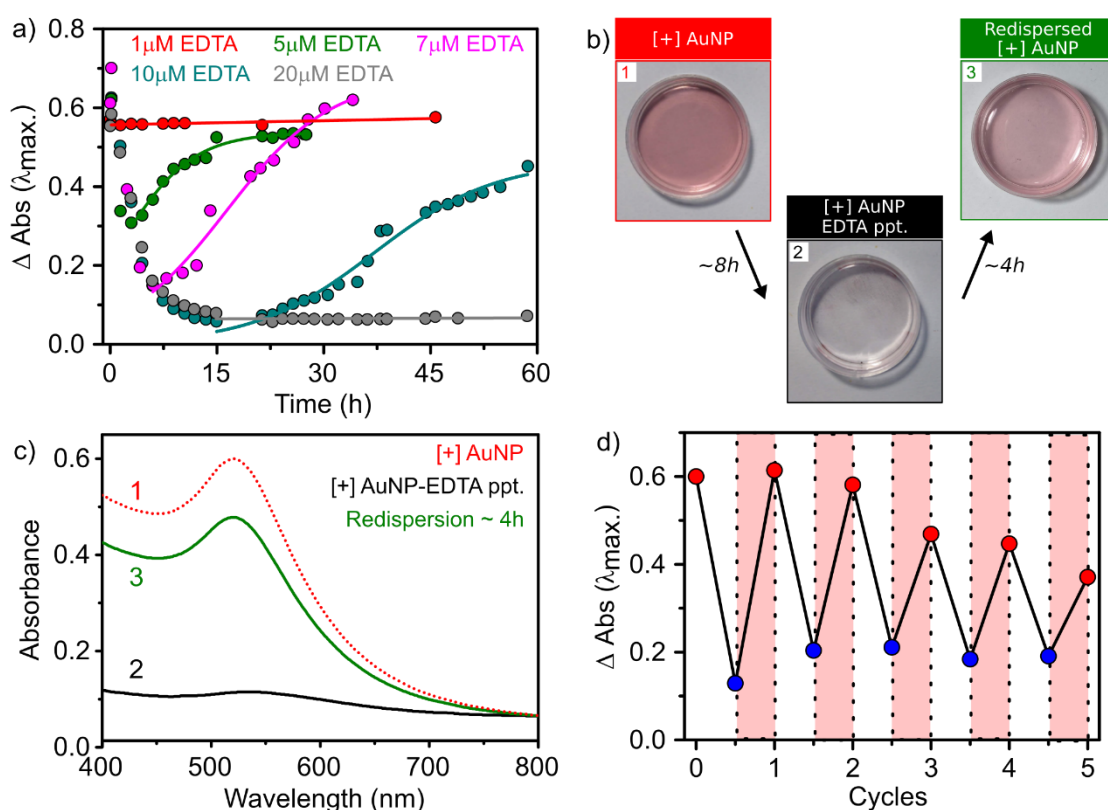


**Figure 3.** Variation in the absorbance of [+] AuNPs upon addition of 10  $\mu\text{M}$  EDTA in (i) single batch, (ii) multiple batches in an open, and (iii) multiple batches in a closed vial. Concentration of trigger in the shaded portion is 10  $\mu\text{M}$ . Arrows show the time at which each aliquot of trigger was added.

### Tunability and Reversibility

Tunability in the lifetime of assembly-disassembly steps is a characteristic feature of any transient self-assembly process. A detailed understanding of various factors involved in the assembly-disassembly steps allowed us to tune the lifetime and reversibility of the present transient self-assembly system. The weakening of the bridging ability of EDTA, upon autonomous pH change, was the key in the disassembly process. Hence, a variation in the amount of EDTA can be conveniently used to control the rate of disassembly, and ultimately the lifetime of AuNP precipitates. With this in mind, [+] AuNPs were exposed to varying concentrations of EDTA and the assembly-disassembly processes were monitored using UV-Vis. studies (Figure 4a). Addition of  $\sim 1 \mu\text{M}$  EDTA failed to activate sufficient number of [+] AuNPs for the self-assembly process, as can be seen from the stagnant nature of the absorption intensity (red curve in Figure 4a). Upon increasing the concentration of EDTA to  $\sim 5 \mu\text{M}$ , an instantaneous decrease in the absorption intensity was observed ( $\Delta \text{Abs. at } \lambda_{\text{max}} = \sim 0.25$ ), indicating the onset of aggregation (green curve in Figure 4a). This decrease in the absorption

intensity ceased after  $\sim 3$  h and the system disassembled completely in  $\sim 15$  h, as it is clear from the reversal of absorbance to the original intensity. A further increase in the amount of EDTA ( $\sim 7 \mu\text{M}$ ) resulted in the formation of complete precipitates in  $\sim 6$  h, which disassembled completely in  $\sim 34$  h. Thus, the time taken to disassemble  $[+]$  AuNP – EDTA aggregates could be conveniently tuned from  $\sim 3$  days to  $\sim 15$  h by decreasing the amount of EDTA (Figure 4a). Alternately, the lifetime of  $[+]$  AuNP – EDTA precipitates was reduced by increasing the exposed area of the dish containing the precipitates. The rationale being that the redispersion of  $[+]$  AuNPs occurs under the influence of atmospheric  $\text{CO}_2$ , and an increase in the exposed area of the container will enhance the dissolution of  $\text{CO}_2$ . A dramatic reduction in the redispersion time from  $\sim 3$  days (in an open vial) to  $\sim 4$  h was observed when the disassembly step was carried out in a  $\sim 3.5$  cm wide petri dish (Figures 4b & c).



**Figure 4.** Tunability in the lifetime and reversibility of transient self-assembly in AuNPs. (a) Variation in  $\Delta \text{Abs}$ . at  $\lambda_{\text{max}}$ . with time for  $[+]$  AuNPs upon the addition of different amounts of EDTA (trigger). (b) Optical photographs of the petri-dish containing  $[+]$  AuNPs,  $[+]$  AuNP – EDTA precipitate, and redispersed  $[+]$  AuNPs marked as 1, 2, and 3 respectively. (c) Variation in the absorption of  $[+]$  AuNPs in the presence of  $10 \mu\text{M}$  EDTA. Here, the redispersion process

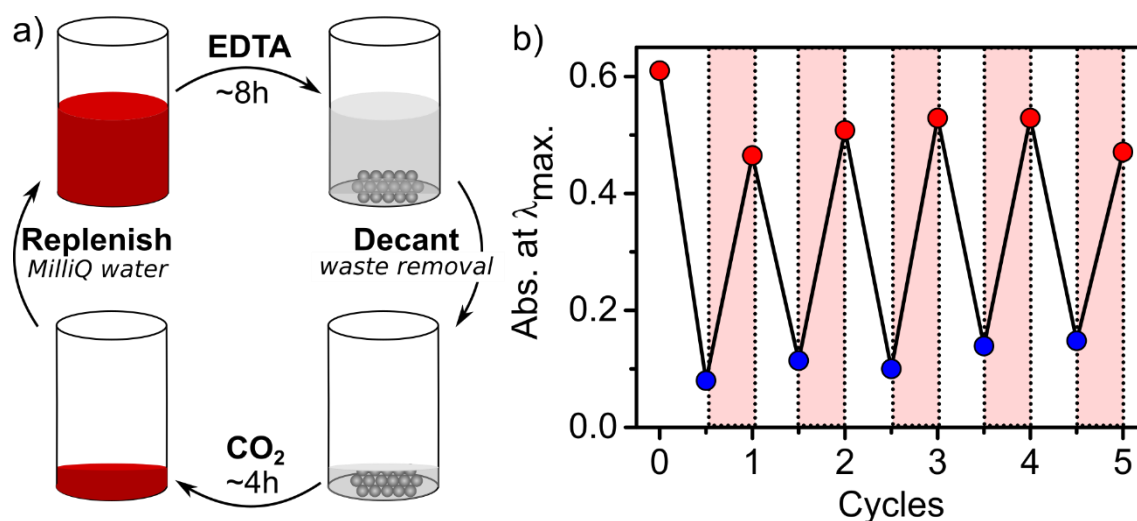
was carried out in a petri-dish, resulting in the faster disassembly of [+] AuNP – EDTA precipitates (in ~4h). (d) Five complete cycles of transient self-assembly of [+] AuNPs.

Next, we discuss about the reversibility of the transient self-assembly process in plasmonic AuNPs. Since the disassembly process was caused by an autonomous decrease in the pH and protonation of EDTA, a mere increase of pH back to ~12 was expected to trigger the next cycle of aggregation. However, no signs of aggregation were observed by increasing the pH of the solution. Similarly, fuelling with a fresh batch of basic solution of EDTA (~7  $\mu$ M) also failed to trigger the aggregation process. To our surprise, the aggregation and precipitation of [+] AuNPs only occurred after the addition of higher amounts of EDTA (~1.5 times more compared to the first cycle). The disassembly step occurred similar to the first cycle, with a plasmon recovery of ~95% (Figure 4d). Surprisingly, the concentration of EDTA had to be continuously increased for each subsequent cycle to efficiently carry out reversibility studies (Figure 4d). The curious observation of demand for higher trigger (EDTA) for each cycle during the reversibility experiments can be rationalized in the following fashion. The aggregation between EDTA and [+] AuNPs is primarily through electrostatic attractions, and the strength of which depends on the ionic strength of the solution. In the present system, spontaneous acidification and decrease in pH of the solution is observed during the autonomous disassembly of [+] AuNP– EDTA precipitates. The produced carbonic acid can react with the base already present in the solution to form a salt ( $\text{NaHCO}_3$ ), thereby increasing the ionic strength of the solution.<sup>44–46</sup> Consequently, the electrostatic attractions will be weaker in the next assembling cycle, demanding for higher amounts of EDTA. We note that the presence of high salt affects the disassembly process as well. Here, for subsequent cycles, noticeable losses in the absorption intensity of redispersed [+] AuNPs was observed (only ~60 % of plasmon intensity was retained at the end of the 5<sup>th</sup> cycle; Figure S8). It has been established in literature

that the waste generated during the process of transient self-assembly interferes with the redispersion process, resulting in a damped response.<sup>5,8</sup>

A long standing challenge in the field is to minimize the interference from the waste, and overcome the damped response observed during the reversibility cycles.<sup>8</sup> To our advantage, the complete sedimentation of NP precipitate (formed during the assembling stage) allowed the easy removal of waste through a simple decantation of the supernatant (Figure 5a). A dramatic decrease in the lifetime of [+] AuNP precipitates was observed from ~3 days (in 3 mL solution) to ~4 h, when the redispersion was performed at a lower volume (~100  $\mu$ L). Moreover, lowering the solution volume helped in minimizing the amount of waste produced in the subsequent disassembly step. This is because lower amounts of CO<sub>2</sub> will now be required to change the pH of a ~100  $\mu$ L solution and switch off the electrostatic attractions, compared to that in 3 mL solution. In order to perform the next cycle of transient self-assembly, the redispersed [+] AuNPs were replenished with MilliQ water to the initial volume of 3 mL, and refuelled with ~10  $\mu$ M EDTA. It is worth mentioning that exactly the same amount of EDTA, as the amount of waste produced in the subsequent disassembly step. This is because lower amounts of CO<sub>2</sub> will now be required to change the pH of a ~100  $\mu$ L solution and switch off the electrostatic attractions, compared to that in 3 mL solution. It is worth mentioning that exactly the same amount of EDTA, as used in the first cycle, was enough to get an immediate aggregation and precipitation of [+] AuNPs. Again, the volume of [+] AuNPs precipitates was reduced by decantation to minimize the waste generated from the second cycle of redispersion. Consequently, the redispersed [+] AuNPs showed negligible losses in the plasmon intensity, indicating minimal interference from the waste. The reversibility cycles were performed for at least 5 times, without much dampening in redispersion response (~95 % of plasmon intensity was retained in each cycles; Figure 5b). Thus, the formation of a transiently stable precipitate

state paved the way for the convenient isolation of activated AuNPs from the excess trigger and waste, without compromising the transient self-assembly process.



**Figure 5.** Easy waste removal and improved reversibility. (a) Schematics showing the sequence of steps undertaken to study the effect of solution volume on the disassembly of [+] AuNP-EDTA precipitates. The formation of complete precipitate allowed the easy removal of waste through simple decantation. (b) Five complete cycles of transient self-assembly of [+] AuNPs, where the redispersion was undertaken in a smaller volume ( $\sim 100 \mu\text{L}$ ). Lowering of the solution volume resulted in a faster disassembly of [+] AuNP – EDTA precipitates ( $\sim 4$  h), along with minimal loss of plasmon intensity during each cycle.

## CONCLUSIONS

The pH and ionic strength dependence of electrostatic interactions was explored to introduce temporal fluctuations in the strengths of interparticle interactions and choreograph a transient self-assembly response in plasmonic AuNPs. The bridging and aggregating ability of EDTA with quaternary ammonium groups was used to trigger the aggregation in [+] AuNP. The observation of pH dependent aggregation of [+] AuNP with EDTA was decisive, as it revealed the factors influencing the stability of NP precipitates and hinted towards an autonomous pathway for the disassembly process. The autonomous changes in the pH and ionic strength values, under the influence of atmospheric CO<sub>2</sub>, resulted in the complete breaking of electrostatic attractions that glued the [+] AuNP - EDTA precipitates. Strikingly, the present

use of temporal fluctuations in electrostatic interactions allowed the realization of transient switching between completely precipitate and redispersed stages of plasmonic NPs. The self-assembly process in [+] AuNP – EDTA system presented here exhibits the key characteristics of transient behaviour like triggered assembly & autonomous disassembly, and tuneable aggregate lifetimes (from days to hours). On top of this, our strategy of using non-destructive ways for disassembly helped in achieving some of the desirable feats in the field of transient self-assembly like easy removal of waste, formation of a transiently stable precipitate state and negligible dampness of the redispersion response. The next logical step will be to impart distinct NP functionalities to such temporal self-assembly process, for which the capability of forming transiently stable NP precipitates will be advantageous.

## CONFLICTS OF INTEREST

There are no conflicts to declare.

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## TOC ENTRY

