Templated out-of-equilibrium self-assembly of branched Au nanoshells

Templated Out-of-Equilibrium Self-Assembly of Branched Au Nanoshells

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Abstract

Out-of-equilibrium self-assembly of metal nanoparticles (NPs) has been devised using different types of strategies and fuels, but the achievement of finite 3D structures with a controlled morphology through this assembly mode is still rare. Here we used a spherical peptide-gold superstructure (PAuSS) as a template to control the out-of-equilibrium self-assembly of Au NPs, obtaining a transient 3D branched Au-nanoshell (BAuNS) stabilized by sodium dodecyl sulphate (SDS). The BAuNS dismantled upon concentration gradient equilibration over time in the solution, leading to NPs disassembly. Notably, BAuNS assembly and disassembly favoured temporary interparticle plasmonic coupling, leading to a remarkable oscillation of their optical properties.

Introduction

Self-assembled systems that operate in out-of-equilibrium states, sustained by a continuous supply of energy, grant the emergence of transient properties and functionalities, frequently unparalleled by their static counterparts.[1,2] Such a dynamic mode is the hallmark of biological systems and the research efforts towards the design of functional assemblies formed far from thermodynamic equilibrium is growing rapidly.[3,4] While being popular building blocks for the development of static self-assembled nanostructures,[5–7] the use of metal nanoparticles (NPs) to devise dynamic systems is still in its infancy.[8–10]

Grzybowski's research group pioneered the topic, by combining gold NPs (AuNPs) bearing acidic head groups with a pH oscillator that controlled the dissociation of the acidic moieties and the subsequent assembly/disassembly of the AuNPs.[11] To date, light has been the most popular stimulus (fuel) to control NP-based out-of-equilibrium systems, usually leveraging the photo-isomerization of azobenzene or spiropyran functionalized NPs.[12–14] Clustering of AuNPs and iron

oxide NPs has also been regulated by a chemical reaction cycle that hydrolyses a carbodiimide-based fuel.[15] A different route to mediate AuNPs self-assembly far from equilibrium was reported by the Klajn's group, who exploited the high local concentration of a surfactant, released near the NP surfaces during their growth, to induce transient assembly of the NPs.[16] Despite several approaches have been devised to drive metal NPs self-assembly far from its thermodynamic equilibrium, it remains highly challenging to achieve the formation of transient assemblies with a finely tuned and finite morphology, feature that could ease the actual application of these systems and expand their practical relevance.

To address this challenge, here we employed a spherical peptide-Au superstructure as a template to control the out-of-equilibrium self-assembly of AuNPs, realizing a branched Au-nanoshell (BAuNS). Owing to its high stability and positive charge, the chosen template attracts $AuCl_4^-$ ions on its surface and, upon Au reduction to the metallic state, a shell composed of interconnected 5 nm AuNPs is formed over its surface. BAuNS is stabilized by sodium dodecyl sulphate (SDS), that reaches a high localized concentration within the branched AuNPs layer. As SDS concentration gradient equilibrated over time in the solution, dismantling of BAuNSs occurred by AuNPs disassembly. Notably, BAuNSs assembly and disassembly favoured temporary interparticle plasmonic coupling, leading to a remarkable oscillation of the AuNPs optical properties.
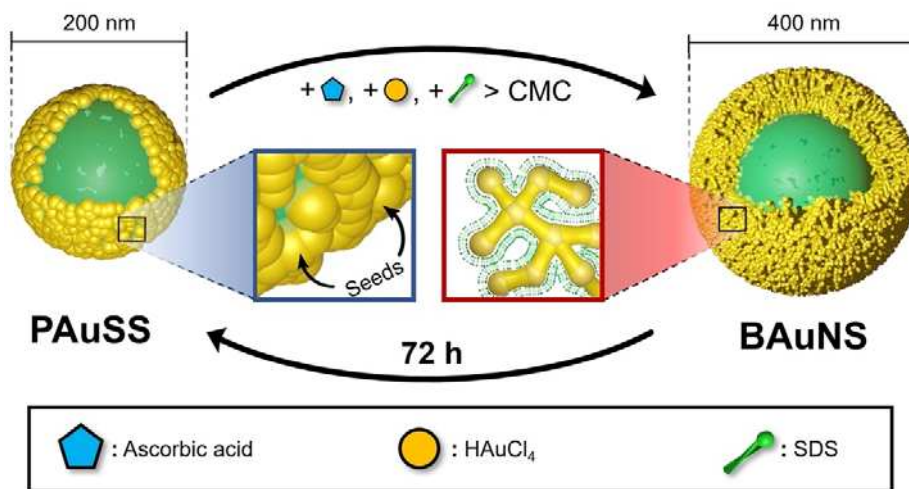
Figure 1 – Schematic representation of the BAuNS formation and its spontaneous disassembly after 72 hours.

Some of us previously reported the synthesis of peptide-Au superstructures (PAuSSs) comprising of an iodinated peptide (DF(I)NKF) core decorated with a monolayer of AuNPs.[17] PAuSSs are highly monodisperse, reproducible, and stable over time (> 1 year) in milliQ water, we thus reasoned that they could act as ideal templates for the synthesis and self-assembly of an additional gold nanolayer. Typically, templated synthesis involves the use of a pre-existing nanofabricate able to modulate the growth of building blocks and their spatial arrangement into larger and well-defined architectures.[18]   Herein, owing to their positively-charged surface (Fig. S4), PAuSSs would attract AuCl$_4^-$ ions and provide seeds for the growth of new AuNPs, that could self-assemble forming a branched layer (Fig. 1). In agreement with a common growth protocol used in aqueous solutions, we selected ascorbic acid (AA) as a mild reducing agent and sodium dodecyl sulphate (SDS) as a surfactant, to stabilize the newly-formed AuNPs layer.[19]

First, following our previously reported one-pot procedure,[17] we obtained a PAuSSs aqueous suspension (see Supporting information, Section 3 for synthetic procedure and characterization).

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Carefully timed additions of HAuCl4, SDS, incubation, and subsequent AA introduction to the PAuSS suspension allowed their evolution towards several different structures, whose morphology depended on reagent ratios (Table S2 and Fig. S5-S10). SDS concentration above its critical micellar concentration (CMC), *i.e.* 8.1 mM at 25 °C, promoted the formation of AuNPs and their templated self-assembly into an interconnected multilayer over the PAuSS surfaces, leading to the formation of branched gold nanoshells, as revealed by TEM characterization (Fig. 2A and S15).

Gold nanoshells represent a spherical layer of gold around a filled or hollow core, that can either be solid or porous,[20,21] with the latter possessing notable catalytic[22] and surface enhanced Raman scattering (SERS) activity.[23,24] To better probe the features of a BAuNS and of its external gold layer we extended the morphological characterization by close-up inspection of their edges *via* TEM. As shown in Fig. 2B, a dense layer of branched nanoparticles was observed, in which individual AuNPs can easily be distinguished as "knots" of the branches. Notably, gold nanostructures having a branched architecture with sharp features or small gaps that favour adsorption of analytes or cargos hold great promise in SERS, photothermal therapy, and other high-end applications.[25,26]

Electron tomography[27] was also performed to further study BAuNS morphological features. To avoid shrinkage caused by the electron beam damage, low dose imaging in combination with fast tomography was used (Fig 2C, Fig. S14 and Video S1). Orthoslices through the 3D reconstructed volume (Fig. 2D and Video S2) and HAADF-STEM projection images (Fig. 2E) showed an evident ring demarking the interface between the peptide core and the external layer, confirming PAuSS as the preferential assembly site of a 40-50 nm thick layer of AuNPs. According to their location on the TEM support grid, two different structures were detected (Fig. 2F and Video S3). When BAuNSs were placed on the edge of a hole in the carbon film of the TEM grids, they retained

their spherical shape, whereas on flat surfaces they assumed a hemispherical shape (Fig. S14), thanks to the ability of the soft peptide core and of the gold external layer to rearrange their shape. Independently from the grid location and possible shape adjustment, BAuNSs retained their structure and the AuNPs external layer remained intact. Interestingly, the (hemi)spherical shape stayed stable regardless of the drying process required to prepare sample for TEM imaging, meaning the peptide core is simultaneously soft enough to permit shape rearrangements according to the surrounding environment and stiff enough to preserve the curved morphology of BAuNSs even in the dry state.
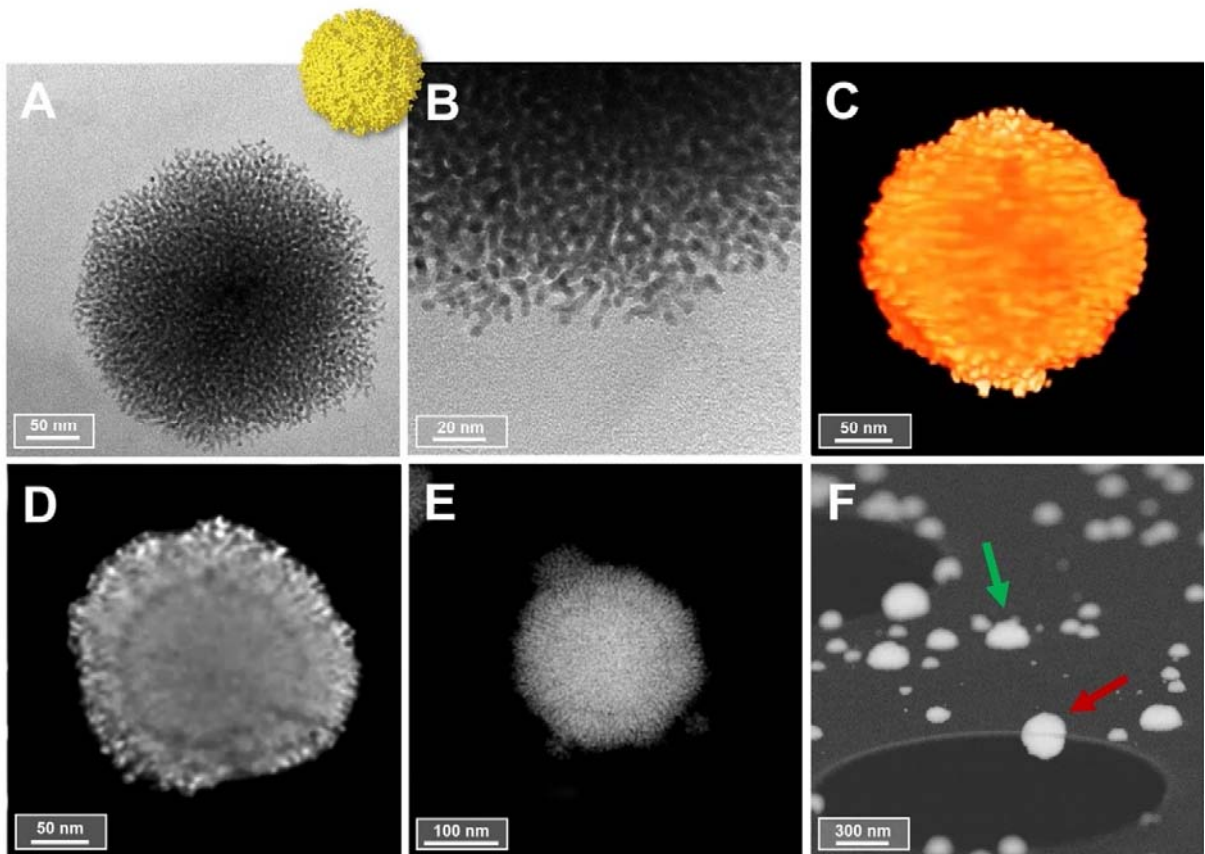

Figure 2 – A) TEM image of a typical BAuNS; B) TEM image showing the edge of a BAuNS, highlighting branches formed by the coalescence of individual AuNPs; C) 3D Visualisation of the tomographic reconstruction of an individual BAuNS; D) Orthoslice through the 3D reconstruction

obtained by electron tomography; E) HAADF-STEM image of a BAuNS, highlighting the interface between the inner core and the outer shell; F) HAADF-STEM image of BAuNSs, displaying their soft nature as spherical (red arrow) or hemispherical (green arrow) assemblies according to their position on the grid.

Over the course of the assembly process, BAuNSs formation was accompanied by several colour changes of the sample solution that could be used to track the Au(III) reduction and AuNP self-assembly process. The PAuSS solution is characterized by a dark blue colour (Fig. 3A). Upon addition of $HAuCl_4$ and SDS to a PAuSSs suspension, mild sample decolouration and LSPR (localized surface plasmon resonance) redshift could be observed (λ_{SPR} = 598 nm) (Fig. 3A). The addition of AA and subsequent formation of BAuNSs led to a further change in the solution colour, that shifted from light blue to red. The intense colour variation of BAuNSs suspension was investigated *via* UV-vis measurements, which revealed a LSPR blueshift (λ_{SPR} = 586 nm), consistent with the observed colour change, accompanied by an increase in absorbance at the same wavelength (Fig. 3B). Persistence of a strong signal at λ = 305 nm in spectra recorded right after AA addition (Fig. 3C) suggested that $HAuCl_4$ reduction did not happen instantaneously, thus reaction kinetics was followed by tracking absorbance of both $HAuCl_4$ and superstructures/nanoshells for several days (Fig. S15). After few hours from AA addition, $HAuCl_4$ signal reached a plateau, suggesting an almost complete consumption of gold salts and no further growth of BAuNSs. Indirect confirmation of the described reaction kinetics was inferred by ζ-potential measurements (Fig. 3D), as positively charged AuSSs (ζ_{pot} = +34 mV) assumed a strongly negative surface charge (ζ_{pot} = -72 mV) during incubation with SDS and $HAuCl_4$ and then equilibrated at a slightly less negative potential (ζ_{pot} = -59 mV).

AA is typically considered a weak reducing agent, meaning that it is able to promote gold salts reduction to achieve controlled growth of Au seeds, limiting secondary nucleation.[19] Preferential attachment of freshly reduced Au atoms to small seeds is favoured by their higher radius of curvature and high energy surface, generally leading to the formation of uniformly sized AuNPs populations, even when starting from rather polydisperse batches. Such an effect of AA was confirmed also in our system, where the AuNPs constituting the external branched layer of BAuNS showed a highly uniform diameter of about 5 nm (Fig. S14E). Moreover, DLS analyses (Fig. 3E) revealed that highly monodisperse PAuSSs gradually increase their hydrodynamic radius, simultaneously becoming more polydisperse as freshly-reduced AuNPs start to cluster around them, mostly generating binary or ternary systems with closely packed structures (Fig. S15). Therefore, incubation of PAuSSs with gold salt and SDS led to a rather polydisperse suspension, which is reflected in its broad LSPR peak (Fig. 3B). AA addition and subsequent BAuNS formation, instead, led to a more monodispersed system, suggesting that BAuNSs are quite uniform in size and shape.

To further verify BAuNS composition, we employed electron energy loss spectroscopy (EELS) technique, which was performed on both PAuSSs and BAuNSs, exploiting iodine atoms as easily traceable labels for DF(I)NKF localization. Rather homogeneous iodine distribution was recorded over the entire PAuSS and BAuNS surfaces, whereas Au signal resulted more concentrated on the edges of PAuSS surface with respect to BAuNSs (Fig. 3F and Fig. S4, S13). The good overlay of EELS signals attributed to I and Au in both structures coupled with an increased Au/I ratio of BAuNSs with respect to PAuSSs emphasises that assembly occurs on pre-existing superstructures, which act as templates for the development of the external shell. Remarkably, substitution of PAuSS with commonly employed Au seeds did not lead either to the formation of BAuNSs, or of

any other system, confirming the essential role of the chosen template in modulating BAuNS formation (Fig S11).
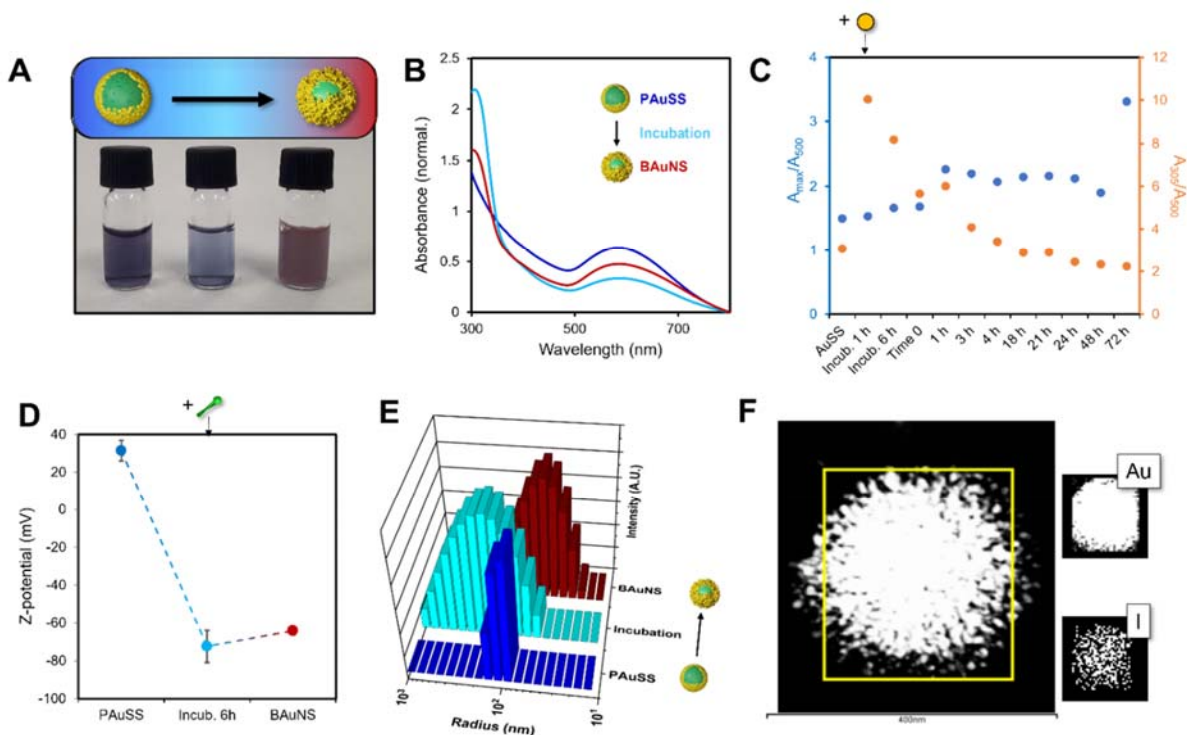

Figure 3 – A) Cartoon and pictures of main stages during BAuNS formation: PAuSSs with a dark blue colour (left), incubated growth solution with a transparent blue colour (center), and BAuNSs with a dark red colour (left); B) UV-vis spectra evolution during BAuNSs formation; C) Normalized changes in absorbance intensity of $HAuCl_4$ consumption (orange) and BAuNSs formation (blue). A_{max} denotes the absorbance at the wavelength of maximum LSPR absorption, A_{500} denotes the absorbance at a wavelength of 500 nm, and A_{305} denotes the absorbance at a wavelength of 305 nm; D) ζ-potential variation during core stages of BAuNSs assembly, highlighting steep decrease when SDS is introduced in the growth solution; E) DLS intensity profiles of PAuSSs (blue), growth solution (light blue), and BAuNSs (red) during core stages of the assembly process; F) EELS map of individual BAuNS with overlapped I and Au signals. On

the right, Au and I maps are reported, displaying rather homogeneous distribution of both elements on the entire analyzed region.

BAuNSs remained stable for 72 hours. After this period of time, BAuNSs normalized absorbance increased and TEM characterization revealed the complete disappearance of BAuNSs in favour of PAuSSs (Fig. 4A, B and Fig. S15). The regression to PAuSSs was determined by the disassembly of the peripheral branched gold layer with consequent release of AuNPs. After several weeks from disassembly, TEM images showed released AuNPs partially coalescing into large gold aggregates present either at PAuSSs surface or dispersed in suspension (Fig. S16), permanently changing the morphological and energetic landscape of the system and, as such, hindering the possibility to undergo further assembly-disassembly cycles (see Supporting Information, Section 6). This behavior revealed the transient and metastable nature of BAuNSs, indicating that, when sufficient amount of surfactant was provided (BAuNSs are not formed when SDS < CMC, see Fig. S8), we could induce the out-of-equilibrium self-assembly of gold nanoshells.

Based on the obtained results, we suggest the following mechanism for the transient formation of BAuNSs (Fig. 4A). First, PAuSSs are formed. Upon addition of $HAuCl_4$ and SDS, the positively charged surface of the employed templates attracts the $AuCl_4^-$ ions and SDS molecules on its surface. AA addition leads to Au reduction and consequent formation of AuNPs capped by SDS, that plays a key role in the out-of-equilibrium assembly of the gold nanoshell. Indeed, SDS is known to cap only specific crystallographic Au planes,[19] and to, overall, have a weak protecting ability. This is due to its tendency to form lamellar micelles that cover only some areas of the surfaces of the growing nanoparticles, leaving some uncapped regions that, as already reported, act as branching points favoring AuNPs to connect with each other and form networked structures.

We thus obtained a branched nanoshell in which SDS reaches high localized concentration, forming lamellar structure that are intercalated between AuNPs (Fig. 4A). As SDS concentration equilibrates within the solution, single SDS-capped AuNPs are gradually released from the branched layer, leading to BAuNSs disassembly. The released AuNPs are not fully stabilized by SDS, thus they coalesce forming larger structures (Fig. 4A).

Traditionally, systems assembled away from their thermodynamic equilibrium are formed driven by a fuel and their disassembly is triggered by either complete fuel consumption/deactivation or by a counter-stimulus. In our system the self-assembly process is triggered by Au(III) reduction, that drives the system to a transient out-of-equilibrium state featuring steep concentration gradients of SDS throughout the sample. BAuNSs disassembly is, instead, spontaneous, and solely determined by SDS concentration equalization in the sample. Although different from traditional examples of out-of-equilibrium systems designed using peptides and polymers,[28,29] spontaneous disassembly has already been shown for transient systems obtained with nanoparticles.[16,30] Notably, SDS role was corroborated by evaluating the impact of its concentration on BAuNSs formation and features. Indeed, no BAuNSs were observed when SDS concentration was below its CMC (Fig. S8). Conversely, when BAuNSs were synthesized employing a higher SDS concentration, it was possible to extend their lifetime to 96 hours, confirming the key role of SDS concentration equilibration in the solution in triggering BAuNS disassembly (Fig. S18). Of note, untreated PAuSSs remained stable for more than one year, indicating that PAuSSs are thermodynamically stable structures, which, upon addition of SDS, AA, and $HAuCl_4$, favours the formation of highly energetic and unstable structures, *i.e.*, BAuNSs, that transiently exists far from thermodynamic equilibrium.

Engineering metastable NP-based systems, able to undergo interconversion between an out-of-equilibrium state and a thermodynamically favourable one, grant access to spatiotemporal control of optical response, with the emergence of transient plasmonic responses.[16,31] Such an oscillation of optical properties was observed also in our system, that showed a consistent bathochromic shift upon incubation with SDS and $AuCl_4^-$ (Fig. 4C), due to their absorption over the template and the change of the surface features in terms of composition and charge. BAuNS assembly was accompanied by a relevant hypsochromic shift (Fig. 4D), determined by the AuNPs layer formation and the final relatively low core size:shell thickness ratio characterizing BAuNSs.[32] Finally, after 72 hours from AA addition to the system, BAuNSs disassembly into AuSSs caused the system to regain its initial optical feature (Fig. 4E). Indeed, almost no change in the LSPR wavelength was observed between freshly synthesized PAuSSs and PAuSSs that have undergone the out-of-equilibrium assembly dynamics.
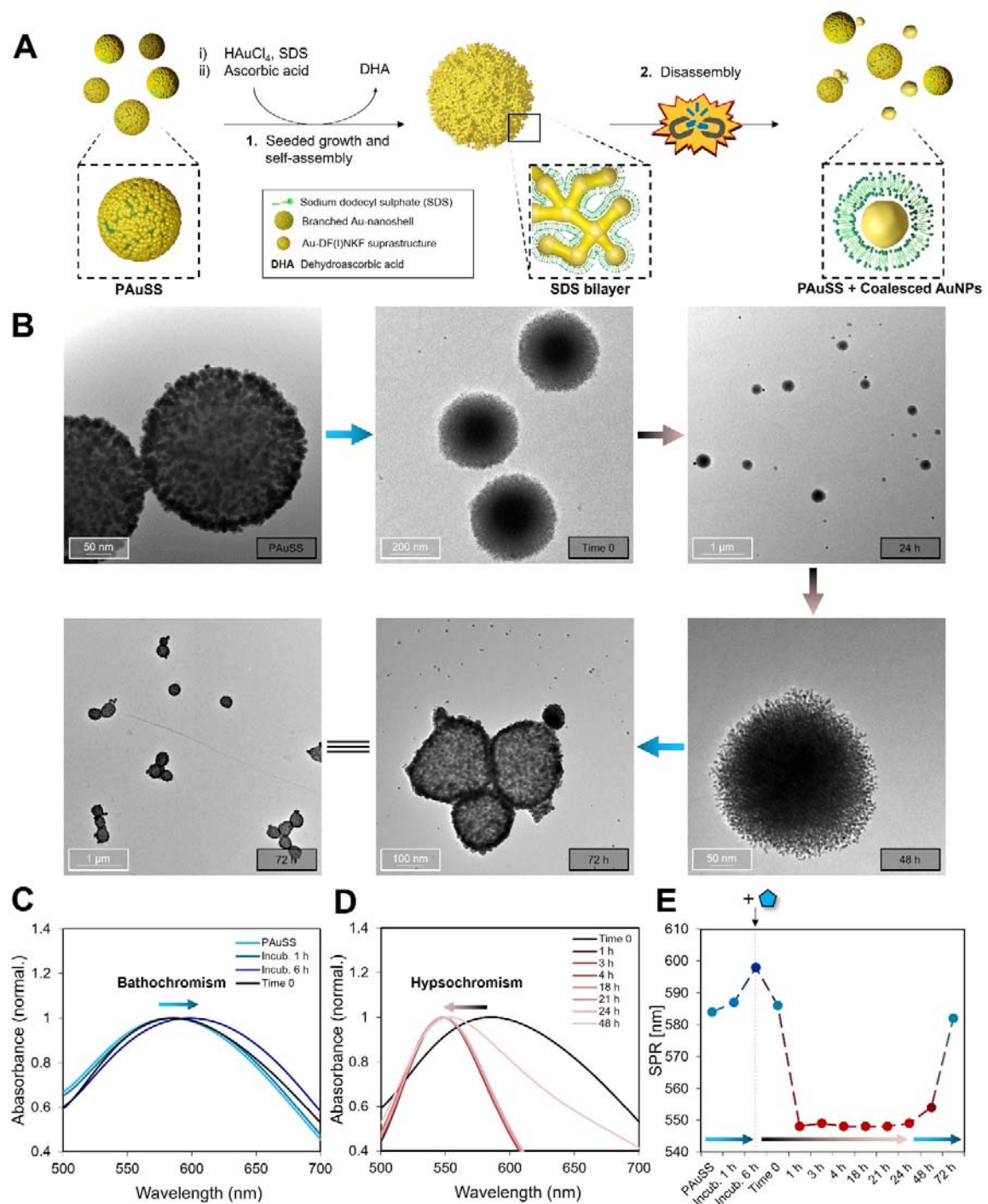
Figure 2 – A) Schematic representation of the proposed mechanism underlying the system dynamics; B) TEM images acquired at different stages of the disassembly process; C) UV-vis spectra displaying the changes to the normalized absorbance during BAuNS assembly; D) UV-vis

spectra displaying the changes to the normalized absorbance during BAuNS disassembly; E) Surface plasmon resonance (SPR) peak position variation during consecutive assembly and disassembly of BAuNSs.

In summary, we applied a common seed-mediated approach for the growth of AuNPs on previously developed peptide-Au superstructures, achieving out-of-equilibrium self-assembly of branched Au nanoshells. We showed that formation of the nanoshells is promoted by a balance between nucleation of novel AuNPs favoured by the reducing agent and their stabilization by SDS lamellar bilayers intercalated between AuNPs. Branched Au nanoshell were found to be transient with a lifetime of 72 hours, indicating that their formation happens in out-of-equilibrium conditions, featuring high intraparticle SDS concentration. As SDS concentration equalizes within the solution, disassembly of the systems happens spontaneously. Notably, when employing common Au seeds, branched nanoshells were not formed, highlighting the relevance of templates in the design of out-of-equilibrium systems based on nanoparticles with a controlled morphology. The transient nature of the obtained nanoshells favours temporary interparticle plasmonic coupling, leading to a remarkable oscillation of optical properties. Overall, our approach represents a simple, yet efficient, strategy to achieve the formation of transient 3D gold nanostructures with a precise morphology, exploiting an out-of-equilibrium self-assembly process. We envisage that self-assembled AuNPs systems that allow dynamic control over their plasmonic properties might represent an innovative approach for the design of transient optical switches and sensors, possibly paving the way towards the development of nanoscale materials with temporal optical features.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Materials and methods; synthesis and characterization of PAuSSs; control samples synthesis and characterization; synthesis, characterization and out-of-equilibrium self-assembly of BAuNSs;

3D tomographic reconstruction of drop-on-hole edge BAuNSs (mp4);

2D tomograms of drop-on-hole edge BAuNSs (mp4);

3D tomographic reconstruction of drop-on-flat surface BAuNSs (mp4);

2D tomograms of drop-on-flat surface BAuNSs (mp4);

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Author Contributions

A.M. conceived the experiments, performed the majority of the experiments and wrote the manuscript; C.P. wrote and revised the manuscript, conceived the experiments and contributed to the discussion of the results; A.G. synthesized the peptide; A.F. performed EELS analyses; D.A.E. and S.B performed STEM measurements and tomographic reconstructions, and contributed to the discussion of results; P.M. conceived the experiments, contributed to the discussion of results, and revised the manuscript.

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

AA, ascorbic acid; AuNPs, gold nanoparticles; BAuNSs, branched gold nanoshells; CMC, critical micellar concentration; DLS, dynamic light scattering; EELS, electron energy loss spectroscopy; LSPR, localized surface plasmon resonance; NPs, nanoparticles; PAuSSs, peptide-Au superstructures; SDS, sodium dodecyl sulphate; SERS, surface enhanced Raman scattering; STEM, scanning transmission electron microscopy; TEM, transmission electron microscopy; UV-vis, ultraviolet-visible.

REFERENCES

(1)   Mattia, E.; Otto, S. Supramolecular Systems Chemistry. *Nat. Nanotechnol.* **2015**, *10* (2), 111–119.

(2)   Grzybowski, B. A.; Huck, W. T. S. The Nanotechnology of Life-Inspired Systems. *Nat. Nanotechnol.* **2016**, *11* (7), 585–592.

(3)   Walther, A. Viewpoint: From Responsive to Adaptive and Interactive Materials and

Materials Systems: A Roadmap. *Adv. Mater.* **2020**, *32* (20), 1905111.

(4)   Ragazzon, G.; Prins, L. J. Energy Consumption in Chemical Fuel-Driven Self-Assembly. *Nat. Nanotechnol.* **2018**, *13*, 882–889.

(5)   Paterson, S.; Thompson, S. A.; Gracie, J.; Wark, A. W.; de la Rica, R. Self-Assembly of Gold Supraparticles with Crystallographically Aligned and Strongly Coupled Nanoparticle Building Blocks for SERS and Photothermal Therapy. *Chem. Sci.* **2016**, *7* (9), 6232–6237.

(6)   Buntara Sanjeeva, K.; Pigliacelli, C.; Gazzera, L.; Dichiarante, V.; Baldelli Bombelli, F.; Metrangolo, P. Halogen Bond-Assisted Self-Assembly of Gold Nanoparticles in Solution and on a Planar Surface. *Nanoscale* **2019**, *11* (39), 18407–18415.

(7)   Kotov, N. A. Particle Self-Assembly: Superstructures Simplified. *Nat. Nanotechnol.* **2016**, *11*, 1002–1003.

(8)   Nie, Z.; Petukhova, A.; Kumacheva, E. Properties and Emerging Applications of Self-Assembled Structures Made from Inorganic Nanoparticles. *Nat. Nanotechnol.* **2010**, *5*, 15–25.

(9)   Grzelczak, M.; Vermant, J.; Furst, E. M.; Liz-Marzán, L. M. Directed Self-Assembly of Nanoparticles. *ACS Nano* **2010**, *4* (7), 3591–3605.

(10)   Dichiarante, V.; Pigliacelli, C.; Metrangolo, P.; Baldelli Bombelli, F. Confined Space Design by Nanoparticle Self-Assembly. *Chem. Sci.* **2021**, *12* (5), 1632–1646.

(11)   Lagzi, I.; Kowalczyk, B.; Wang, D.; Grzybowski, B. A. Nanoparticle Oscillations and Fronts. *Angew. Chem. Int. Ed.* **2010**, *49* (46), 8616–8619.

(12)   Yucknovsky, A.; Mondal, S.; Burnstine-Townley, A.; Foqara, M.; Amdursky, N. Use of Photoacids and Photobases To Control Dynamic Self-Assembly of Gold Nanoparticles in Aqueous and Nonaqueous Solutions. *Nano Lett.* **2019**, *19* (6), 3804–3810.

(13)   Zhao, H.; Sen, S.; Udayabhaskararao, T.; Sawczyk, M.; Kučanda, K.; Manna, D.; Kundu, P. K.; Lee, J.-W.; Král, P.; Klajn, R. Reversible Trapping and Reaction Acceleration within Dynamically Self-Assembling Nanoflasks. *Nat. Nanotechnol.* **2016**, *11*, 82–88.

(14)   Kundu, P. K.; Das, S.; Ahrens, J.; Klajn, R. Controlling the Lifetimes of Dynamic Nanoparticle Aggregates by Spiropyran Functionalization. *Nanoscale* **2016**, *8* (46), 19280–19286.

(15)   Grötsch, R. K.; Wanzke, C.; Speckbacher, M.; Angı, A.; Rieger, B.; Boekhoven, J. Pathway Dependence in the Fuel-Driven Dissipative Self-Assembly of Nanoparticles. *J. Am. Chem. Soc.* **2019**, *141* (25), 9872–9878.

(16)   Sawczyk, M.; Klajn, R. Out-of-Equilibrium Aggregates and Coatings during Seeded Growth of Metallic Nanoparticles. *J. Am. Chem. Soc.* **2017**, *139* (49), 17973–17978.

(17)   Pigliacelli, C.; Sanjeeva, K. B.; Nonappa; Pizzi, A.; Gori, A.; Bombelli, F. B.; Metrangolo, P. In Situ Generation of Chiroptically-Active Gold-Peptide Superstructures Promoted by Iodination. *ACS Nano* **2019**, *13* (2), 2158–2166.

(18)   Jones, M. R.; Osberg, K. D.; MacFarlane, R. J.; Langille, M. R.; Mirkin, C. A. Templated Techniques for the Synthesis and Assembly of Plasmonic Nanostructures. *Chem. Rev.* **2011**, *111* (6), 3736–3827.

(19)   Kuo, C.-H.; Chiang, T.-F.; Chen, L.-J.; Huang, M. H. Synthesis of Highly Faceted

Pentagonal- and Hexagonal-Shaped Gold Nanoparticles with Controlled Sizes by Sodium Dodecyl Sulfate. *Langmuir* **2004**, *20* (18), 7820–7824.

(20)   Liu, C.; Luo, L.; Zeng, L.; Xing, J.; Xia, Y.; Sun, S.; Zhang, L.; Yu, Z.; Yao, J.; Yu, Z.; Akakuru, O. U.; Saeed, M.; Wu, A. Porous Gold Nanoshells on Functional NH 2 -MOFs: Facile Synthesis and Designable Platforms for Cancer Multiple Therapy. *Small* **2018**, *14* (35), 1801851.

(21)   Park, T.-H.; Jeong, D.-W.; Lee, J. H.; Jang, D.-J. Seed-Assembly-Mediated Fabrication and Application of Highly Branched Gold Nanoshells Having Hollow and Porous Morphologies. *Nanotechnology* **2022**, *33* (15), 155605.

(22)   Park, T.-H.; Lee, H.; Lee, J.; Jang, D.-J. Morphology Evolution of Ag/Au Nanocomposites via Temperature-Controlled Galvanic Exchange to Enhance Catalytic Activity. *RSC Adv.* **2017**, *7* (13), 7718–7724.

(23)   Chauvin, A.; Lafuente, M.; Mevellec, J. Y.; Mallada, R.; Humbert, B.; Pina, M. P.; Tessier, P.-Y.; El Mel, A. Lamellar Nanoporous Gold Thin Films with Tunable Porosity for Ultrasensitive SERS Detection in Liquid and Gas Phase. *Nanoscale* **2020**, *12* (23), 12602–12612.

(24)   Chew, W. S.; Pedireddy, S.; Lee, Y. H.; Tjiu, W. W.; Liu, Y.; Yang, Z.; Ling, X. Y. Nanoporous Gold Nanoframes with Minimalistic Architectures: Lower Porosity Generates Stronger Surface-Enhanced Raman Scattering Capabilities. *Chem. Mater.* **2015**, *27* (22), 7827–7834.

(25)   Sanz-Ortiz, M. N.; Sentosun, K.; Bals, S.; Liz-Marzán, L. M. Templated Growth of Surface

Enhanced Raman Scattering-Active Branched Gold Nanoparticles within Radial Mesoporous Silica Shells. *ACS Nano* **2015**, *9* (10), 10489–10497.

(26)   Van De Broek, B.; Devoogdt, N.; Dhollander, A.; Gijs, H. L.; Jans, K.; Lagae, L.; Muyldermans, S.; Maes, G.; Borghs, G. Specific Cell Targeting with Nanobody Conjugated Branched Gold Nanoparticles for Photothermal Therapy. *ACS Nano* **2011**, *5* (6), 4319–4328.

(27)   Ishikawa, T. Electron Tomography. In *Encyclopedia of Cell Biology*; Bradshaw, R. A., Stahl, P. D., Eds.; Elsevier, 2016; Vol. 2, pp 22–31.

(28)   Sorrenti, A.; Leira-Iglesias, J.; Sato, A.; Hermans, T. M. Non-Equilibrium Steady States in Supramolecular Polymerization. *Nat. Commun.* **2017**, *8* (May), 1–8.

(29)   Sheehan, F.; Sementa, D.; Jain, A.; Kumar, M.; Tayarani-Najjaran, M.; Kroiss, D.; Ulijn, R. V. Peptide-Based Supramolecular Systems Chemistry. *Chem. Rev.* **2021**, *121* (22), 13869–13914.

(30)   Rao, A.; Roy, S.; Pillai, P. P. Temporal Changes in Interparticle Interactions Drive the Formation of Transiently Stable Nanoparticle Precipitates. *Langmuir* **2021**, *37* (5), 1843–1849.

(31)   Liu, L.; Gao, Z.; Jiang, B.; Bai, Y.; Wang, W.; Yin, Y. Reversible Assembly and Dynamic Plasmonic Tuning of Ag Nanoparticles Enabled by Limited Ligand Protection. *Nano Lett.* **2018**, *18* (8), 5312–5318.

(32)   Hu, M.; Chen, J.; Li, Z.-Y.; Au, L.; Hartland, G. V.; Li, X.; Marquez, M.; Xia, Y. Gold Nanostructures: Engineering Their Plasmonic Properties for Biomedical Applications.

Chem. Soc. Rev. **2006**, *35* (11), 1084–1094.