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

Alessandro Marchetti,^[a] Alessandro Gori,^[b] Anna Maria Ferretti,^[b] Daniel Arenas Esteban,^[c] Sara Bals,^[c] Claudia Pigliacelli,^{*[a]} Pierangelo Metrangolo^{*[a]}

[a] A. Marchetti, Dr. C. Pigliacelli, Prof. P. Metrangolo
Laboratory of Supramolecular and Bio-Nanomaterials (SBNLab)
Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta"
Politecnico di Milano
Via L. Mancinelli 7, 20131 Milano, Italy
E-mail: claudia.pigliacelli@polimi.it; pierangelo.metrangolo@polimi.it

[b] Dr. A. Gori, Dr. A.M. Ferretti
Istituto di Scienze e Tecnologie Chimiche
National Research Council of Italy
Via M. Bianco 9, 20131 and Via G. Fantoli 16/15, 20138 Milano, Italy

[c] Dr. D. Arenas Esteban, Prof. S. Bals
Electron microscopy for Materials research (EMAT)
University of Antwerp
Groenenborgerlaan 171, 2020 Antwerpen, Belgium

Supporting information for this article is given via a link at the end of the document.

Abstract: Out-of-equilibrium self-assembly of metal nanoparticles (NPs) has been devised using different types of strategies and fuels, but achieving 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 sample solution, leading to NPs disassembly and regression to PAuSS. Notably, BAuNS assembly and disassembly promoted temporary interparticle plasmonic coupling, leading to reversible and tuneable changes of their plasmonic properties, a highly desirable behaviour in the development of optoelectronic nanodevices.

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.^[3-5] While being popular building blocks for the development of static self-assembled nanostructures,^[6-8] the use of metal nanoparticles (NPs) to devise dynamic systems is still in its infancy.^[9-11]

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.^[12] 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.^[13-15] Clustering of AuNPs and iron oxide NPs has also been regulated by a chemical reaction cycle that hydrolyses a carbodiimide-based fuel.^[16] 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.^[17] Overall, when driving metal NPs self-assembly far from thermodynamic equilibrium, it remains highly challenging to achieve the formation of transient assemblies with a finely tuned and finite morphology. This key feature could ease the actual application of these systems and expand their practical relevance in the design of optoelectronic nanodevices, such as optical switches or waveguides, sensors and switchable catalysts.^[18]

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

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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 equilibrates over time in solution, dismantling of BAuNSs occurs by AuNPs disassembly. Notably, BAuNSs assembly and disassembly favoured temporary interparticle plasmonic coupling, leading to a tuneable change of the AuNPs optical properties.

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.^[19] Key figures of merit of PAuSSs is that they are highly monodisperse,

robust, and stable over time (> 1 year) in milliQ water. As templated synthesis typically 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,^[20] we reasoned that our PAuSS could act as ideal templates for the synthesis and self-assembly of an additional gold nanolayer. In our vision, owing to their positively-charged surface (Fig. S4), PAuSSs would attract AuCl_4^- ions and provide seeds for the templated growth of new AuNPs that self-assemble forming a further NPs 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.^[21]

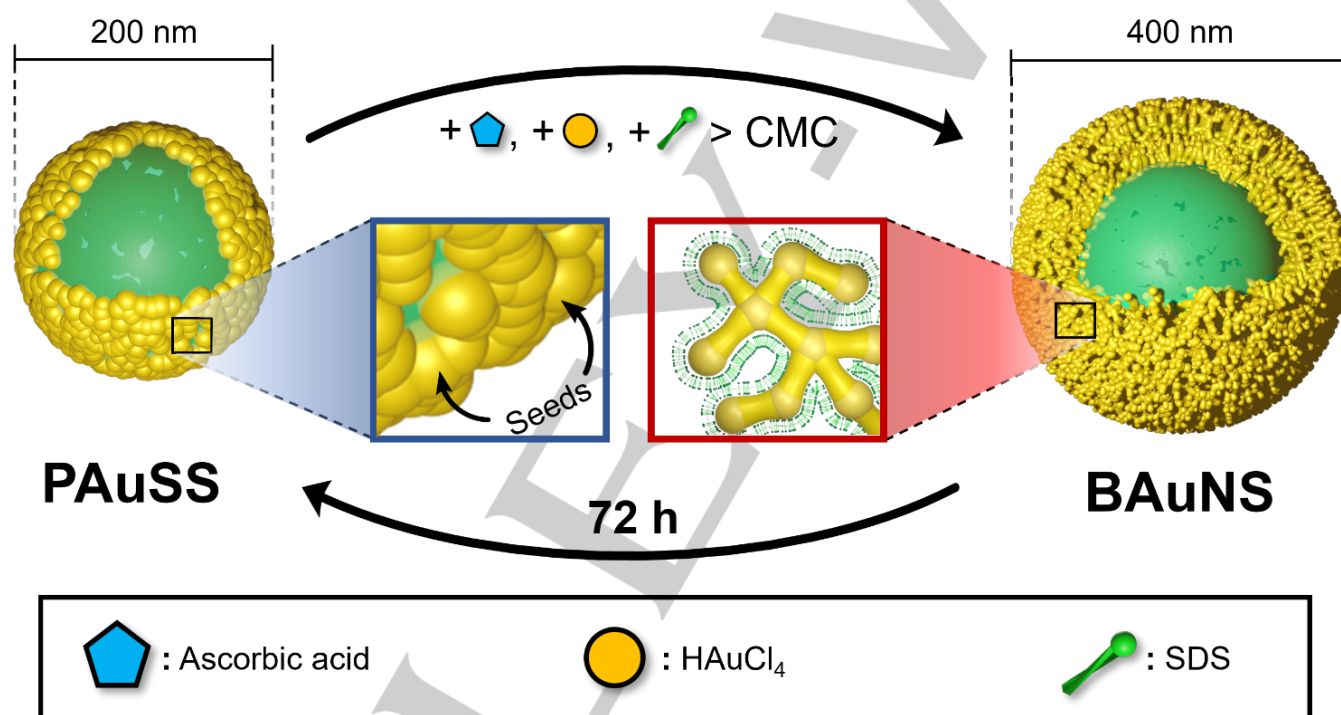


Figure 1. Schematic representation of the BAuNS formation and its spontaneous disassembly after 72 hours.

First, following our previously reported one-pot procedure,^[19] we obtained a PAuSSs aqueous suspension (see Supporting information, Section 3 for synthetic procedure and characterization). Carefully timed additions of HAuCl_4 , SDS, incubation, and subsequent AA introduction to the PAuSS suspension allowed their evolution towards several different structures, whose morphology depended on reagents 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,^[22,23] with the latter possessing notable catalytic^[24] and surface enhanced Raman scattering (SERS) activity.^[25,26] To better probe the features of a BAuNS and its external gold layer we extended the

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morphological characterization by close-up inspection of its 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.^[27,28]

Electron tomography^[29] 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. Conversely, 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 form. 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 remained 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.

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 HAuCl₄ and SDS to a PAuSSs suspension, mild sample decolouration and LSPR

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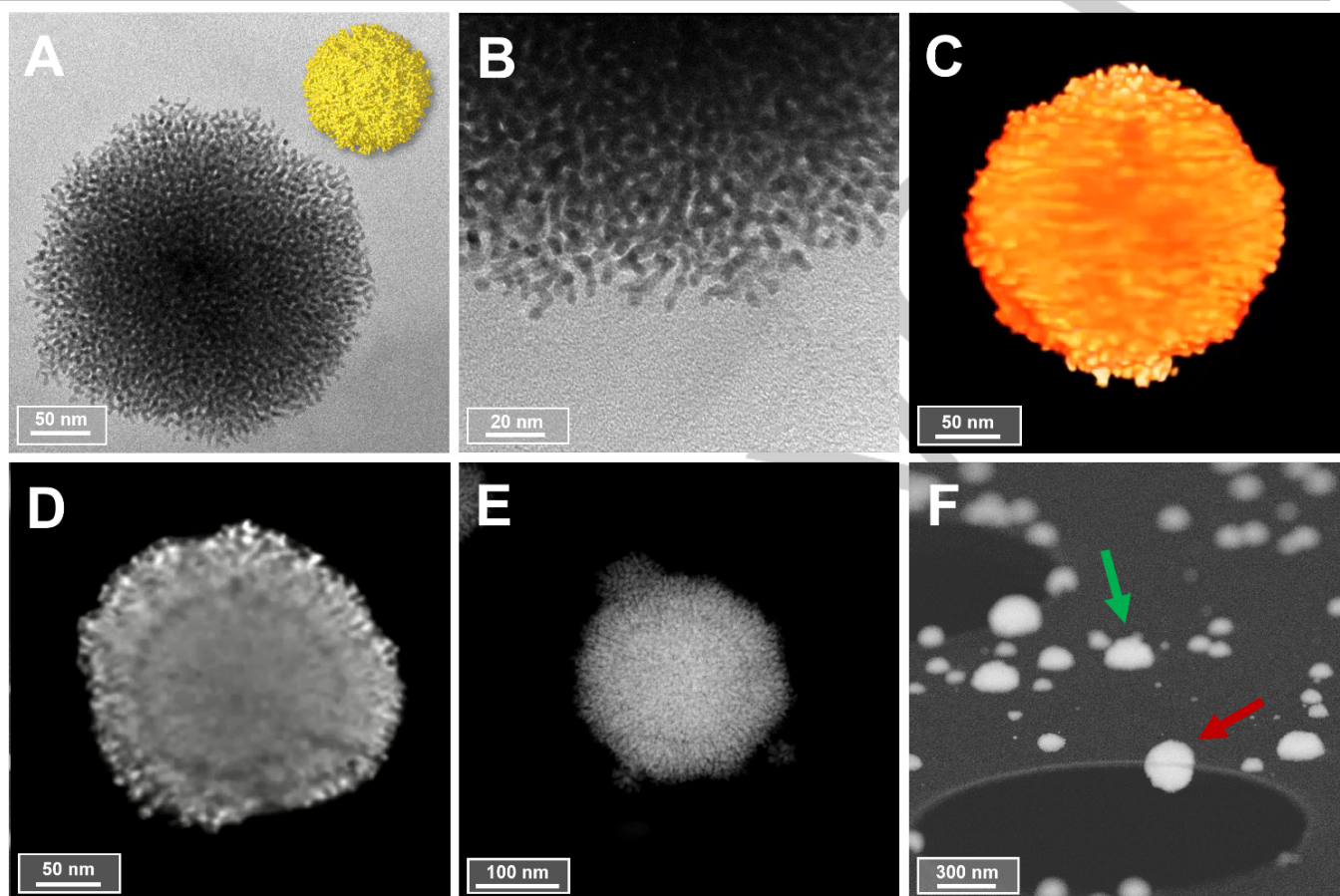


Figure 2. A) TEM image of a typical BAuNS; B) TEM image showing the edge of a BAuNS, highlighting branches formed by the coalescence of individual AuNPs; C) 3D visualisation of tomographic reconstruction of an individual BAuNS; D) Orthoslice through the 3D reconstruction obtained by electron tomography;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

(localized surface plasmon resonance) redshift ($\lambda_{\text{SPR}} = 598 \text{ nm}$) could be observed (Fig. 3A). The addition of AA and subsequent formation of BAuNSs led to a further change in the solution colour, that turned from light blue to red. The intense colour variation of BAuNSs suspension was investigated via UV-vis measurements, which revealed a LSPR blueshift ($\lambda_{\text{SPR}} = 586 \text{ nm}$), consistent with the observed colour change, accompanied by an increase in absorbance at the same wavelength (Fig. 3B). Persistence of a strong signal at $\lambda = 305 \text{ nm}$ 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 PAuSSs ($\zeta_{\text{pot}} = +34 \text{ mV}$) assumed a strongly negative surface charge ($\zeta_{\text{pot}} = -72 \text{ mV}$) during incubation with SDS and HAuCl_4 and then equilibrated at a slightly less negative potential ($\zeta_{\text{pot}} = -59 \text{ mV}$).

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.^[21] 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

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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, yielded a more monodispersed system, suggesting that BAuNSs are quite uniform in size and shape.

To further verify BAuNS composition, we employed energy dispersive X-ray spectroscopy (EDX) 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 EDX elemental maps attributed to I and Au in both structures coupled

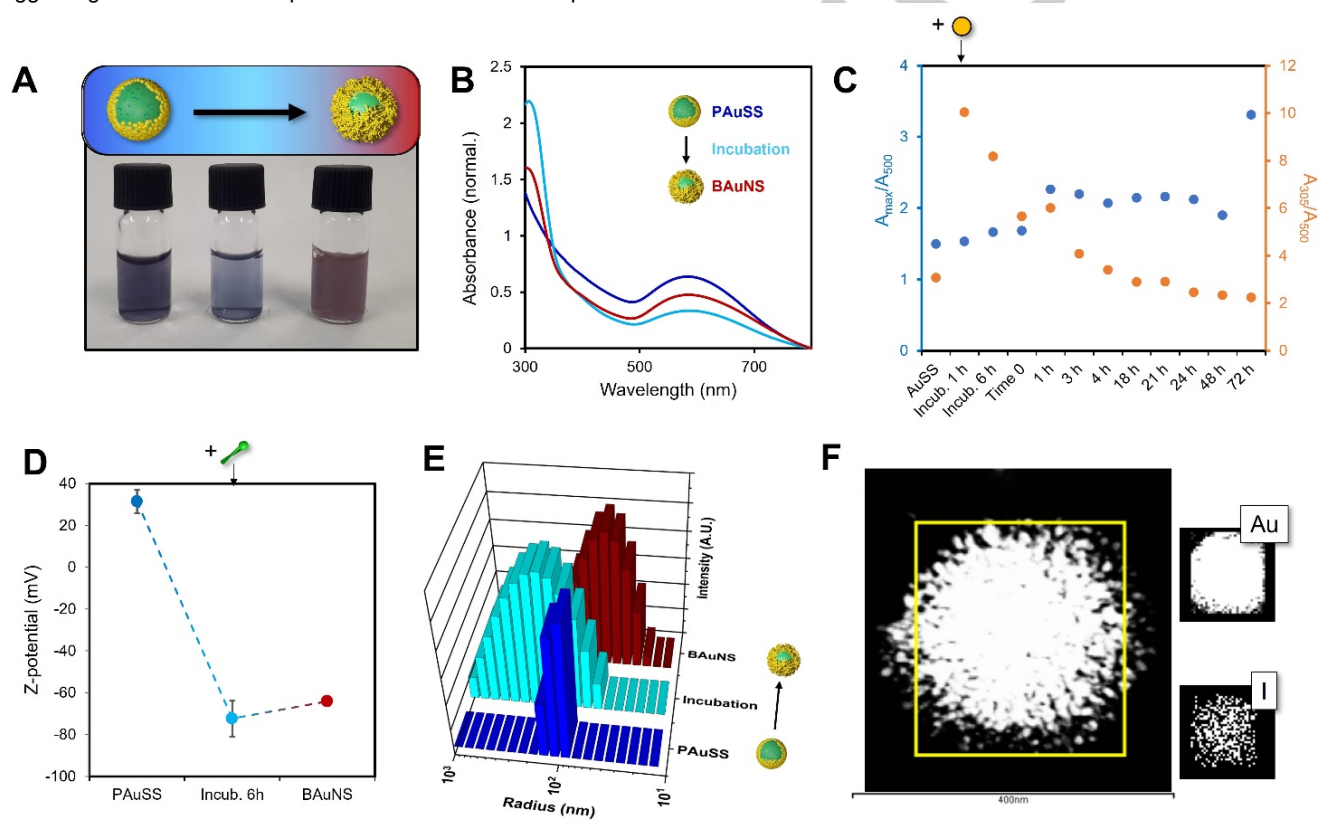


Figure 3. A) Cartoon and pictures of main stages during BAuNS formation: PAuSSs with a dark blue colour (left), incubated growth solution with a transparent blue colour (center), and BAuNSs with a dark red colour (right); B) UV-vis spectra evolution during BAuNSs formation; C) Normalized changes in absorbance intensity of HAuCl₄ 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) EDX 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 analysed region.

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).

BAuNSs remained stable for 72 hours. After this period of time, their normalized absorbance increased and TEM characterization revealed the complete disappearance of BAuNSs in favour of

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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 four 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 behaviour revealed the transient and metastable nature of BAuNSs, indicating that, when sufficient amount of surfactant was provided (BAuNSs are not formed when $\text{SDS} < \text{CMC}$, 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 and to, overall, have a weak protecting ability.^[21] 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 favouring AuNPs to connect with each other forming 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 thanks to the drive of 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

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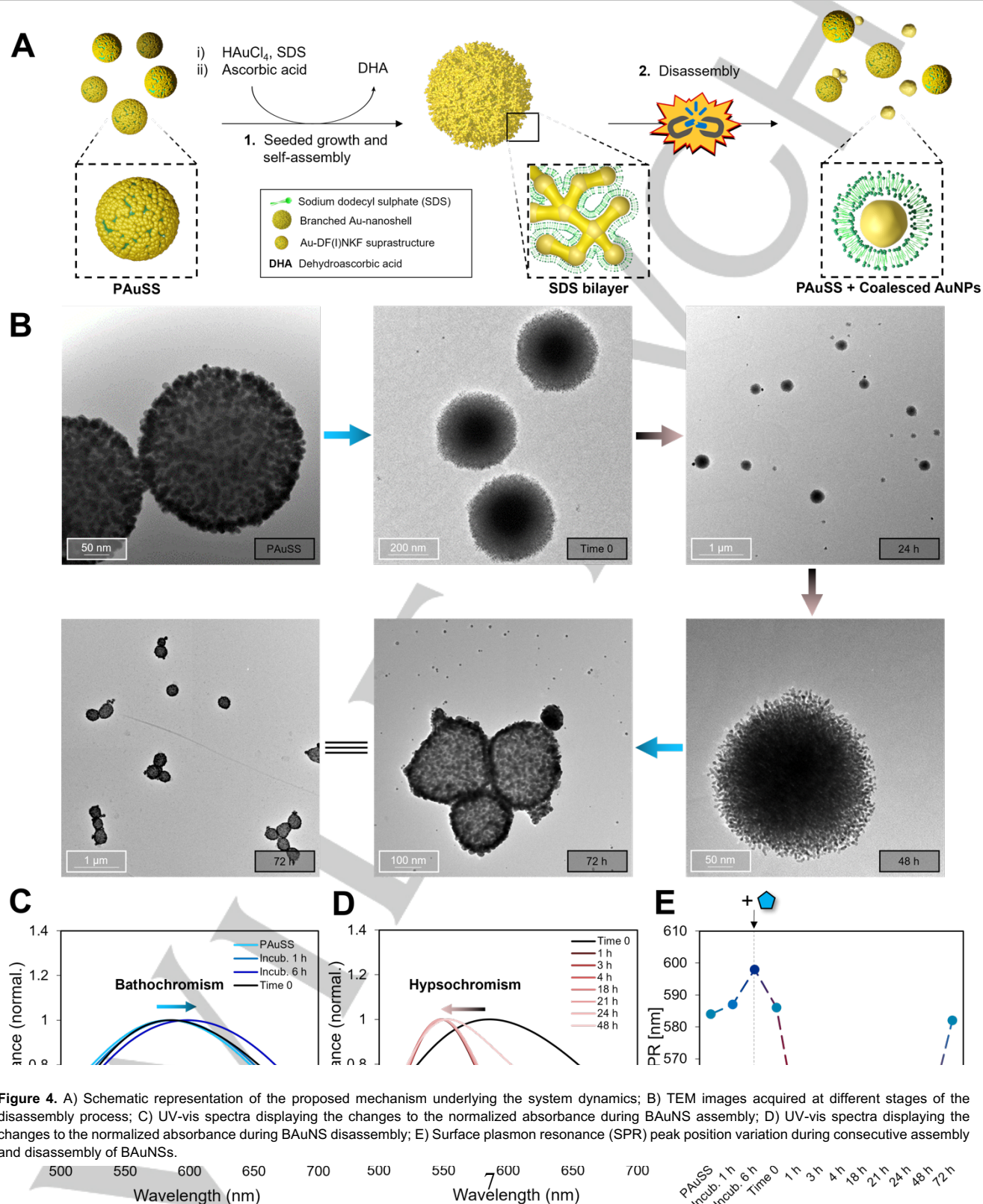


Figure 4. A) Schematic representation of the proposed mechanism underlying the system dynamics; B) TEM images acquired at different stages of the disassembly process; C) UV-vis spectra displaying the changes to the normalized absorbance during BAuNS assembly; D) UV-vis spectra displaying the changes to the normalized absorbance during BAuNS disassembly; E) Surface plasmon resonance (SPR) peak position variation during consecutive assembly and disassembly of BAuNSs.

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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,^[30,31] spontaneous disassembly has already been shown for transient systems obtained with nanoparticles.^[17,32] 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 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 HAuCl₄, 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.^[17,33] Such a reversible change of optical properties was observed also in our system, that showed a consistent bathochromic shift upon incubation with SDS and AuCl₄⁻ (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.^[34] Finally, after 72 hours from AA addition to the system, BAuNSs disassembly into PAuSSs 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.

In summary, we applied a 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 tailored 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 tuneable and reversible change of optical properties. Overall, our approach represents a simple, yet efficient, strategy to achieve the formation of transient 3D gold nanostructures with an organic core and 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.

Acknowledgements

P.M. is grateful to the European Research Council (ERC) for the Starting Grant ERC-2012-StG_20111012 FOLDHALO (Grant Agreement no. 307108) and the Proof-of-Concept Grant ERC-2017-PoC MINIRES (Grant Agreement no.789815). A. M. and P. M. are thankful to the project Hydrogex funded by Cariplo Foundation (grant no. 2018-1720). D.A.E. and S.B. acknowledges financial support from ERC Consolidator Grant Number 815128 REALNANO and Grant Agreement No. 731019 (EUSMI).

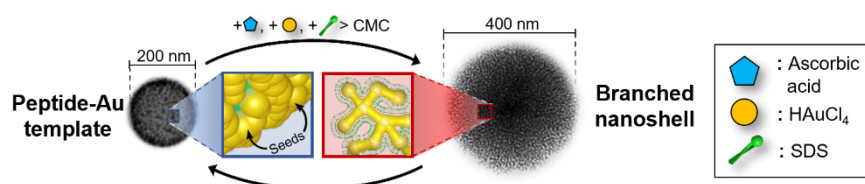
Keywords: Self-assembly • Out-of-equilibrium • Nanoparticles • Branched Nanostructures • Gold Nanoshells

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Out-of-equilibrium self-assembly of metal nanoparticles (NPs) achieving 3D structures with controlled morphology is still rare. Here we used a peptide-gold superstructure as template to control the out-of-equilibrium self-assembly of Au NPs, obtaining a transient 3D branched Au-nanoshell stabilized by surfactant (SDS). The nanoshell dismantled upon concentration gradient equilibration, leading to disassembly and regression to the template.

Institute and/or researcher Twitter usernames: @SupraBioNanoLab, @PierMetra, @ClaudiaPigliac1