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Formation and Thermal Stability of Au-SiO₂ Nanohybrids: Insights into Mechanism and Morphology using Electron Tomography

Paromita Kundu*, Hamed Heidari, Sara Bals, N. Ravishankar and Gustaaf Van Tendeloo

Gold-based heterostructures are important in different fields of application starting from catalysis to biomedicine^[1-4]. For catalytic application, reactions are often carried out at higher temperatures and thus retaining the size of the catalyst particles is critical as the active surface area inversely scales with the size^[5]. A good control over morphology, stability and ordering of the heterounits is a prime requirement for most applications. In this context, SiO₂ based metal hybrids are desired for their easiness to synthesize, good thermal and chemical stability, inertness as a support/coating material and tunable optical properties which is size dependant. Different strategies exist to obtain these hybrids, with various kind of distribution and morphology, via chemical routes^[6-9] but often the attachment of the nanoparticle on the SiO₂ sphere is not favorable due to the high interfacial energy or negatively charged silica surface and hence functionalization of SiO₂ is employed to modify the interfacial energies. For instance, Au does not nucleate favorably on SiO₂ surface without functionalization^[7, 10]. However, particles attached directly on SiO₂ and held by a monolayer of linkers on the surface are often less stable due to the high mobility of Au on SiO₂, as well as the low thermal stability of the molecular chains. Therefore, new strategies are required to design more stable hybrid structures. At the same time, it is necessary to understand the mechanism of formation and the morphological changes that such structures might undergo in a course of reaction as a function of temperature. In heterostructures, the ordering of the component units often determines their functionality. It is therefore important to determine the distribution of catalyst nanoparticles on support materials with different morphologies. For such heterostructures, conventional imaging techniques like TEM and STEM may give information on the size of the nanostructures. However, it is important to realize that these techniques yield 2D projection images, which can yield misleading information concerning the shape, morphology and distribution of the heterounits. For instance, metal nanoparticles coated with a silica layer and vice-versa have been

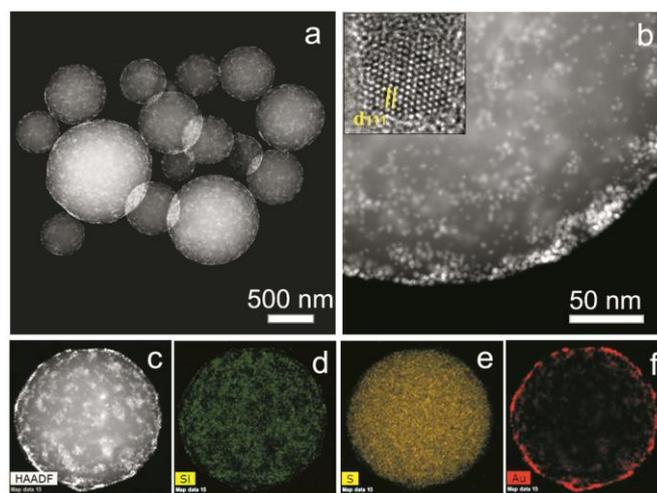


Figure 1. (a) and (b) Low and high magnification HAADF-STEM image of as-synthesized hybrid, respectively, shows the Au particles and their average distribution on the SiO₂ spheres and inset of (b) shows the HRTEM from a Au particle, resolving the {111} and {100} planes. (c-f) show HAADF image of a selected hybrid particle with the elemental maps for Si-K, S-K and Au-L lines.

reported but the uniformity or continuity of the coating cannot be confirmed from 2D projection images only. Hence, the actual morphology of nanostructures often remains elusive without a 3D characterization. Electron tomography is a state-of-the-art technique to perform such an investigation. A 3D reconstruction of an object is obtained from a series of its 2D projection images and can give precise information on the shape, position and distribution of the heterounits^[11-12].

In this report, we present a facile synthetic route to Au decorated SiO₂ spheres in which the Au nanoparticles are embedded in the outermost layer of the formed silica spheres. The formation of the hybrid is mediated by self-assembling of Au nanoparticles capped with mixture of oleyl amine and MPTMS. HAADF-STEM tomography and x-ray energy dispersive spectroscopy (XEDS) have been performed to investigate the structure and composition of the hybrid. A mechanism has been proposed to understand the formation mechanism of such hybrids in the medium. The thermal stability of the hybrid has been investigated that indicates a low mobility of Au in the hybrid. However, penetration of the particles from the surface into the matrix of the silica sphere was observed from the electron tomography experiments. This study provides useful insights on the morphological changes that may be encountered by similar hybrids in course of temperature dependant processes such as catalysis.

Gold nanoparticles of 2-10 nm size are formed by microwave reduction process using oleyl amine as the reducing and capping agent. After treating these particles with silica precursor, MPTMS,

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

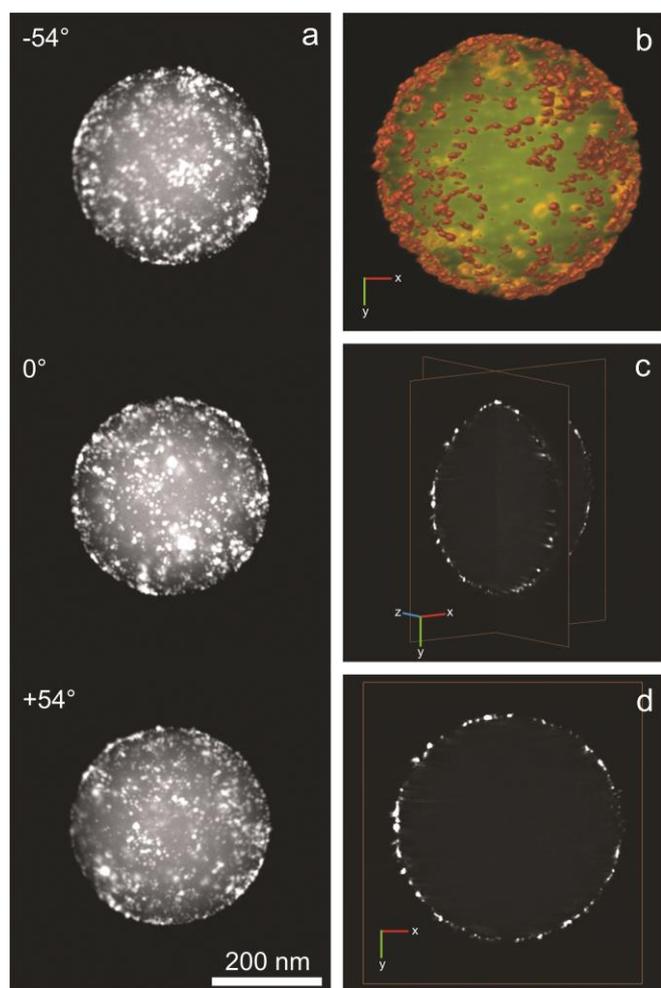


Figure 2. STEM tomography of a Au-SiO₂ particle where (a) 2D projection images at 0° and higher ($\pm 54^\circ$) tilt angles. (b) 3D volume rendering obtained from the reconstruction of the aligned tilt series images, recorded by tilting the sample from -70° to $+56^\circ$ with 2° increment, showing that the Au particles are located on the surface of the sphere. (c) intersection of two different orthoslices and (d) orthoslice in xy-plane show the presence of Au particles, with brighter Z-contrast, only at the surface and the SiO₂ matrix inside corresponds to lighter Z-contrast.

and sodium silicate in ethanol medium, Au-SiO₂ hybrid forms which are 300-500 nm sized spheres with a silica core and Au nanoparticles assembled on its surface as shown in Fig. 1(a,b). The high resolution image (inset of b) shows an image of a faceted Au particle with the {111} and {001} planes resolved. The size of the Au particles was retained in the hybrid although they were loosely clustered at several places. HAADF-STEM images, presented in Fig. 1(a,b) show the distribution of the Au nanoparticles on the SiO₂ spheres, however, it is difficult from such 2D images to determine the location of the Au particles on the silica. It is impossible to conclude if they are present only at the surface or if they are embedded into the matrix of the silica spheres. STEM-EDX elemental mapping is performed to confirm the composition of the hybrid (Fig. 1c-f). Fig. 1d shows the Au-L map which indicates a large density of Au on the periphery in comparison to the centre. The Si-K and S-K maps are given in Fig. 1(e & f), respectively, and O-K map closely overlaps with the one of the Si (supporting information, S1); it is therefore clear that the SiO₂ along with S containing MPTMS forms the dense three dimensional mass on

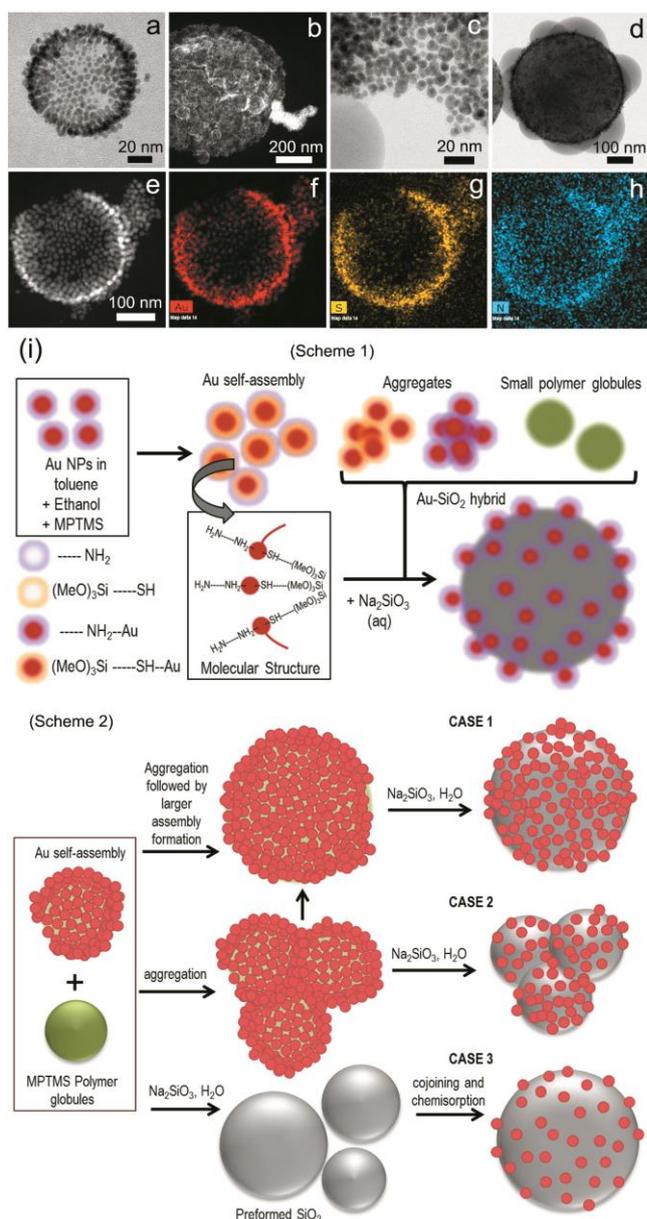


Figure 3. Intermediate stages of formation of the Au-SiO₂ hybrid as in (a) self assembled Au nanoparticles, (b) aggregation of smaller self assemblies, (c) thiol and amine capped Au particles randomly aggregated and partially adsorbed on the preformed SiO₂ sphere and (d) conjoining of the smaller SiO₂ spheres to a Au-SiO₂ sphere. (e-h) HAADF-STEM image of a Au particles self assembly and the elemental maps derived from Au-L, S-K and N-K lines. (i) Schematic representation describing, scheme1- the possible mechanistic route leading to the hybrid formation and scheme 2- possible routes to Au-SiO₂ hybrid from the Au self-assemblies.

which the Au nanoparticles are attached presumably via the -SH (thiol) moieties of MPTMS. However, the presence of N (N-K map in supporting information, S1) in close proximity to the Au implies that the oleyl amine capping exists along with the thiol but it remains mostly on the Au surface outside the silica matrix. This is also evident from the line scan profile (see supporting information, S1). To reconstruct the 3D shape of the hybrids, HAADF-STEM tomography was performed and HAADF-STEM images were acquired by tilting the specimen from +f to -f degrees (where f varies for different samples and is typically within $\pm 70^\circ$) with

increments of 2° . Examples of 2D projection images are presented in Fig. 2a. The Au particles appear with higher intensity because of the chemical sensitivity of the HAADF-STEM technique. 3D reconstructions were obtained using 30 iterations of the SIRT algorithm^[5]. The visualisations, presented in Fig. 2b show that the fully formed spheres yield Au nanoparticles only at the surface and not embedded in the matrix. This is especially obvious from the orthoslices presented in Fig. 2(c,d), where the Au particles are clearly present only at the surface of the SiO₂ matrix; a 3D animation is presented in the supporting information, S2.

Formation of Au-SiO₂ hybrids with the observed morphology and composition has never been investigated earlier. However, understanding the formation mechanism could provide useful insight to tune the reaction parameters and conditions in order to exercise control over size, shape and distribution. Previous reports describe competitive reaction schemes for the thiol containing silane precursors to undergo hydrolysis, polymerization and monolayer formation on Au^[13]. As these reactions are largely reactant concentration dependant, it is difficult to resolve the steps sequentially towards the formation of the hybrids discussed here. However, based on the investigation of the intermediate stages during reaction, we propose a formation mechanism of these structures. Fig. 3(a-d) shows different type of Au nanoparticles assemblies and aggregates of formed silica spheres where some of them are already coated with Au nanoparticles that resulted after 4-5 hours of reaction. Of these types, such as the self-assembly as shown in Fig. 3a, is found to be present in large majorities during the reaction. Fig. 3e shows a HAADF-STEM image of the assembled Au particles. The STEM-EDX elemental maps in Fig. 3(f-h) present evidence of the specific binding of the S and N containing ligands to the Au. The formation of these products can be understood considering the binding of two types of ligands to the Au particles, their interaction with the solvent medium and the chemistry involved in formation of the silica. The Si-K and O-K maps (in supporting information, S3) reveal the absence of SiO₂ core and that the assemblies are hollow. In Fig. 3i we describe schematically the stages of formation of the Au-SiO₂ hybrid in solution (an elaborate reaction scheme in supporting information, S4). An aliquot of a particular concentration of MPTMS in ethanol (polar medium) when added to the oleyl amine capped Au nanoparticles suspended in toluene (a non-polar medium), ligand exchange occurs due to higher affinity of -SH compared to -NH₂ towards Au and results in a mixed ligand arrangement on the Au particles (as shown in the schematic molecular structure) where the amine bilayer formation is possible^[9]. Due to the increased polarity of the medium by addition of ethanol, the non-polar part of MPTMS, i.e. the silane end, tends to face the core with one of the amine ends of bilayer of oleyl amine facing the solvent as described above. Electron tomography performed on these structures shows that these are 3D spherical assemblies (see movie in supporting information, S5) but soft structures, therefore, attaining a dome-shaped morphology when deposited on a TEM grid as understood from the 2D projection images in Fig. 4a. Fig. 4b presents the 3D rendering of the reconstructed tilt series showing the particles assembly. The orthoslices in Fig. 4c further confirms that there is no SiO₂ matrix at the core supporting the Au particles assembly. These structures could coalesce to yield bigger assemblies in due course as in Fig. 3b. Also, the free end of the MPTMS chain can undergo polymerisation or self-assemble on the formed SiO₂ spheres depending on the MPTMS concentration^[14]. In our case, initially the concentration is high enough (0.56 M) to trigger polymerization and result in globular structures as shown in Fig. 3i scheme. Both of these soft-

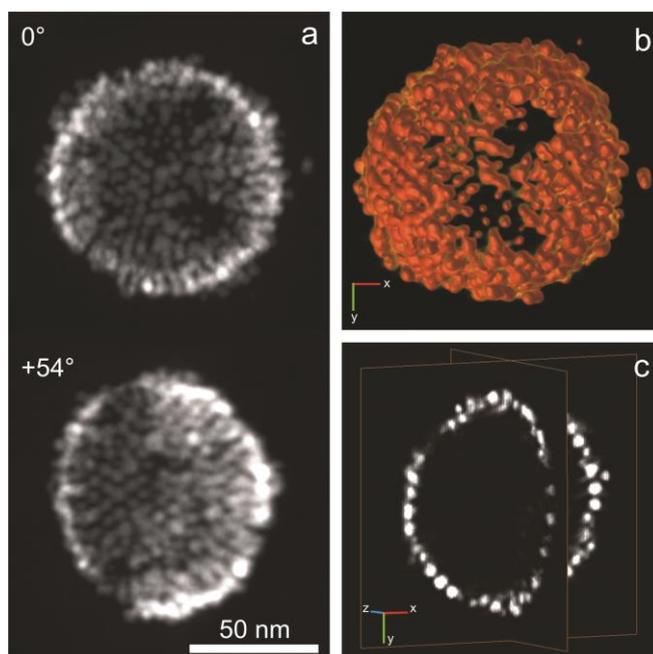


Figure 4. STEM tomography of the intermediate self-assembly of Au nanoparticles. (a) 2D projection images at 0° and $+54^\circ$ tilt angles, indicating a dome-like shape. (b) 3D volume rendering from the reconstruction of the aligned tilt series images, recorded by tilting the sample from -66° to $+68^\circ$ with 2° increment. (c) intersection of two different orthoslices showing that there are no particles located inside the assembly.

template structures could coalesce to yield bigger assemblies in due course; which can rearrange to produce larger hollow self-assemblies. However, when such assemblies are drop-cast on the grid we observe larger folded irregular shaped assemblies lying almost flat on the grid due to the soft-template(see supporting information, S6).

The silane end of the MPTMS can undergo thermal hydrolysis and subsequent condensation in presence of an alkaline medium to form silica^[15] but in presence of sodium silicate, silica formation can be triggered even at room temperature^[8]. There can be three cases operating to result in Au-SiO₂ hybrid (scheme 2 in Fig. 3i). Case 1, where the silane part facing the core of the larger hollow assemblies undergo hydrolysis and subsequent condensation to form SiO₂. However, only this would result in hollow silica shell with particles on it which are not the final products here. Instead, with addition of Na₂SiO₃ (aq) solution, the reactant can diffuse in followed by SiO₂ nucleation and growth within the 3D polymerized globules and the the Au particles self-assemblies, forming a SiO₂ framework. Case 2, in which the smaller assemblies aggregate and start forming SiO₂ by the same mechanism as in case 1. This would result in a Au particles packed hybrid which is not the end product. In another way, i.e. case 3, it can be the growth of the preformed SiO₂ spheres by conjoining of the smaller ones and chemisorption of the 3D self-assemblies, with or without Au, on them via Si-O-Si linkage as in Fig. 3(c & d). This might result in fewer number of Au particles on the SiO₂ spheres. However, the self-assemblies being the major kind of intermediate products, the first mechanism must be dominating.

Heating experiments performed on the hybrid indicates interesting morphological changes. The nanostructures were initially heated to 200°C in a furnace in air and was further heated *in situ* upto 485°C for microscopic study. HAADF-STEM imaging shows that the heterostructures did not undergo any morphological

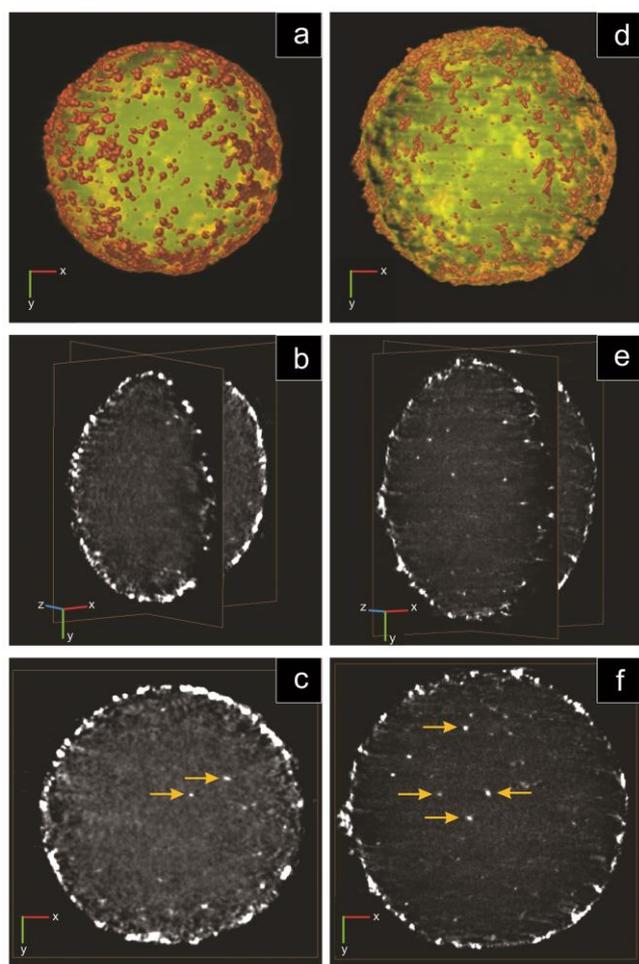


Figure 5. Electron tomography of a Au-SiO₂ particle heated to 200°C and 485°C. For 200°C, (a) 3D volume rendering obtained from the reconstruction of the aligned tilt series images, recorded by tilting the sample from -62° to +64° with 2° increment, showing that the Au particles are located at the surface of the sphere as well as inside the matrix. (b) Intersection of two different orthoslices revealing that the particle remains spherical and (c) orthoslice in xy-plane confirming the presence of Au particles at the surface as well as inside the matrix of the sphere (as marked). For 485°C, (d-f) show the corresponding results for sample tilt from -66° to +70° with 2° increment. Orthoslices confirm the retention of morphology of the hybrid but migration of a larger number of Au particles inside the matrix (as marked).

changes on heating (supporting information, Fig. S7). The hybrid is stable up to 400°C; however, heating at 485°C shows few bigger Au particles. It is evident from the increased intensity in some regions due to thickness contrast. From these 2D projection images we can conclude that there is no migration of the Au nanoparticles on the SiO₂ surface and hence no clustering or growth of the particles due to aggregation up to 400°C. The clustering which appears, in 2D projection, after heating to 485°C could also be apparent due to random migration of particles and their placement inside the matrix^[16]. Electron tomography performed on the heated samples (200°C, 485°C) shows that the Au particles are indeed located inside the SiO₂ matrix, more at 485°C, but not coarsened due to heating. It shows no change in the shape of the hybrid particles at 200°C and 485°C which is evident from the HAADF-STEM images, acquired at different tilt angles (see supporting information, S8). Fig. 5a and 5d shows the volume rendering and the orthoslices in Fig. 5(b,e) reveals the presence of particles on the surface of as well as inside

the spheres. It is clear from the orthoslices in Fig. 5(c,f) that more Au particles migrated into the SiO₂ matrix (marked by arrows) at higher temperature (485°C) (3D animation in supporting information, S9). As there was no significant migration of the particles on the silica surface, the presence of the particles inside the spheres could be due to the collapse of the C-chain of the MPTMS ligands^[15].

At sufficiently higher temperature (above 400°C), the damage of the organic mass is more which leads to migration of the particles inside matrix in random manner. Therefore, penetration of the Au particles into the matrix might result in finer channels leading to a porous hybrid structure. This study reveals that polymeric SiO₂ matrix acts as a stable support for the Au particles, preventing them from surface migration and aggregation. We therefore conclude that the hybrid has good thermal stability and could be a better porous catalyst for several reactions^[17] unlike the Au attached on bare/functionalized silica surface.

In summary, we demonstrated a novel chemical synthesis route to stabilize Au nanoparticles on polymeric SiO₂. A 3D characterization is carried out by electron tomography to understand the distribution of the Au particles, which has not been reported earlier, and elemental mapping confirms the composition in the hybrid. These techniques play a crucial role in understanding the shape, composition and distribution of the heterounits of/in the hybrid, respectively. A mechanism is proposed based on the intermediate assembled structures of Au and SiO₂. Thermal stability test reveals the material to be a potential candidate for catalysis and biotechnology.

Experimental Section

Synthesis of Au nanoparticles: 4 mg HAuCl₄, (assay 49%) was dissolved in 5 ml ethylene glycol (EG) and 50 μL of oleyl amine added to it. Solution was subjected to microwave radiation for 1 min in a domestic microwave (2.45 GHz) operated at 800 watt. The mixture was cooled. The amine capped Au nanoparticles were extracted by phase transfer using dry toluene and used for synthesizing the hybrid as follows.

Synthesis of Au-SiO₂ hybrid: To 2.5 ml of Au sol, 1 ml of ethanol containing 10 μL of (3-mercaptopropyl) trimethoxysilane (MPTMS) was added while stirring. After 20 mins 40 μL of 2M Na₂SiO₃ (aq) solution was added dropwise under stirring and left for 20 mins. Then the mixture was left for about 12 hours until the hybrid settled down at the bottom of the solution. Separation was done by centrifugation and washing with water and ethanol, and dried.

Intermediate stage products were collected after 4-5 hours of reaction.

Electron tomography and *in situ* heating: Samples were prepared on a formvar coated C grid. For intermediate products, the solution was diluted and dropcast on grid for analysis. Electron tomography and the *in situ* heating was carried out in Tecnai G2 microscope operated at 200 kV in STEM mode using a camera length of 91 mm. STEM-EDX elemental mapping was carried out in TITAN³ microscope with chemiSTEM technology. It being equipped with SuperX-EDX detector system, is capable of detecting lighter elements as well.

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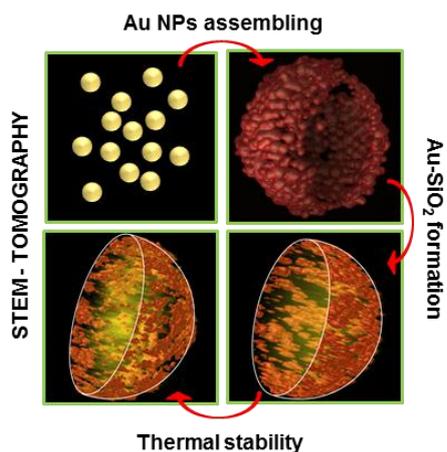
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Au-SiO₂ in 3D

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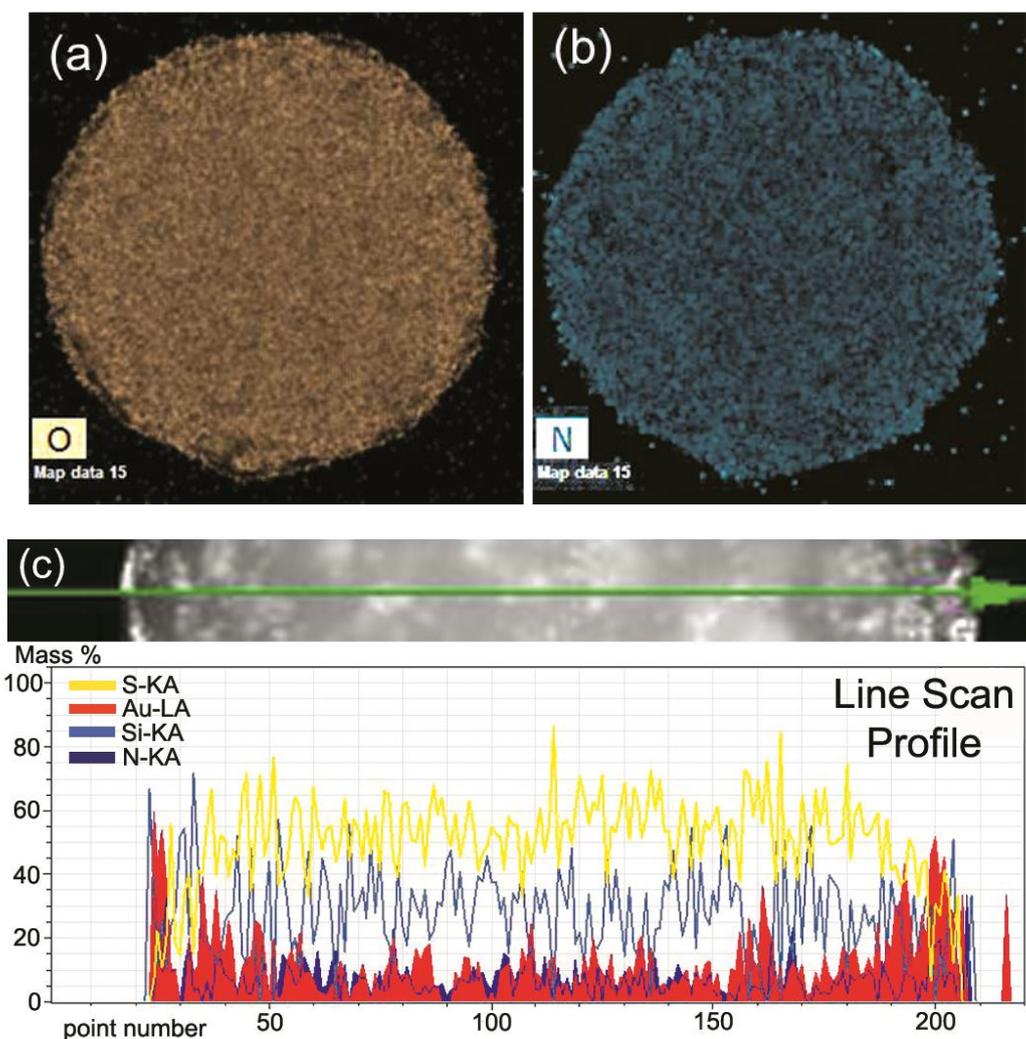
Formation and Thermal Stability of Au-SiO₂ Nanohybrids: Insights into Mechanism and Morphology using Electron Tomography



A simple approach to synthesize fine Au particles decorated on SiO₂ spheres is demonstrated and a rationale is discussed for the formation mechanism. Electron tomography is used extensively to understand the morphology of, and changes occurred on heating the hybrid. It shows excellent thermal stability appropriate for several applications including catalysis. The protocol being general can be extended to make similar hybrids of SiO₂.

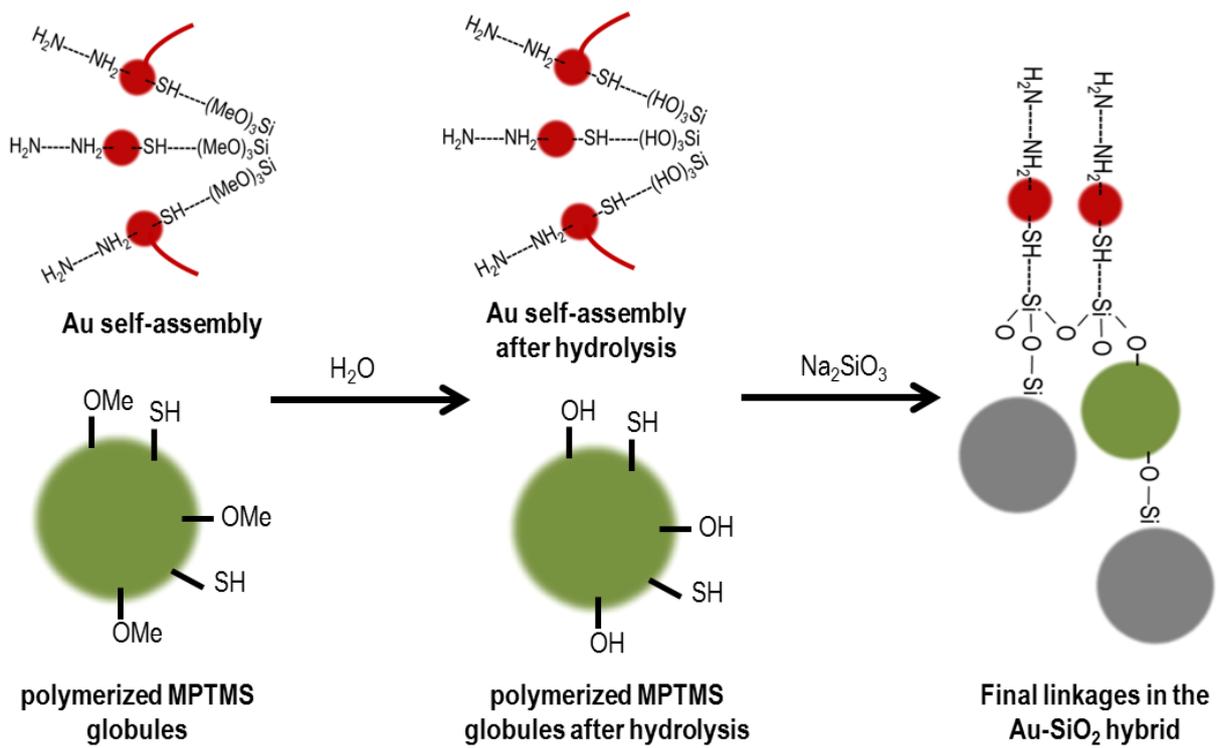
Supporting Information

S1. STEM-EDX elemental map from (a) O-K line and (b) N-K line for the hybrid, as synthesized (c) a line profile showing the distribution of Au particles that confirms its higher density at the outer surface.

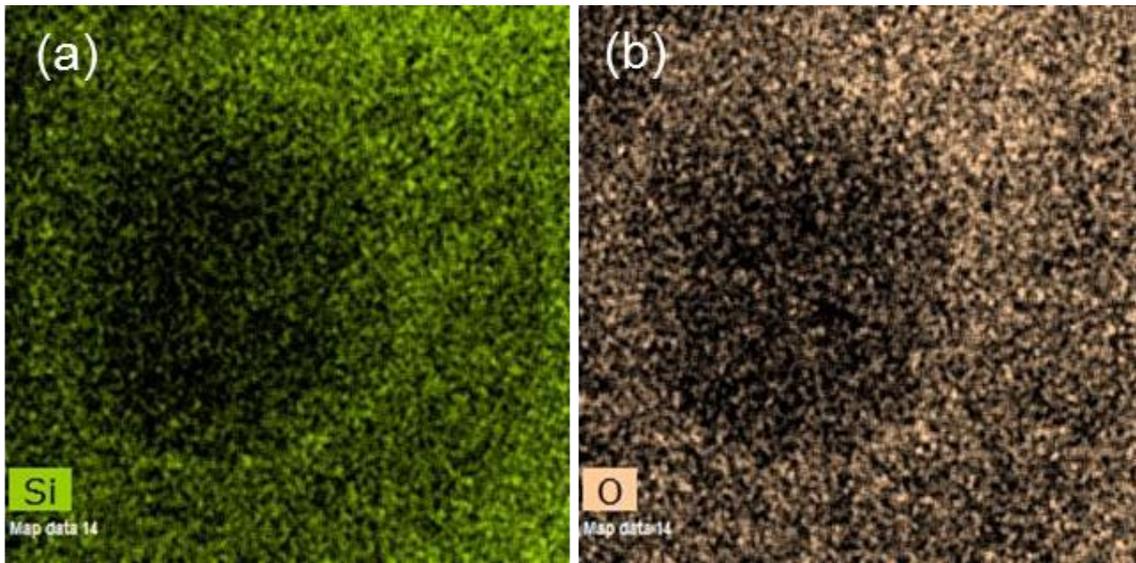


S2. Movie: 3D Volume rendering and the orthoslices for AuSiO₂ hybrid, as synthesized, showing that there are no Au particles embedded inside the matrix.

S3. Reaction scheme showing the final linkages in the Au-SiO₂ hybrid

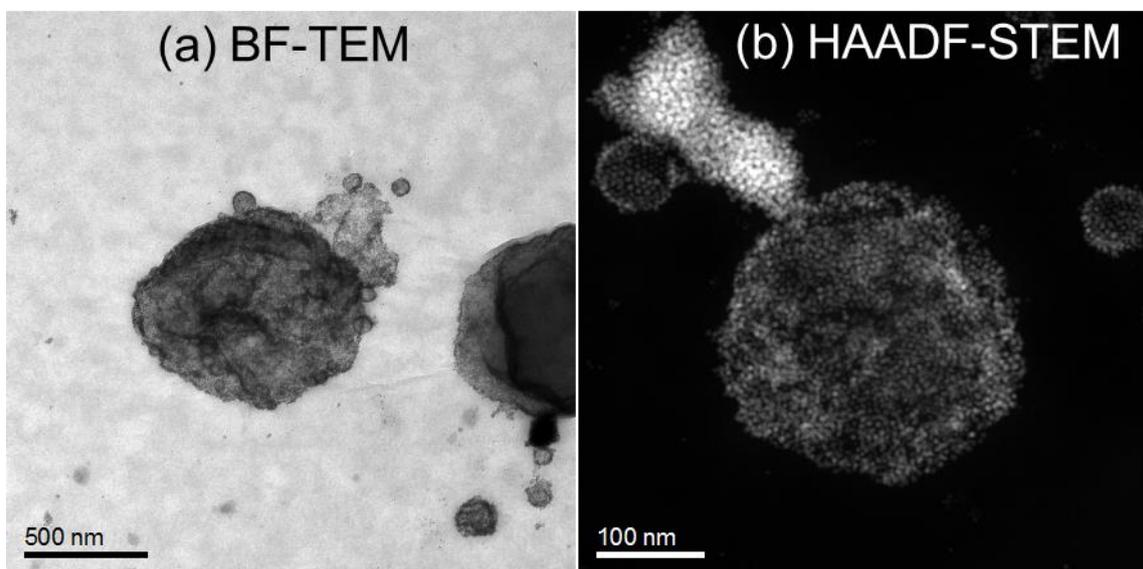


S4. STEM-EDX elemental map from (a) Si-K line and (b) O-K line for the smaller intermediate Au self-assembly formed in course of reaction.

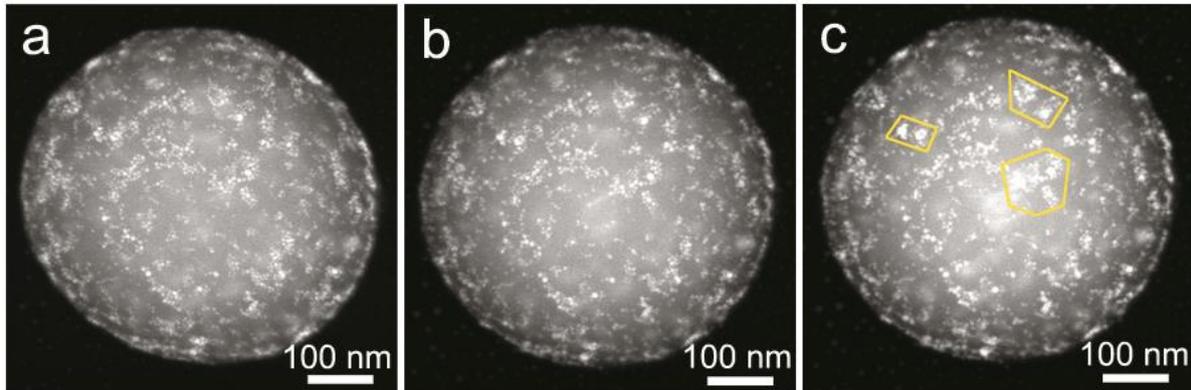


S5. Movie: Intermediate self-assembly – volume rendering and orthoslices.

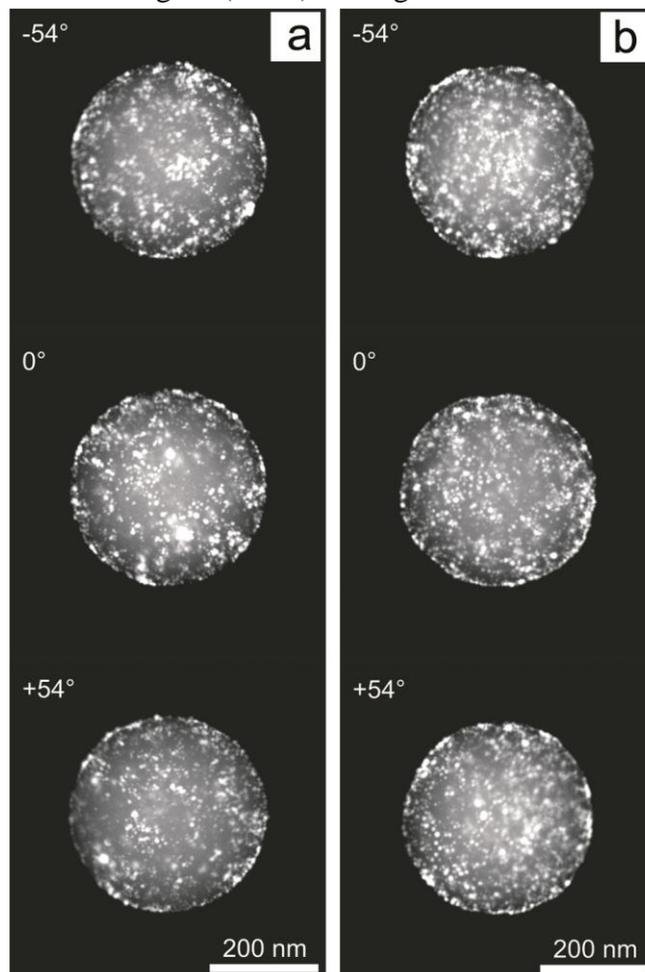
S6. Showing the aggregated self-assemblies lying in irregular shapes on the grid; as the assemblies are supported by the polymeric soft template, their shapes end to distort when drop-casted on the grid.



S7. Thermal stability test of the hybrid when heated from room temperature to (a) 200°C, (b) 400°C and finally (c) 485°C. The HAADF-STEM images acquired from the same particle reveals an apparent morphological stability of the hybrid until 400°C. At higher temperatures clustering of Au particles result due to their lateral migration (as the regions are marked).



S8. Electron tomography of a Au-SiO₂ particle after heating to (a) 200°C and (b) 485°C. 2D projection images at 0° tilt and higher ($\pm 54^\circ$) tilt angles for both cases.



S9. Movie: 3D animation for AuSiO₂ hybrid heated to 485°C showing Au particles inside the matrix.