

Atomically Precise Nanocluster Assemblies Encapsulating Plasmonic Gold Nanorods

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Abstract: The self-assembled structures of atomically precise, ligand-protected noble metal nanoclusters leading to encapsulation of plasmonic gold nanorods (GNRs) is presented. Unlike highly sophisticated DNA nanotechnology, this strategically simple hydrogen bonding-directed self-assembly of nanoclusters leads to octahedral nanocrystals encapsulating GNRs. Specifically, the *p*-mercaptobenzoic acid (*p*MBA)-protected atomically precise silver nanocluster, $\text{Na}_4[\text{Ag}_{44}(\text{pMBA})_{30}]$, and *p*MBA-functionalized GNRs were used. High-resolution transmission and scanning transmission electron tomographic reconstructions suggest that the geometry of the GNR surface is responsible for directing the assembly of silver nanoclusters via H-bonding, leading to octahedral symmetry. The use of water-dispersible gold nanoclusters, $\text{Au}_{\sim 250}(\text{pMBA})_n$ and $\text{Au}_{102}(\text{pMBA})_{44}$, also formed layered shells encapsulating GNRs. Such cluster assemblies on colloidal particles are a new category of precision hybrids with diverse possibilities.

Atomically precise monolayer-protected nanoclusters of noble metals^[1–3] such as $\text{Au}_{25}(\text{SR})_{18}$, $\text{Ag}_{25}(\text{SR})_{18}$, $\text{Ag}_{44}(\text{SR})_{30}$, and $\text{Au}_{102}(\text{SR})_{44}$ owing to their small size and quantum confinement of electrons lead to discrete energy levels, making their optical absorption spectra reminiscent of dye molecules. Near-infrared emission and unusual catalysis are some of the fascinating properties of such clusters. Over the past one decade, there has been tremendous progress in the

synthesis, characterization, and studies of their diverse properties. Recent reports of inter-nanocluster reactions^[4] and isomorphous transformations^[5] have expanded the scope of their science. Moreover, it has been recently shown that by tuning the inter-nanocluster H-bonding, free-standing 2D nanosheets and capsids with monolayer thick shells can be achieved using *p*MBA-protected gold nanoclusters.^[6,7] On the other hand, noble metal nanoparticles, especially gold nanorods (GNRs),^[8,9] owing to their anisotropic surface plasmonic excitations and extreme sensitivity to chemical environments have been one of the most intensely researched nanosystems. The unique plasmonic properties of gold nanoparticles have been exploited recently to achieve plasmon-molecular resonance coupling using small organic dye molecules^[10] as well as quantum dots.^[11] Such a plasmon-exciton coupling shows remarkably altered fluorescence (enhanced or quenched), possibly allowing the amplification of plasmonic signals in devices. Therefore, it is relevant to investigate whether colloidal-scale molecules such as atomically precise quantum clusters affect the plasmon of nanoparticles when placed at sufficient proximity. In this context, the *p*MBA-protected silver nanocluster ($\text{Na}_4[\text{Ag}_{44}(\text{pMBA})_{30}]$),^[12,13] which is of great interest owing to its intense and broad multiband optical absorption property,^[14] is a suitable candidate because of its facile synthesis and the presence of H-bonding ligands. Furthermore, earlier study from our group has shown that Ag_{44} can show fundamentally different assemblies to direct hierarchical structures when interacted with 1D (anisotropic) tellurium nanowires.^[15] With these motivations, we undertook an investigation into the precision assemblies of noble metal nanoclusters on GNR surfaces in solution. In our experiments we observed a quantitative transformation of clusters to composite cages where one nanorod was incorporated per cage. This fascinating observation warranted a detailed structural investigation, as such assemblies have been achieved previously using highly sophisticated DNA nanotechnology.^[16]

The GNRs ($d \approx 10$ nm, $l \approx 30$ nm) were synthesized according to an established method^[17] in presence of cetyltrimethylammonium bromide (CTAB) and are denoted as GNR@CTAB (Supporting Information, Figure S1). To incorporate the hydrogen bonding functionalities on GNR surfaces, ligand exchange was performed using *p*MBA and the resulting *p*MBA protected nanorods are denoted as GNR@*p*MBA (Figure 1b; Supporting Information, Figure S2). The ligand exchange was monitored by measuring the zeta (ζ) potential (Supporting Information, Figure S2) which changed from +51 mV (GNR@CTAB) to −2.6 mV

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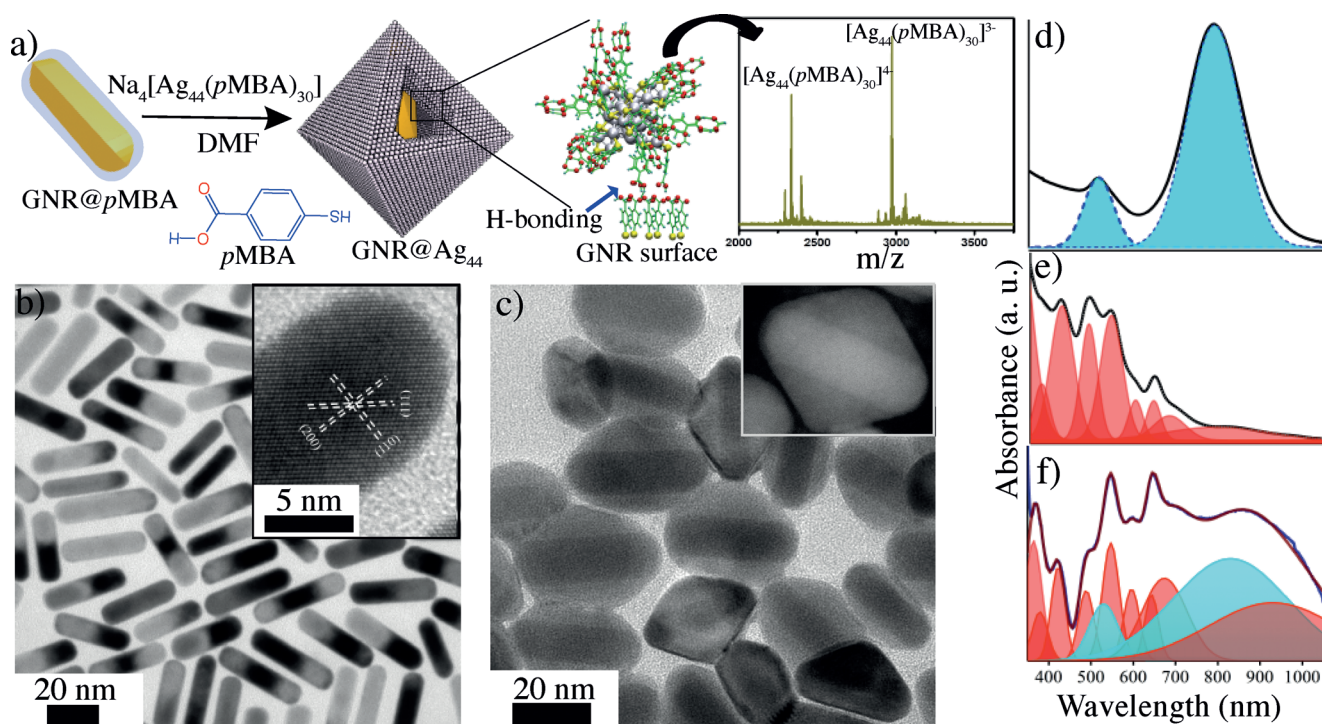


Figure 1. a) Representation of the self-assembly of Ag_{44} (curved arrow directs to the ESI MS of the cluster) on the GNR@pMBA surface, b) TEM image of GNR@pMBA (inset shows an HRTEM image of a single nanorod), c) TEM image of GNR@Ag_{44} (inset shows dark field STEM image of a composite particle), and d)–f) UV/Vis spectra of GNR@pMBA , Ag_{44} , and GNR@Ag_{44} , respectively.

(GNR@pMBA). The presence of sulfur and the existence of Au–S bond in GNR@pMBA were confirmed using Raman spectroscopy, scanning transmission electron microscopy, energy-dispersive X-ray (EDX STEM) spectroscopy, and X-ray photoelectron spectroscopy (Supporting Information, Figures S2, S3). The modified GNRs were purified and redispersed either in *N,N*-dimethylformamide (DMF) or water for further experiments. The silver nanocluster $\text{Na}_4[\text{Ag}_{44}(\text{pMBA})_{30}]^{13-}$ and water dispersible gold nanoclusters, $\text{Au}_{102}(\text{pMBA})_{44}^{18-}$ and $\text{Au}_{250}(\text{pMBA})_n^{19-}$ (from here on abbreviated as Ag_{44} , Au_{102} , and Au_{250} , respectively), were prepared according to previous reports (see the Supporting Information for detailed synthesis and characterization). Figure 1a pictorially describes the self-assembly of Ag_{44} on GNR@pMBA . In our experiment, a dispersion of GNR@pMBA in DMF was allowed to interact with Ag_{44} dissolved in DMF (characterized by absorption spectroscopy and electrospray ionization (ESI) mass spectrometry; Supporting Information, Figure S4), at room temperature. This allowed Ag_{44} clusters to assemble on GNR surfaces through systematic H-bonding via carboxylic acid dimerization of the bound ligands (Supporting Information, Figure S3a), giving rise to a well-defined geometry of the end product (Figure 1c). After 20 h of incubation time, the product was extracted by centrifugation and was characterized (Supporting Information, Figure S5). The GNR@pMBA has two characteristic plasmonic peaks at 520 nm and 780 nm in its absorption spectrum (Figure 1d), whereas Ag_{44} shows molecule-like electronic spectrum (Figure 1e). When the resulting composite dispersed in DMF was studied, it displayed the absorption spectrum containing the peaks arising from both

GNR@pMBA as well as Ag_{44} as evident from peak fitting (Figure 1f). The supramolecularly self-assembled composite superstructure is denoted as GNR@Ag_{44} , where the individual components preserve their identities. However, significant broadening along with a shift in peak position at the NIR region was observed for the composite material, owing to the electronic interactions between them. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) revealed the formation of self-assembled superstructures encapsulating a single GNR in each nanocrystal (Figure 1c). Remarkably, a systematic optimization leads to a system where neither free GNR nor excess cluster exists in the medium and the final material has a definite morphology. Moreover, stability of this nanohybrid material is comparable with that of the Ag_{44} crystal. It can be redispersed in DMF by mild sonication without breaking the cluster assemblies, even after months of its preparation. The clusters can be regained from the composite only by probe sonication in an acidic medium (Supporting Information, Figure S6).

To gain insights into the morphology of GNR@Ag_{44} , and thus to have a better understanding of the assembly of clusters on the GNR surface, TEM and STEM tomography reconstructions were performed on GNR@CTAB , GNR@pMBA , and GNR@Ag_{44} . GNR@CTAB showed the reported geometry where the sides consist of four $\langle 110 \rangle$ and four $\langle 100 \rangle$ facets arranged alternately (Figure 2a; Supporting Information, Video S1).^[20] However, owing to larger interatomic distances, the bonding between the surface gold atoms is relatively weaker on the $\langle 110 \rangle$ facet compared to the $\langle 100 \rangle$ facet leading to the formation of stronger bonds with

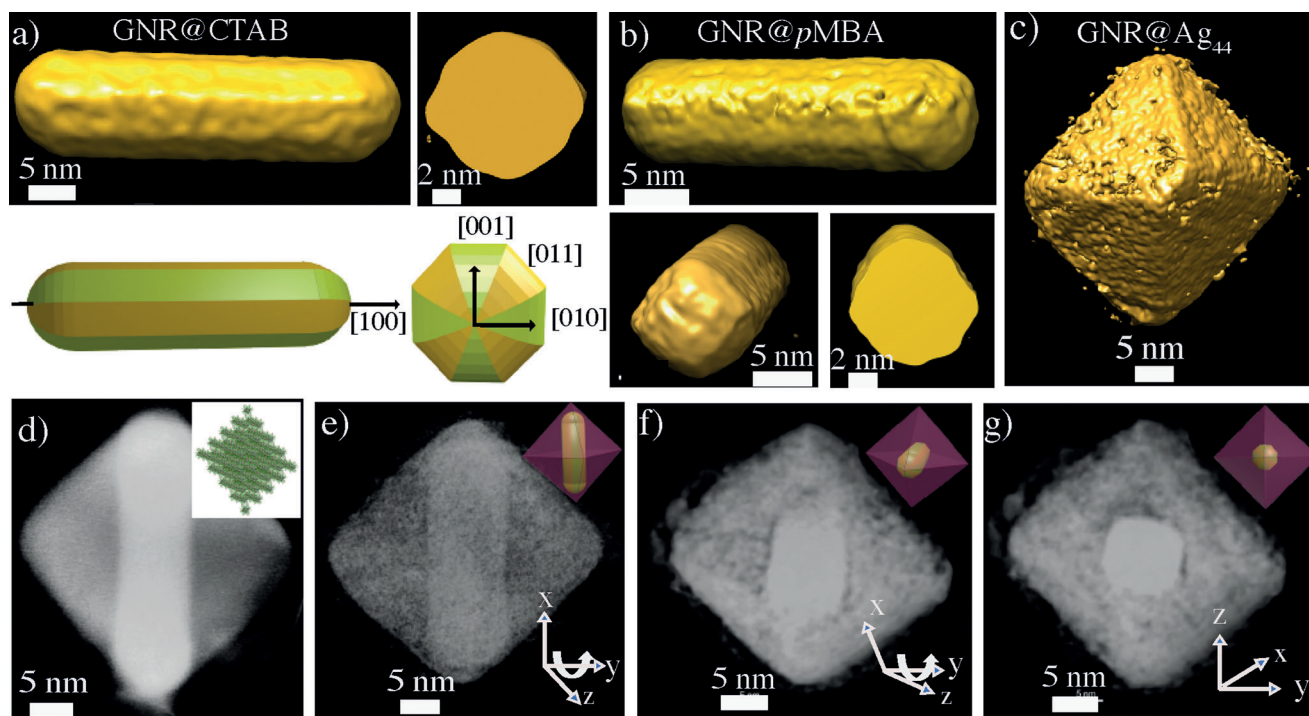


Figure 2. TEM and STEM tomography: a) TEM 3D reconstructed structure of GNR@CTAB (top left) and its cross-sectional view (top right) along with graphical representations of the side (bottom left) and top (bottom right) views showing octagonal geometry; b) side (top) and top (bottom left) views of GNR@pMBA, cross sectional view (bottom right) showing slightly distorted octagonal geometry; c) GNR@Ag₄₄ showing octahedral geometry. d) Dark-field STEM tomography of GNR@Ag₄₄ showing the octahedral nanocage and encapsulation and orientation of GNR within (inset: theoretically obtained Ag₄₄ assembly giving octahedral shape). e)–g) Rotational views of the nanocomposite along y axis (insets show corresponding representations).

adsorbed or bonded atoms (here *p*MBA molecules) on the former surface. In this process, the Au <100> surface undergoes bond breaking in the inner layers whereas Au <110> shows a missing row reconstruction.^[21,22] This leads to a distortion of the inherent octagonal shape of the GNR surface, when functionalized by *p*MBA (Figure 2b; Supporting Information, Video S2). The GNR@Ag₄₄, as shown in Figure 2c and 2d is octahedral. There are reports of similar geometry when gold,^[23] silver,^[24] or palladium^[25] shells have been grown on GNRs. It is evident that there is a competing growth on the two sets of side facets of GNRs. Upon preferential growth of the metals on the <110> surface facets compared to the <100>, there is a gradual enlargement of the latter and finally all <110> facets disappear.^[25] Although it was technically impossible to detect the surface facets of the cluster cages owing to the beam intolerance of the clusters in that high resolution, we suggest that in this case also the Ag₄₄ clusters assemble faster on the <110> surface facets than <100> causing the similar geometry. Herein, the nanorods are oriented diagonally, which denotes the size of the cages, by the length of nanorods. Figure 2e–g shows the views of the stepwise rotation of a single GNR@Ag₄₄ particle by an overall angle of 90° along the y axis. From these results, it can be further confirmed that Ag₄₄ self-assemble on GNR surfaces leading to an octahedral shape (Supporting Information, Video S3) where the GNR is oriented along the corners. Ag₄₄ is known to crystallize into a triclinic lattice^[26] in which each cluster has a specific orientation, which satisfies

translational periodicity. In presence of some specific counterion, it is also known to form an isotropic FCC arrangement.^[27] Directional hydrogen bonding between the ligands is mainly responsible for the intercluster (both intralayer and interlayer) interactions leading to the crystals. Based on the crystal morphology, only a cubic crystal lattice system can give rise to a bulk crystal form which is octahedral. We suggest that the underlying lattice structure of our octahedral assemblies is FCC in which the orientations of the hydrogen bonds between two connected cluster units may have disorder, but isotropic van der Waals interactions hold the FCC lattice together. The *p*MBA molecules attached to the GNR interact with the *p*MBA molecules on Ag₄₄ clusters, weakening the hydrogen bonding between the ligands of individual clusters. The GNR@pMBA surface imposes orientational constraints to the assembly and an ordered orientation of the clusters may not be possible. A careful observation of different stages of growth suggests that in the beginning, the Ag₄₄ was attached almost evenly to the entire surface of the GNRs (Supporting Information, Figure S7b). Gradually, as the sides (body) of the GNRs exhibited more van der Waals interaction compared to the pyramidal tips owing to their larger surface area, Ag₄₄ started to assemble on the side (body) surfaces preferentially. This interaction was highest at the center of the sides (body) of the GNRs, since it has the greatest number of significant contributions from both halves of the rods which gradually gets lower towards the tips of the GNRs. This, coupled with the preferential attachment of cluster units to

the $\text{Au} \langle 110 \rangle$ than $\text{Au} \langle 100 \rangle$ surface facets of GNR@pMBA , results in the anisotropic growth. As a result, the overall morphology of the nanocages encapsulating a single GNR happens to be an octahedron. An inset in Figure 2d shows a model of the octahedral crystal of Ag_{44} derived from its FCC lattice. TEM tomographic images of some other shapes obtained owing to the incomplete growth of clusters are shown in the Supporting Information, Figure S8. In a medium with $\text{pH} > 7$, where pMBA exists in its anionic form, the assembly did not take place. Also, when the cluster was added to GNR@CTAB without functionalizing with pMBA , the assembly was not observed (Supporting Information, Figure S9), suggesting that the hydrogen bonding is the basis of the structure.

To validate the generality of our approach, we used the water-dispersible gold nanocluster Au_{250} (Figure 3a) to perform the assembly. Unlike Ag_{44} , the gold nanoclusters assembly on GNRs was carried out in water ($\text{pH} \approx 7$) keeping

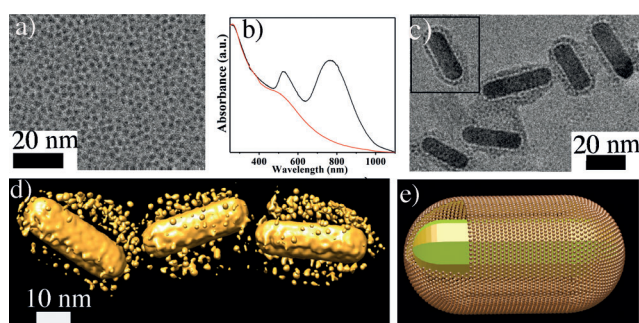


Figure 3. GNR@pMBA with Au_{250} nanoclusters in water: a) TEM image of Au_{250} , b) UV/Vis absorption spectra of Au_{250} (red) and GNR@Au_{250} (black), c) TEM images showing layered shell around GNR@pMBA when treated with aqueous Au_{250} , d) 3D reconstructed structures from the TEMs and e) 3D graphical representation of GNR@Au_{250} .

all the other conditions the same. On reacting with GNR@pMBA , the gold nanoclusters formed a similar nano-assembly named as GNR@Au_{250} , whose optical spectrum is also a composite of the components (Figure 3b). However, unlike GNR@Ag_{44} , the composite shows no specific morphology, rather it gave either one or multilayer shell structures (Figure 3c). Figure 3d (Supporting Information, Video S4) show the TEM tomography reconstruction of GNR@Au_{250} (Figure 3e shows the graphical representation of the same). Absence of any specific morphology in this case, even on completion of the reaction, can be due to the fact that Au_{250} has to be partially deprotonated to facilitate water dispersibility.^[6,7] As a result, not all of the ligands are involved in H-bonding, which decreases the packing density. Similar structures have been obtained on treating GNRs with Au_{102} (Supporting Information, Figure S10). Thus, irrespective of the solvent this approach can be useful to condense any noble metal nanocluster, protected by hydrogen-bond-forming ligand on GNRs, which act as the nucleating sites.

In conclusion, we have shown that composite nanostructures composed of two well-defined regimes of nano-systems, namely gold nanorods and the $\text{Na}_4[\text{Ag}_{44}(\text{pMBA})_{30}]$

cluster, can be created by non-covalent assembly. Systematic hydrogen-bond-induced self-assembly of Ag_{44} clusters on the pMBA functionalized gold nanorods encapsulates the GNRs completely, leading to octahedral composite nanocages. Interestingly, this hybrid nanomaterial shows unusually high stability at room temperature. The identities of GNR and the cluster are manifested in the spectroscopic properties of the composite. This simple method of controlled self-assembly of colloidal objects may be useful for creating larger hierarchical structures. Using Au_{250} we have shown that this approach is rather general in terms of nanoclusters and the solvent involved. However, luminescent quantum clusters might show metal-enhanced luminescence when they reside close to the plasmonic nanoparticles which should improve the detection limits of nanocluster-based sensors. Thus, creation of such precision assemblies with low polydispersity addresses the most crucial issues of controlled nanoparticle encapsulation and suggests a direction forward for the synthesis of more complex materials.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: atomically precise nanoclusters · hydrogen bonding · plasmonic gold nanorods · self-assembly · supramolecular chemistry

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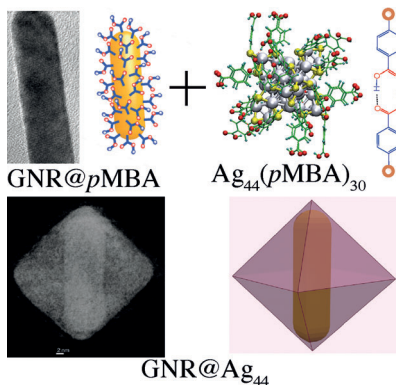
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Communications

Gold Nanorods

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Atomically Precise Nanocluster
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GNRs inside: Atomically precise nanoclusters were assembled on surface reconstructed plasmonic gold nanorods (GNRs), resulting in octahedral composite crystals. *pMBA* = *p*-mercaptobenzoic acid.