Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Atomically Precise Nanocluster Assemblies Encapsulating Plasmonic Gold Nanorods

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Author Contributions

Ann Candice Fernandez initiated this work as a summer student at IITM.

Supporting Information

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Chemicals used:

Tetrachloroauric acid trihydrate ($HAuCl_4$, $3H_2O$), Cetyltrimethyl ammonium bromide (CTAB) and ascorbic acid were purchased from Sigma Aldrich. Silver nitrate ($AgNO_3$, 99%), 4-mercaptobenzoic acid (*p*MBA, 97%), trisodium citrate dihydrate (99%), and sodium borohydride ($NaBH_4$, 99.99%) were purchased from Aldrich. Dimethylformamide (DMF, AR grade), dimethyl sulfoxide (DMSO, AR grade), toluene (AR grade), methanol (AR grade), ammonium acetate, citric acid, sodium chloride (NaCl) and sodium hydroxide (NaOH) pellets were procured from RANKEM, India. All the chemicals were used without further purification. De-ionized water was used in all the experiments.

Experimental Details

Synthesis of Gold nanorods:

Gold nanorod (GNR) synthesis was performed following a seedless synthetic protocol as reported from our group[1] with a slight modification. Briefly, to a 50 mL solution of 100 mM CTAB, 2.5 mL of 10 mM $HAuCl_4$, $3H_2O$, 325 µL of 10 mM $AgNO_3$, and 350 µL of 100 mM ascorbic acid were added sequentially. All the solutions were mixed under mild stirring in a synthesizer keeping the temperature fixed at 28 ℃. The solution was incubated for 5 min and 500 uL of freshly prepared $NaBH_4$ solution (1.67 mM in ice cold DI water) was added in one shot. Prior to $NaBH_4$ addition, the stirring was stopped and the mixture was kept unperturbed overnight. After this, the GNRs were washed with water to remove the excess CTAB from the solution. For getting better uniformity, fractional centrifugation was carried out; i.e., the GNR solution was centrifuged at 7000 rpm for 20 min, the precipitate containing the larger particles were discarded. The supernatant was then separated and centrifuged stepwise at 12000 and 14000 rpm in a similar way. TEM study has shown that the precipitate after centrifuging at 12000 rpm furnished the best uniformity. This precipitate was redispersed in deionized (DI) water and again centrifuged twice at 12500 rpm each time for 15 min. At every step, the precipitate was shaken under vortex to prevent aggregation.

Synthesis of Ag_{44}(*p*MBA)$_{30}$ and purification:

We followed the procedure by Desireddy et al.[2] In brief, 128 mg of $AgNO_3$ and 173 mg of *p*MBA were added in a beaker containing DMSO and water mixed in 4:7 volume ratio under constant stirring. 50% CsOH (in water) was added dropwise until the cloudy thiolates became clear. Once a greenish-yellow color appeared, 283 mg of $NaBH_4$ in 9 mL of water was added dropwise to obtain a brown solution. The color of this solution changed to deep red after 1 h revealing the confirmation of the cluster formation. DMF was used to purify this crude cluster, which precipitated the cluster, and the solution was centrifuged. Then the residue was removed and the cluster was extracted in citric acid containing DMF solution. Thus all the protons of carboxylic acid were protonated making the cluster soluble in DMF. The extracted cluster was again precipitated using toluene, and the solution was centrifuged. Then the acidification step was repeated one more time. After this, the precipitate was redissolved in 25 mL of DMF to get the purified cluster. Notably, when all carboxylates are protonated, there is no need of citric acid, and DMF can extract the cluster directly. Protonation is the key step for this purification.

Synthesis of Au_{102}(*p*MBA)$_{44}$:

The synthesis was performed according to a previously published method.[3] In a typical synthesis 0.209 g (0.50 mmol) $HAuCl_4.3H_2O$ was dissolved in 19 mL of Millipore water (denoted as solution A). In a separation container 0.292 g (1.89 mmol) *para*-mercaptobenzoic acid (*p*MBA) was dissolved in 18.43 mL of water containing 0.57 mL of 10 M NaOH (denoted as solution B). Then, in the following order, 75 mL of methanol, 17.8 mL of previously prepared solution A and 15.5 mL of previously prepared solution B were quickly added to a 1 L reaction vessel containing 51.5 mL of water equipped with a stirring bar and a screw cap. The reaction mixture was stirred at room temperature. After 20 h, when a white precipitate was formed, 20.8 mg (0.55 mmol) solid $NaBH_4$ was added to it. The reaction mixture turned black immediately upon the addition of solid $NaBH_4$ and after stirring for 5 h, methanol was added to the reaction vessel until the total volume was approximately 800 mL followed by the addition of 40 mL 5 M NH_4OAc. The reaction mixture was centrifuged at 3500 rpm for 5 min. The supernatants were discarded and the black precipitate was air dried for 1 and dissolved in 400 µL of water. To the solution, 1 mL 2 M NH_4OAc was added, followed by methanol until the total volume was 90 mL and centrifuged at 3500 rpm for 10 min. The resulting supernatant was discarded and the black precipitate was allowed to air dry for 15 min. The air-dried sample was further subjected for fractional precipitation to obtain atomically precise nanoclusters.

Purification of Au_{102}(*p*MBA)$_{44}$ by fractional precipitation:

All particles in each conical were dissolved in about 9.24 mL millipore water and then combined into one 50 mL conical flask. To it, 2 M 0.76 mL NH_4OAc and 2.5 mL methanol were added and the suspension in the conical was mixed and centrifuged at 3500 rpm for 12 min. The resulting supernatant was then decanted into a new 50 mL conical flask, to which 12.5 mL methanol were added, the suspension in the conical was once again mixed and centrifuged at 3500 rpm for 12 min. Supernatant was then decanted into a new 50 mL conical and methanol was added until the total volume was 45mL. The suspension in the conical was mixed and divided into two 50 mL centrifuge tubes which were then centrifuged at 3500rpm for 15 min. The resulting supernatant was decanted and the precipitate (Au_{102}(*p*MBA)$_{44}$) was air-dried.

Synthesis of $Au_{\sim250}$(*p*MBA)$_n$.

This also was synthesized using a reported procedure.[4] About 0.246 g (1.60 mmol) of *p*MBA was dissolved in 19 mL of methanol and 0.107 g (0.27 mmol) of $HAuCl_4{\cdot}3H_2O$ was dissolved in 9.7 mL of methanol. Then 9.07 mL of 33 mM $HAuCl_4$ solution was mixed with

18.14 mL of 84 mM *p*MBA solution. Next, 68 mL of water was added to this mixture followed by dropwise addition of 2.69 mL 2 M NaOH with stirring, while maintaining the pH ~11). The solution was transferred into a 1 L capped plastic reaction vessel and after 20 h of vigorous stirring at room temperature, a mixture of 23.21 mL of methanol and 68.28 mL of water were added. Then 2.37 mL of freshly prepared 0.19 M aqueous $NaBH_4$ solution was added and the reaction was stirred for another 4.5 h. The reaction was quenched by adding 16 mL of 0.1M NaCl solution and 32 mL of methanol. The mixture was centrifuged at 3500 rpm for 15 min. The supernatant was decanted and the black precipitates were allowed to air dry. The solid was dissolved in 1:3 methanol/water mixture and centrifuged at 3500 rpm for 15 min. Supernatant was removed and solid product $Au_{\sim 250}(p\text{MBA})_n$ was allowed to dry under ambient conditions.

Surface functionalization of GNRs by *p*MBA: In order to make the GNRs react with $Ag_{44}(p\text{MBA})_{30,}$ their surfaces were functionalized by *p*MBA which essentially replaced the CTAB molecules. For that, the clean GNRs were incubated in 0.1 mM aqueous *p*MBA solution (1:1 v/v) for 3 h. Then it was centrifuged again and the supernatant containing excess *p*MBA was discarded. To ensure uniform functionalization, this process was repeated thrice. At the final step, the precipitate was redispersed in the appropriate medium (DMF for silver cluster and water for gold clusters) to carry out further studies.

Reaction between GNR@*p*MBA and Ag_{44}: To the GNR@*p*MBA dispersed in 1 mL of DMF, 300 uL, as-synthesized Ag_{44} cluster was added. The mixture was shaken well initially for proper mixing and then kept undisturbed at room temperature for 20 h.

Reaction between GNR@*p*MBA and Au nanoclusters: In order to study the self-assembly, the nanoclusters (1.0 mg) was dissolved in 100 µL of 1.0 M sodium hydroxide solution and diluted the total volume to 1.0 mL using milliQ water. This partially deprotonates the carboxylic acid groups (~22 –COOH groups) and stabilizes the nanocluster dispersion. Due to strong electrostatic repulsion aggregation of nanoclusters were prevented and the nanoclusters exist as individual clusters (Cryo-TEM). However, considerable number of COOH groups are still in their protonated form and are available for H-bonding. This property has been utilized to bind the gold nanolcusters to GNR surface. In this case, to the 1 mL of aqueous dispersion of GNR@*p*MBA, 100 uL and 50 uL of as synthesized Au_{250} and Au_{102} clusters were added respectively.

Instrumentation

The UV-vis absorption spectra were recorded using a PerkinElmer Lambda 25 UV-vis spectrometer. A Waters Synapt G2-Si high definition mass spectrometer equipped with electrospray ionization was used in the negative mode. All TEM measurements were made using a JEOL 3010 (JEOL Japan) transmission electron microscope. Raman measurements were made using a Confocal Raman micro spectrometer (Witec GmbH, Germany) with 532 nm and 633 nm laser excitation.

SerialEM and 3D reconstruction: Electron tomographic tilt series were acquired with the SerialEM software package. Samples were tilted between ± 69^o angles with 2^o increment steps. Prealignment of tilt image series was done and the fine alignment and cropping were executed with IMOD. The images were binned 2-4 times to reduce noise and computation time. Maximum entropy method (MEM) reconstruction scheme was carried out with a custom-made program on Mac or Linux cluster with regularization parameter value of l = 1.0e-3. The STEM imaging was performed using JEOL JEM-2800 high throughput electron microscope operated at 200 kV with simultaneous bright field (BF) and dark field (DF) STEM imaging.

Making of the Hexagonal crystal structure of $Ag_{44}(p\text{MBA})_{30}$ cluster:

It was built by replacing the octahedral lattice points by $Ag_{44}(p\text{MBA})_{30}$ clusters and the octahedral $Ag_{44}(p\text{MBA})_{30}$ crystal structure was visualized using visual molecular dynamics (VMD) software).

Results and Discussion

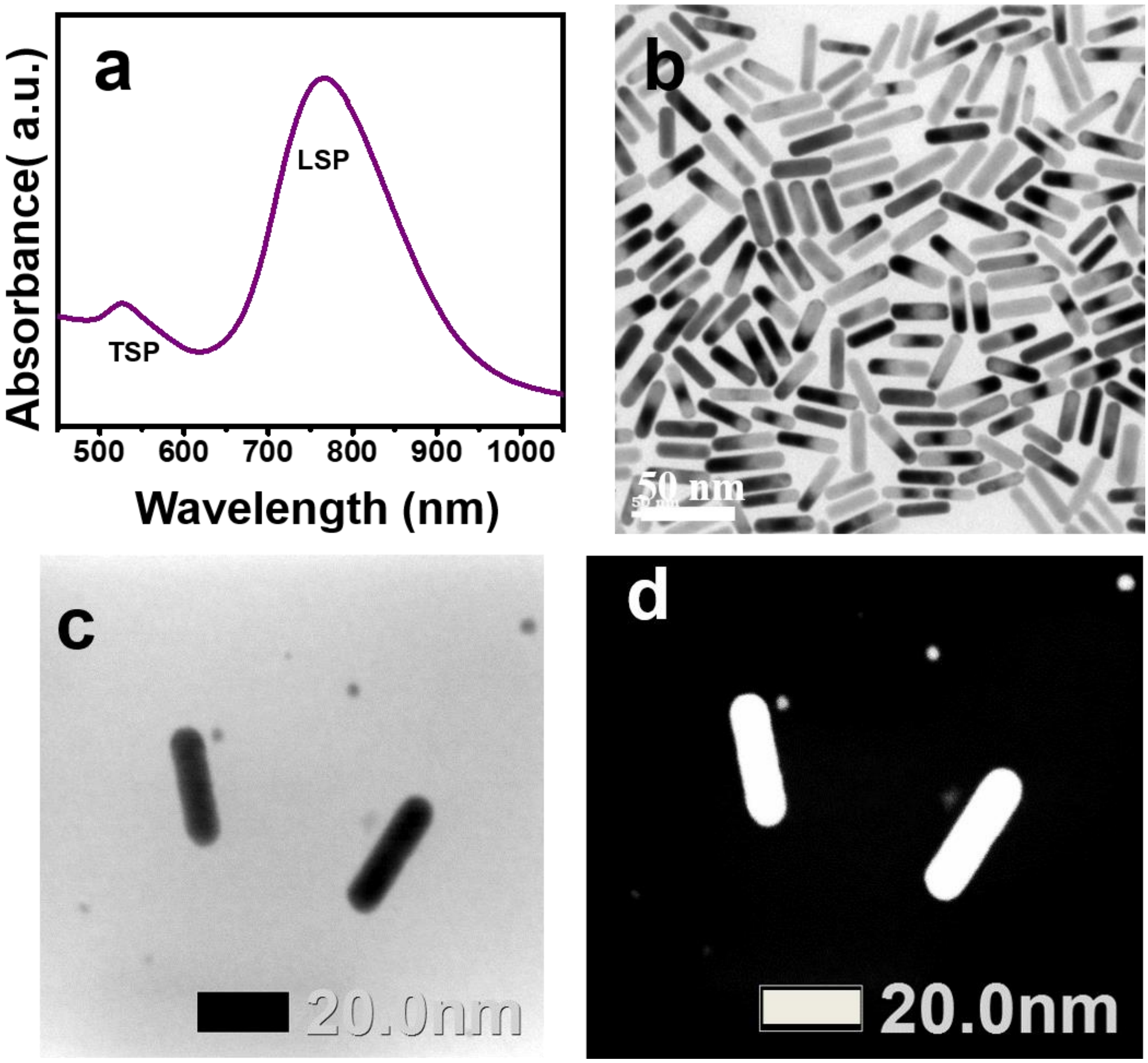

Figure S1. Characterization of GNR@CTAB : (a) Absorption spectrum showing transverse (TSP) and longitudinal surface plasmon (LSP) resonances (b) TEM image, (c) bright field and (d) dark field STEM images.

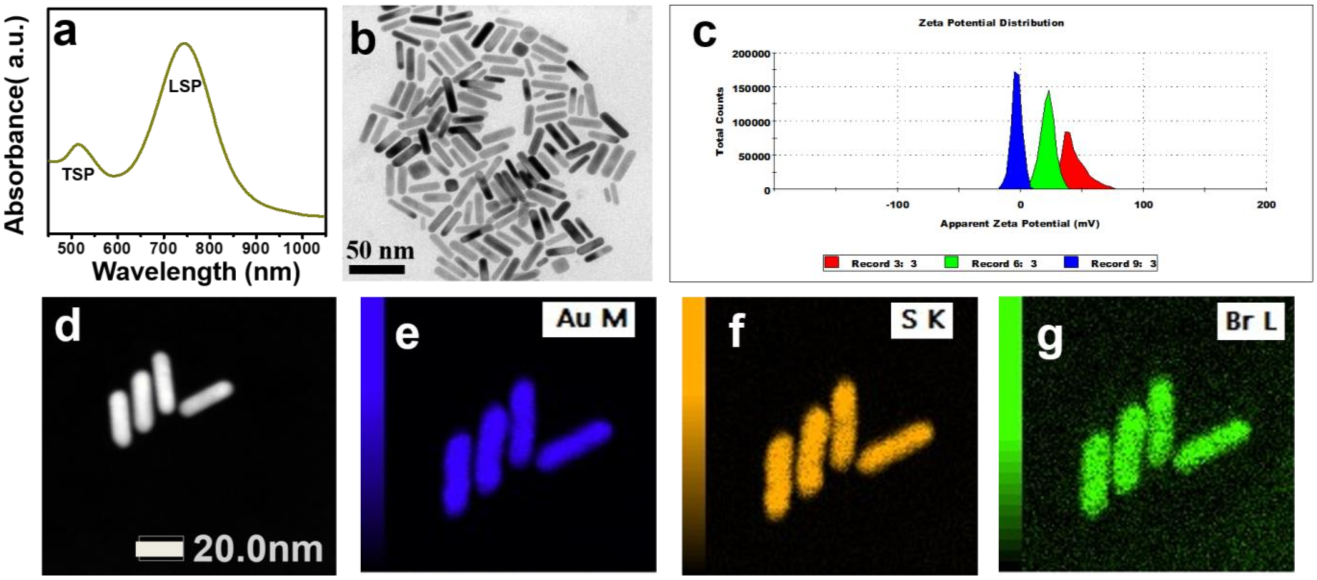

Figure S2. Characterization of GNR@*p*MBA : (a) Absorption spectrum showing transverse (TSP) and longitudinal surface plasmon (LSP) resonances (b) TEM image, (c) change in zeta potential with MBA functionalization on GNR surfaces: GNR@CTAB, 1 step MBA functionalized GNR and 3 step MBA functionalized GNR are denoted by red, green and blue curves, respectively; (d) dark field STEM image, STEM elemental mapping of Au (e), (f) S and (g) Br. Images d-g has the same scale bar.

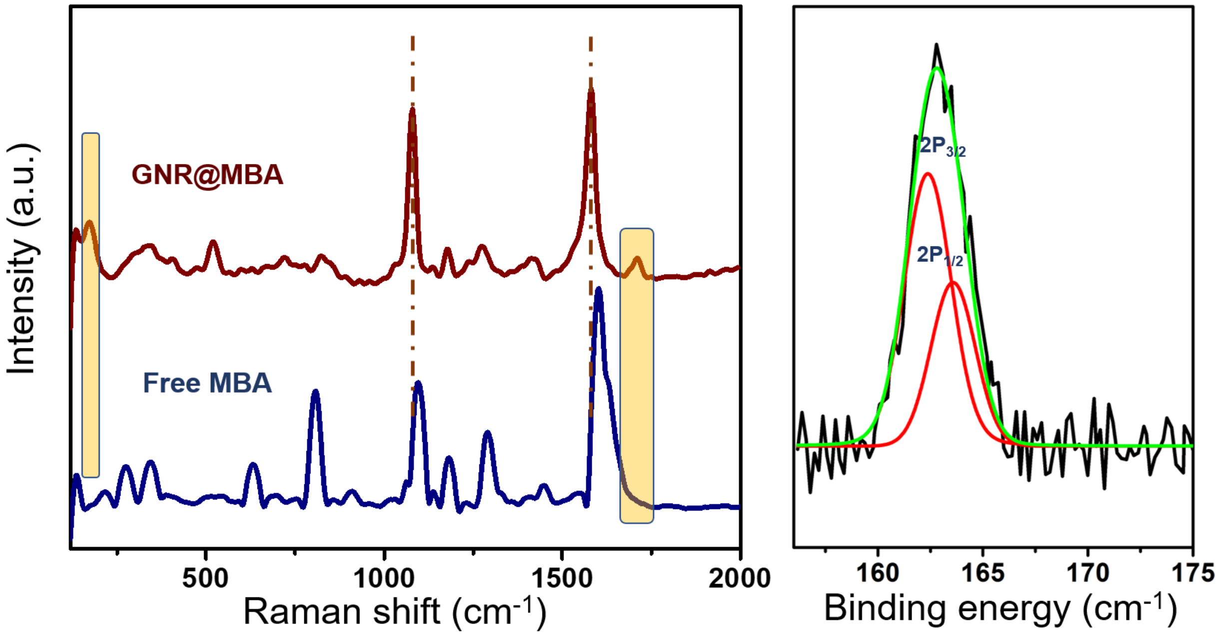

Figure S3. Proof of Au-S bond in GNR@*p*MBA: (a) comparative Raman spectra of free MBA and GNR@*p*MBA shows an intense Au-S-C stretching (ref 5) at 175 cm^{-1} in the case of GNR@*p*MBA. The new peak at 1710 cm^{-1} corresponds to C=O stretching corresponding to the neutral -COOH group. The presence of peaks at 1590 and 1080 cm^{-1} in GNR@*p*MBA assigned to the aromatic ring vibrations show little shift as a result of the binding to the metal surface. The peaks at 1370-1380 cm^{-1} are ascribed to the presence of a small number of COO- groups (ref 6). The specific peaks are marked. (b) The peak at 162.5 eV in XPS is the characteristic feature of Au-S bond.

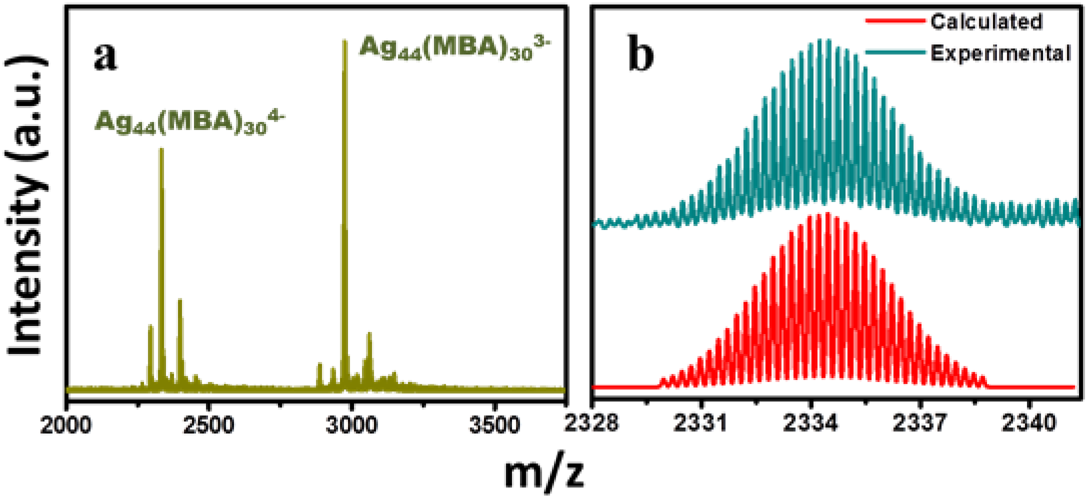

Figure S4. Characterization of Ag_{44}(*p*MBA)$_{30}$: (a) ESI mass spectrum and (b) Expanded view of molecular ion peak [Ag_{44}(*p*MBA)$_{30}$]$^{4-}$ along with the theoretical spectrum of the same ion.

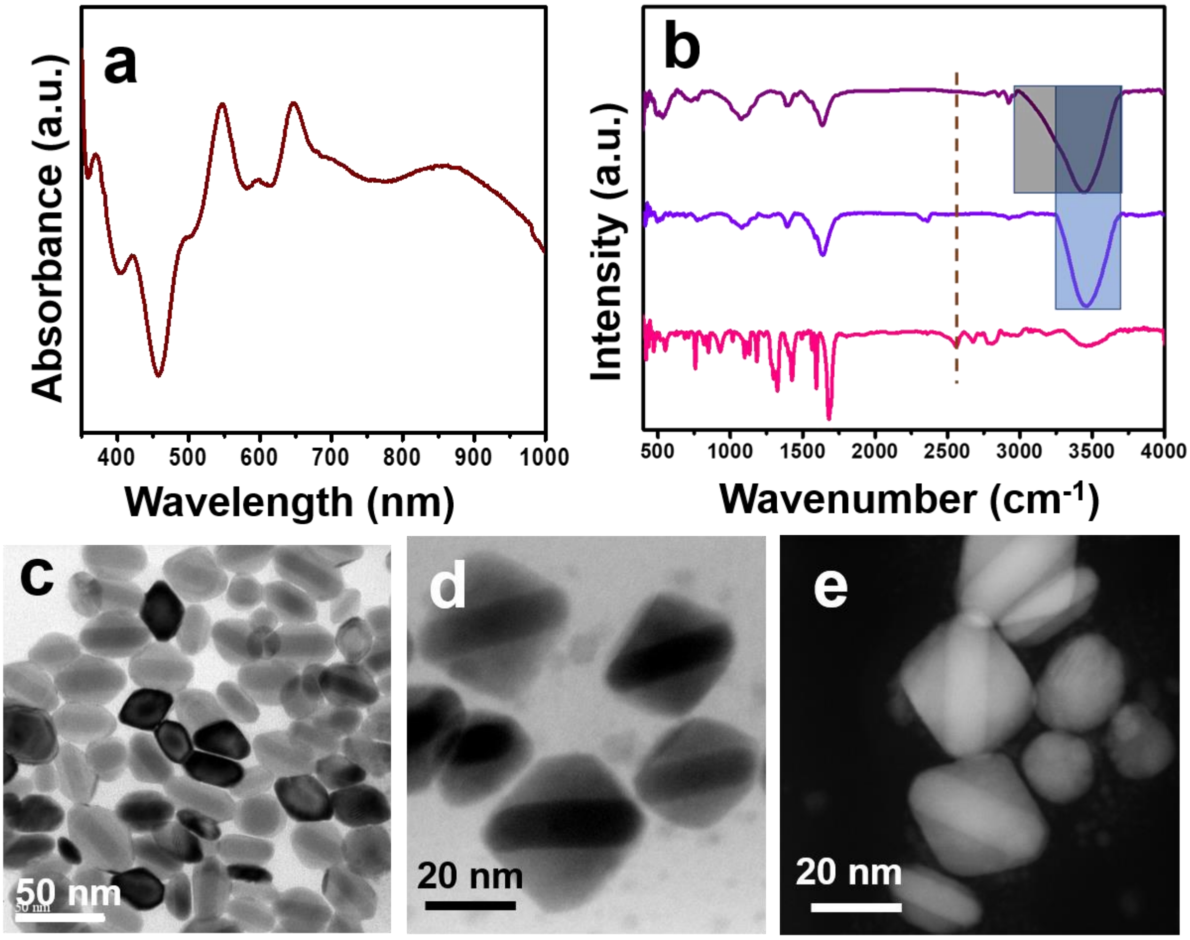

Figure S5. Characterization of GNR@Ag$_{44}$: (a) Absorption Spectrum, (b) Comparative infrared spectra of free *p*MBA, Ag$_{44}$ and GNR@Ag$_{44}$ – all in the solid state. Significant broadening of the signal near 3500 cm^{-1} is an indication of H- bonding between *p*MBA moieties in the final composite material. The characteristic S-H peak at 2550 cm^{-1} in solid *p*MBA disappears in case of GNR@Ag$_{44}$, which supports the formation of Au-S bond. (c) TEM, (d) Bright Field STEM and (e) Dark Field STEM images of GNR@Ag$_{44}$.

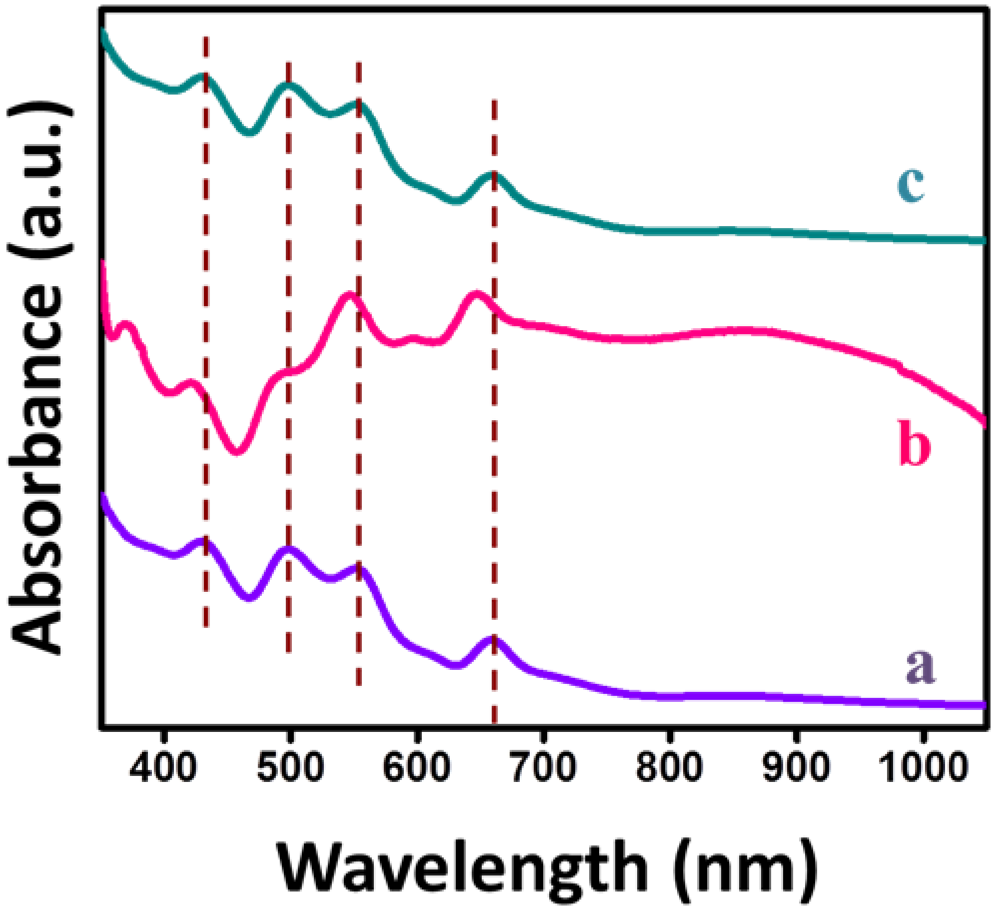

Figure S6. Absorption spectra of (a) Ag_{44} cluster before reaction, (b) GNR@Ag_{44} composite and (c) Ag_{44} cluster separated from the composite using probe sonication in DMF. The peaks at 681, 574, 506, and 440 nm occur at the same positions in a and c, showing that the clusters can be separated from the composite keeping their intrinsic properties intact.

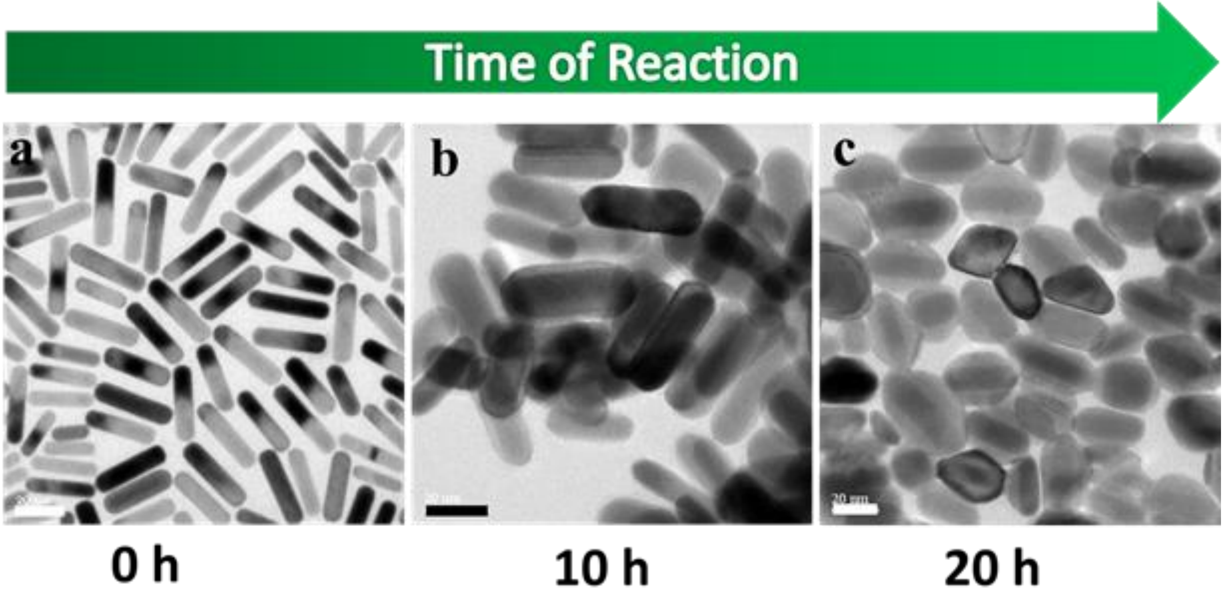

Figure S7. TEM images of the cluster assembly on the GNR@*p*MBA surface after (a) 0 h, (b) 10 h and (c) 20 h. (scale bar shows 20 nm in each case).

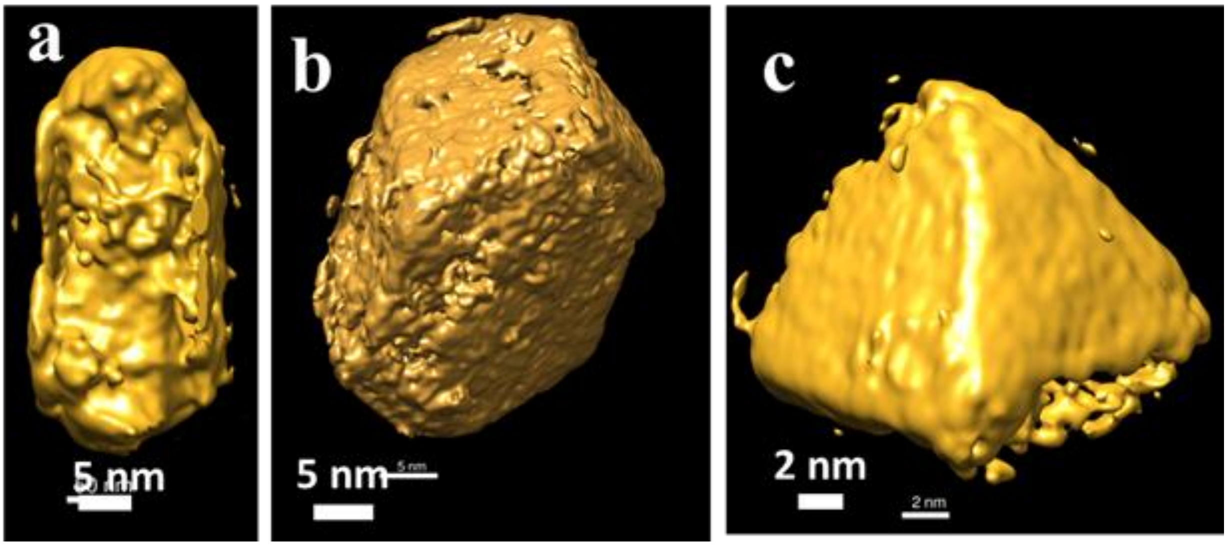

Figure S8. TEM tomography of different other morphologies: (a) limited cluster growth at an initial stage, (b) truncated octahedral structure obtained at a later stage, and (c) square pyramidal structure obtained when clusters assembled at only one side of the GNR@*p*MBA.

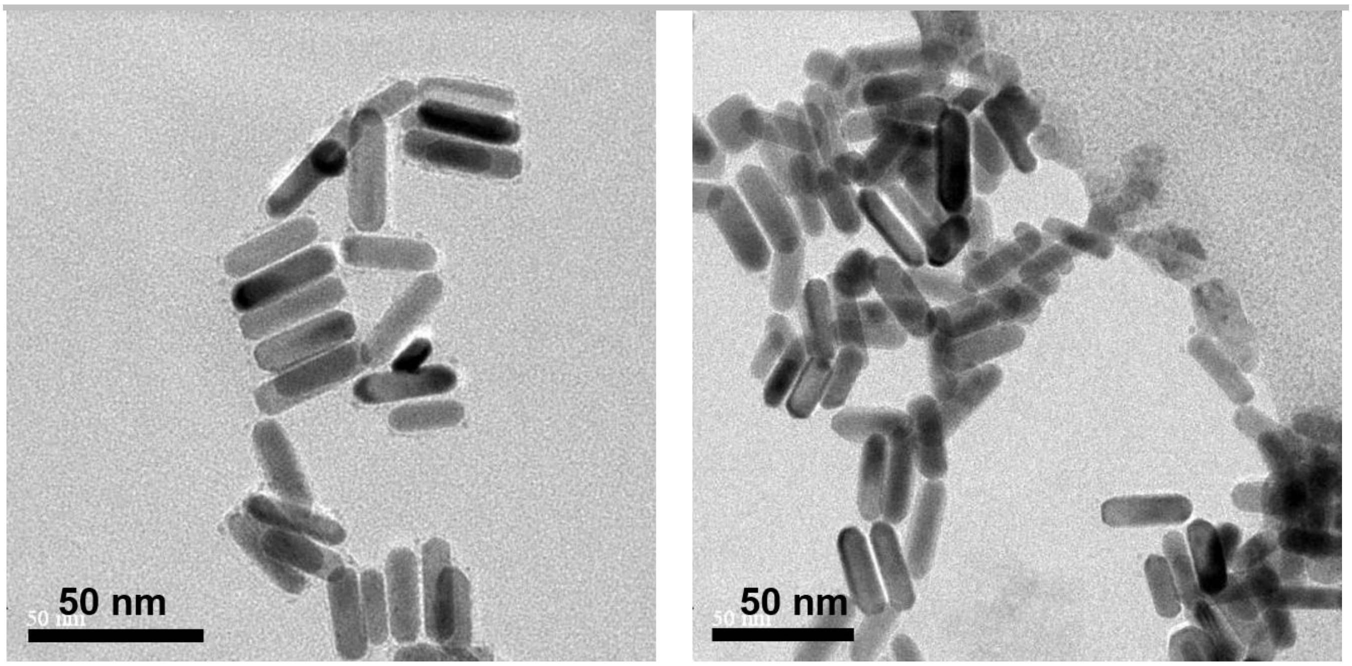

Figure S9. Control experiment when Ag_{44} was added to GNR@CTAB : a) very few clusters are there surrounding the GNRs, b) clusters are there assembling within themselves, but not interacting with the GNRs. This proves that H-bonding functionality has to be there on the GNR surface.

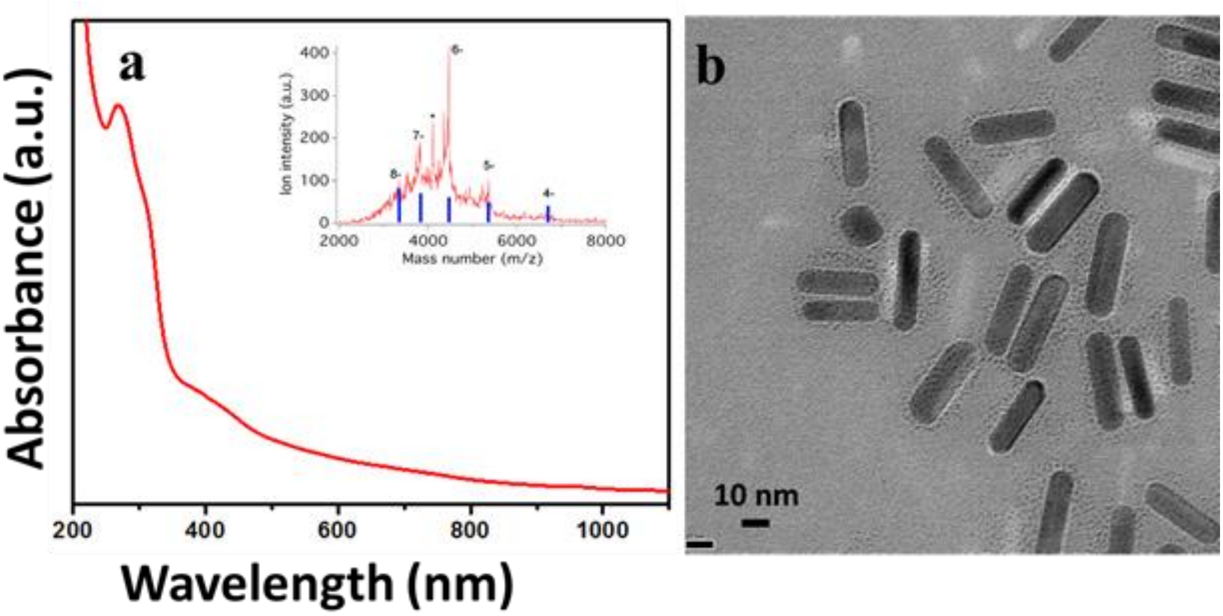

Figure S10. (a) UV-Vis absorption spectrum of $Au_{102}(p\mathrm{MBA})_{44}$ (inset shows the ESI mass spectrum[4] where the calculated mass numbers of $Au_{102}(p\mathrm{MBA})_{44}$ are marked with blue bars and the corresponding charge state is given above each calculated mass number, peak of a minor impurity is marked with an asterisk), and (b) TEM image of GNR@Au_{102}.

Supporting videos are given separately.

Video S1: TEM Tomographic reconstruction of GNR@CTAB.
Video S2: TEM Tomographic reconstruction of GNR@*p*MBA.
Video S3: TEM Tomographic reconstruction of GNR@Ag_{44}.
Video S4: TEM Tomographic reconstruction of GNR@Au_{250}.

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