Supporting information for the paper:

Coalescence of Atomically Precise Clusters on Graphenic Surfaces

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S1. Supporting information

Experimental Section

**Synthesis of graphene:** Graphene has been prepared by the modified Hummer’s process followed by reduction of GO to RGO.\(^1\) Initially, 1 g of graphite powder (purchased from R. K. Scientific) was taken in a round bottle flask. To that, 12 mL of concentrated H\(_2\)SO\(_4\) was added and the mixture was kept at 90 °C for an hour. 2 g of K\(_2\)S\(_2\)O\(_8\) and 2 g of P\(_2\)O\(_5\) were added under stirring condition. The mixture was kept at the same temperature for 6 h for pre-oxidation of graphite. Then the mixture was cooled to room temperature and filtered. The filtrate was discarded and the pre-oxidized GO was kept for drying in hot air overnight. About 24 mL of concentrated H\(_2\)SO\(_4\) was added to this pre-oxidized GO and kept at ice cold condition. Then 3 g of KMnO\(_4\) was added slowly with constant stirring and allowed to stand for 6 h. Then 400 mL of distilled water was added slowly under stirring condition and kept at room temperature for an hour. To stop the reaction, 5 mL of 20% H\(_2\)O\(_2\) was added to it and kept undisturbed overnight. The bright yellow precipitate confirmed the formation of GO. The solution was decanted and the precipitate was collected. It was washed with 1% HCl for three times. This solution was centrifuged to collect GO and then dried in vacuum for 24 h. About 1 g of dried GO was weighed and re-dispersed in 500 mL of water such that the concentration of the GO solution was 0.5 wt %. Unwanted ions were removed from the solution by dialysis. This GO solution was used as the stock solution for the preparation of graphene. About 100 mL of this GO (0.1 wt %) solution was taken in a round bottom flask. To that 700 µL of ammonia (25%) and 65 µL of hydrazine (35%) was added and the solution was kept at 80 °C for two hours. The solution was cooled to room temperature. Then it was centrifuged and washed with distilled water for two times. The ppt was dispersed in requisite amount of water so that final concentration is 0.01 wt %. 
S2. Supporting information

Evolution of $\text{Au}_{25}(\text{PET})_{18}$ - MALDI MS study

*Figure S2.* Time dependent MALDI MS data during the synthesis of $\text{Au}_{25}\text{PET}_{18}$. It shows that the formation of $\text{Au}_{25}$ takes 36 hours. (Where PET, $\text{SCH}_2\text{CH}_2\text{Ph}$, is a ligand protecting the cluster core)
S3. Supporting information

Comparison of the MALDI MS spectra of PET protected gold cluster $[\text{Au}_{135}(\text{PET})_{57}]$ with native lysozyme (Lyz) and lysozyme-gold cluster (Au@Lyz)

![MALDI MS spectra](image)

**Figure S3.** Comparison of the spectra of PET protected gold cluster $[\text{Au}_{135}(\text{PET})_{57}]$ with native lysozyme (Lyz) and lysozyme-gold cluster (Au@Lyz). The peak that is shifted from the native protein in Au@Lyz is due to the Au cluster nucleated within the protein. 2M, 3M, are dimer, trimer, etc. of the protein and the corresponding cluster features. M also shows a dication ($M_{2^+}$) feature. Lysozyme and Au@Lysozyme data have been published by Ananya et. al.²
S4. Supporting information

MALDI MS spectrum of the intermediate product and its laser flux-dependent study

**Figure S4.** (A) MALDI MS spectrum of the intermediate product shows that Au$_{33}$, Au$_{38}$, Au$_{55}$ have been formed during the conversion process of Au$_{25}$ to Au$_{135}$. (B) Laser flux-dependent study of the intermediate product.
S5. Supporting information

TEM, effect of electron beam irradiation on Au$_{25}$ and graphene-supported Au$_{135}$

**Figure S5.** (A) and (A1) TEM images of Au$_{25}$ clusters before and after electron beam irradiation. Size of Au$_{25}$ grows fast upon electronbeam irradiation. A1 was collected after 10 minutes of irradiation. (B) and (B1) Same data for supported Au$_{135}$ clusters. Some clusters are marked with circles. Size of the graphene-supported Au$_{135}$ clusters do not change upon electron beam irradiation.
S6. Supporting information

Laser flux-dependent study of Au$_{25}$ and graphene-supported Au$_{135}$

Figure 6. (A) Laser flux-dependent study of Au$_{25}$ showing that as the laser intensity increases, intensity of the parent peak (Au$_{25}$) decreases and fragmented peak (Au$_{21}$) increases. At very high laser power, the parent peak has almost vanished. (B) Laser flux study-dependent of graphene-supported Au$_{135}$ shows that with the increase of laser intensity, peak broadening occurs with a peak at lower mass, due to fragmentation. Inset: Change of dication with the increase of laser intensity.

Reference: