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Electronic Supporting Information

A Protecting Group Approach toward Au-Silica Janus Nanostars

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Experimental section:

All chemicals were supplied by Sigma and used as received unless otherwise indicated. $HAuCl_4 \cdot 3H_2O$ (99%), sodium citrate tribasic dihydrate (98%), 4-mercaptobenzoic acid (4-MBA 90%), polyacrylic acid solution (PAA Mw=25000g/mol, 35% H_2O), ammonium hydroxide (28-30%), tetraethylortosilicate (TEOS, 98%), silver nitrate (99%), L-Ascorbic acid (L-AA, 99%), hydrochloric acid (Panreac, 37%). 2-propanol (Scharlab, 99.8%); absolute ethanol (Scharlab) and Milli-Q water were used as solvents. All the glass material was washed with Aqua Regia (care must be taken as it is a highly oxidizing liquid) and rinsed gently with Milli-Q water prior to use.

Preparation of Au-SiO_2 Janus particles. Au@citrate spheres (40 nm av. diameter, 27 mL) were prepared as previously reported,[1] centrifuged at 2100g for 20 min, washed with the same volume of water and dispersed again in water (10 mL). The seeds were added dropwise under vortex stirring to a mixture of 2-propanol (38 mL) and H_2O (12 mL), containing 4-MBA (400 μL, 5 mM in EtOH) and PAA (400 μL, 0.645 mM in H_2O). After gentle stirring for 30 min to induce self-assembly of the ligands over the surface, ammonium hydroxide (1.8 mL) was added under fast stirring, followed by dropwise addition of TEOS (12 mL, 8.96 mM in 2-propanol) and was stored for ~12h under slow stirring. [Au] ≈ 0.3 mM; pH ≈ 11.

Preparation of Au-SiO_2 Janus stars. First 6-10 mL of the as synthesized Janus particles was centrifuged at 2100g for 30 min. The supernatant was centrifuged again under the same conditions and then the precipitates were collected, washed with half the volume of water at 1900g for 20 min and redispersed in 10 mL of water. To this solution were quickly added: $HAuCl_4$ (19.8 μL, 0.1265 M), HCl (10 μL, 1 M), $AgNO_3$ (100 μL, 3

[1] N. G. Bastús, J. Comenge, V. Puntes, *Langmuir* **2011**, 27, 11098–11105.

mM) and L-AA (50 μL, 0.1 M) as previously reported for nanostars growth.[2] After 30-60s the particles were collected by centrifugation at 1100g for 5 min and washed with 5 mL of water (the maximum possible amount of supernatant was removed). The particles were transferred under sonication into a solution of 4-MBA in ethanol (5 mL, 20 μM), and washed with ethanol (5 mL) to remove excess 4-MBA.

Preparation of Au Janus stars. Au-SiO_2 Janus stars were dispersed in an aqueous solution of 4-MBA (5 mL, 20 μM) and washed 3-fold with water (5 mL) to remove 4-MBA in excess. The process initially led to dissolution of the inner part of the silica semishell, which was completely removed after two days.

Instrumentation:

Visible-NIR spectra were measured in 1cm path length quartz cuvettes using an Agilent 8453 spectrophotometer. Conventional Transmission Electron Microscopy (TEM) analysis was performed with JEOL JEM 2100F and 1400F transmission electron microscopes operating at acceleration voltages of 200 and 100 kV, respectively. HAADF-STEM tomography series and high resolution HAADF-STEM images were acquired using an aberration corrected cubed FEI-Titan 60-300 electron microscope operated at 200kV. The acquisition of all the tomography series was performed by using the Xplore 3D automatic acquisition software from FEI and the alignment of the series by using the Inspect 3D software from FEI. The reconstruction of all the series was performed by using the Simultaneous Iterative Reconstruction Technique (SIRT) as implemented in Inspect 3D.

[2] H. Yuan, C. G. Khoury, H. Hwang, C. M. Wilson, G. A. Grant, T. Vo-Dinh, *Nanotechnology* **2012**, 23, 075102.

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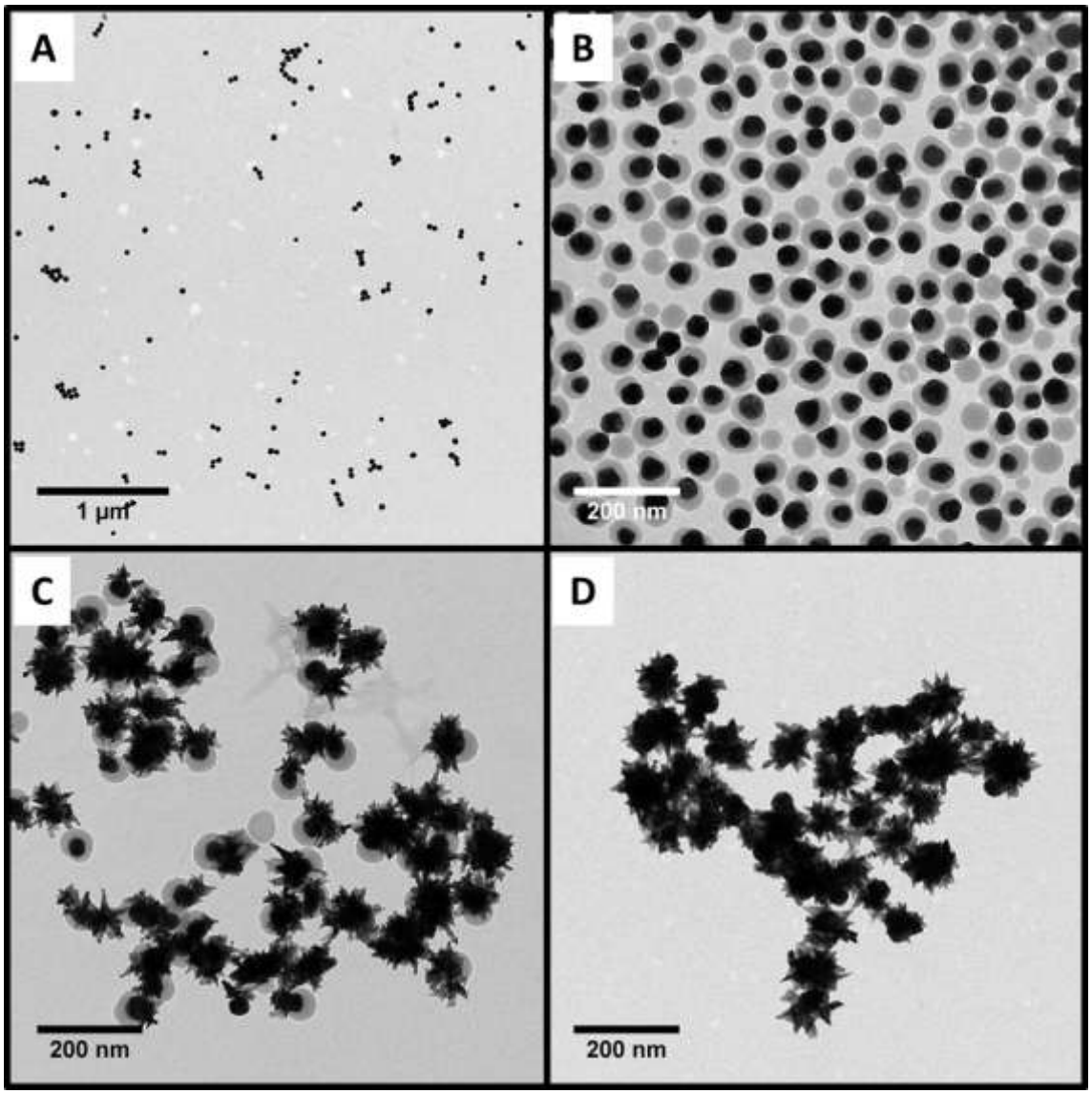

Figure S1. Representative low magnification TEM micrographs: **(A)** ~40 nm Au@citrate seeds; **(B)** Au-SiO_2 Janus particles; **(C)** Au-SiO_2 Janus nanostars and **(D)** Au Janus stars after SiO_2 removal.

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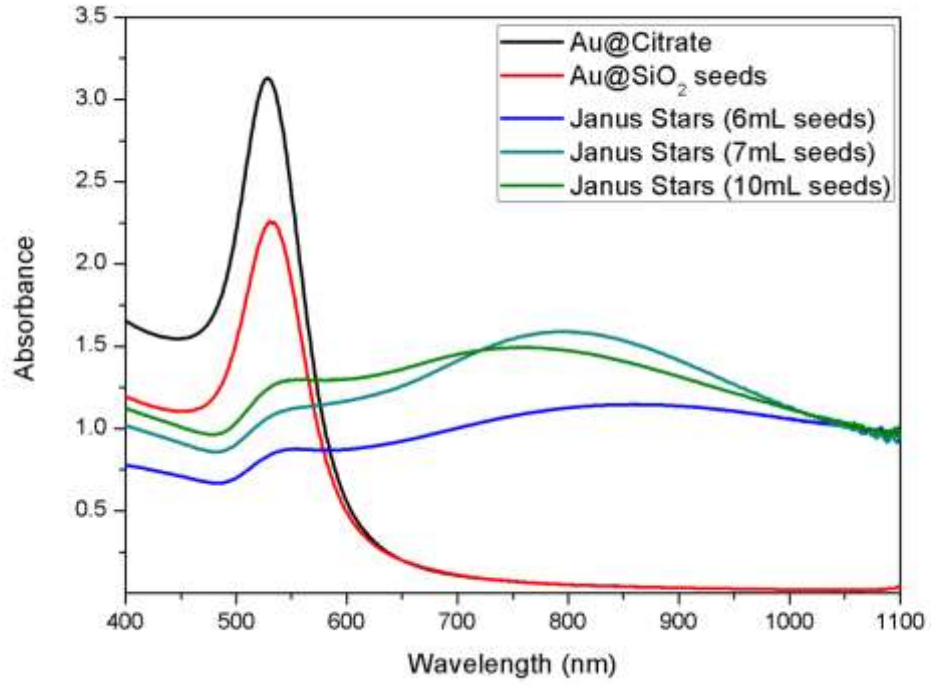

Figure S2. Vis-NIR spectra of 40 nm Au@citrate (black), Au-SiO_2 Janus seeds (red) and Au-SiO_2 Janus stars made from different amounts of seed solution as indicated in the labels.

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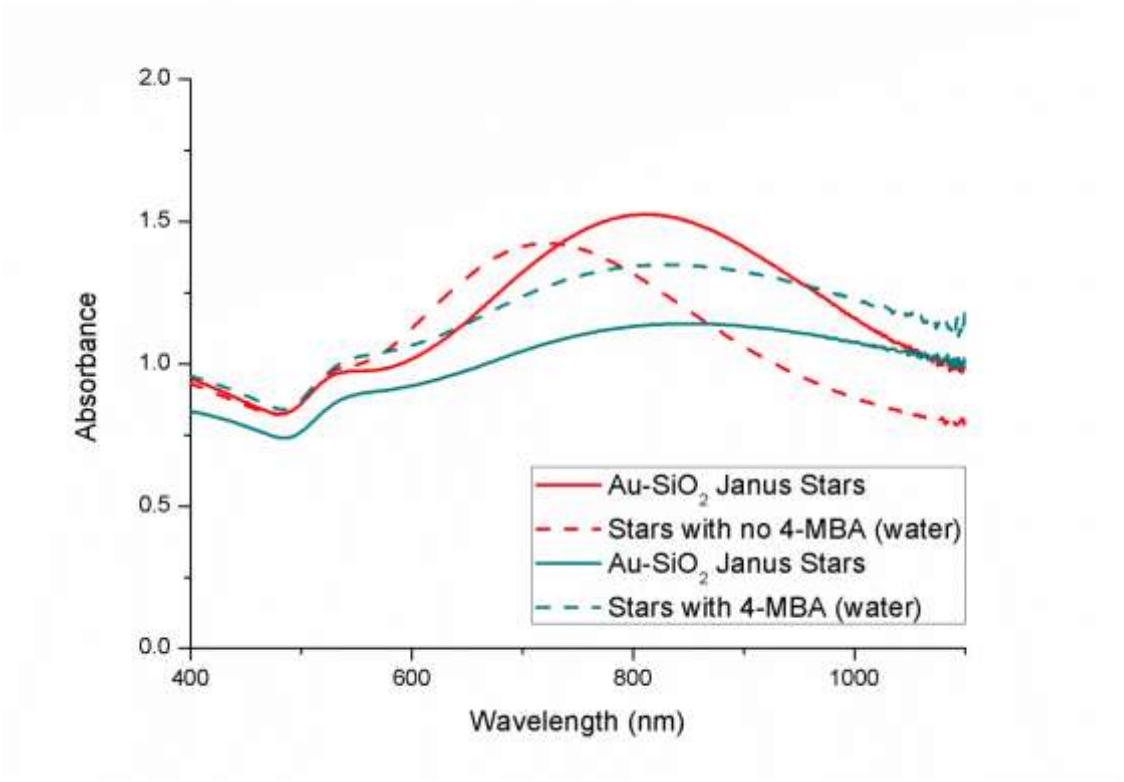

Figure S3. Evolution of Vis-NIR spectra of aqueous solutions of Au-SiO_2 Janus nanostars in the absence and presence of 4-MBA. A 100 nm blueshift is observed after two days when no 4-MBA was added, indicating reshaping of the spikes and silica dissolution (red lines). Only a minor blueshift can be seen when 4-MBA was present in the aqueous Janus nanostars solution, indicating silica dissolution maintaining the spiky shape (blue lines).

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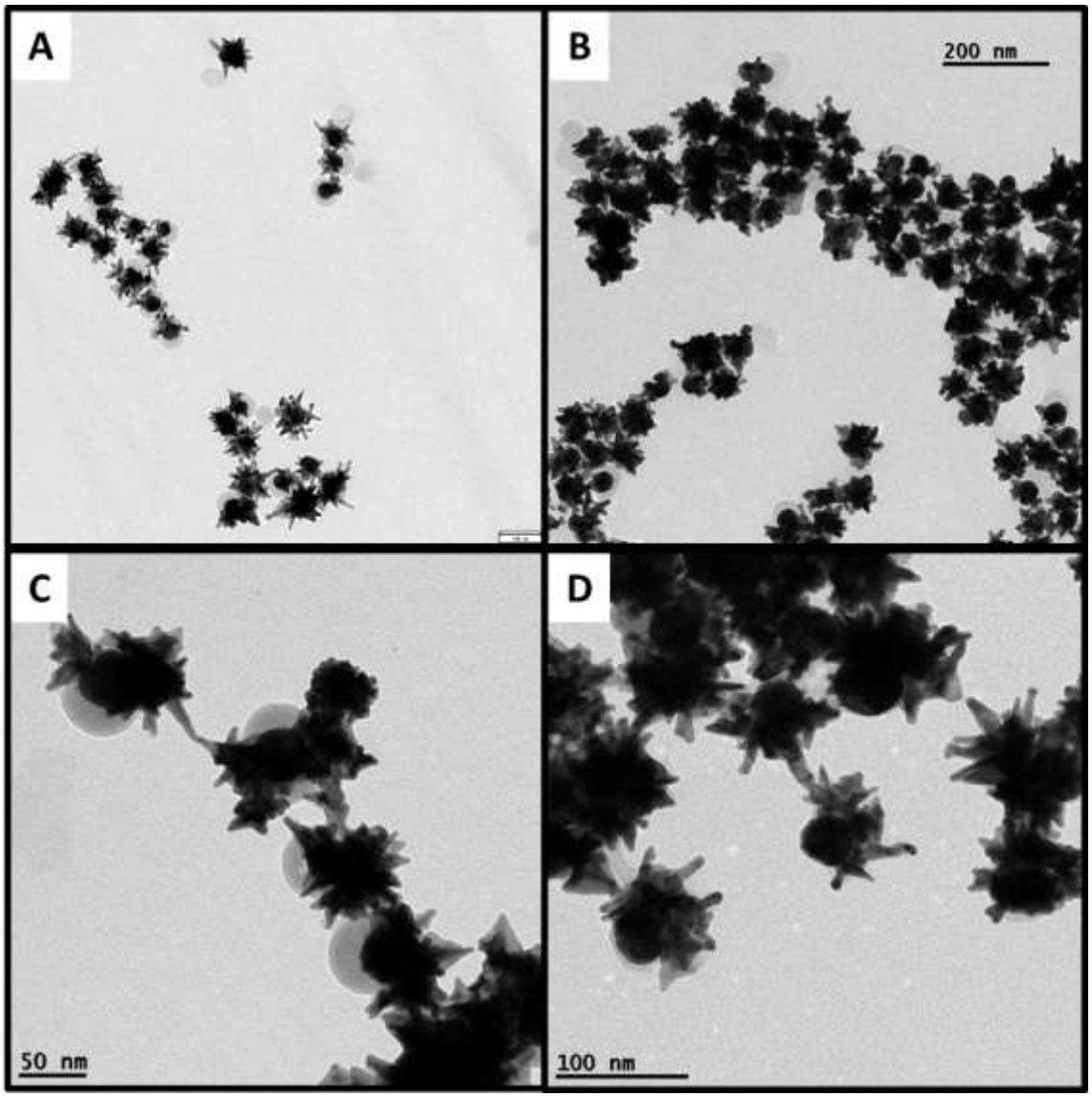

Figure S4. (A,B) TEM micrographs of Au-SiO_2 Janus nanostars before (**A**) and after reshaping and silica dissolution in water in the absence of 4-MBA (**B**). **(C,D)** TEM micrographs of Au-SiO_2 Janus nanostars before (**C**) and after storage in 4-MBA aqueous solution (**D**), showing preservation of the spikes but dissolution of the silica semishells.

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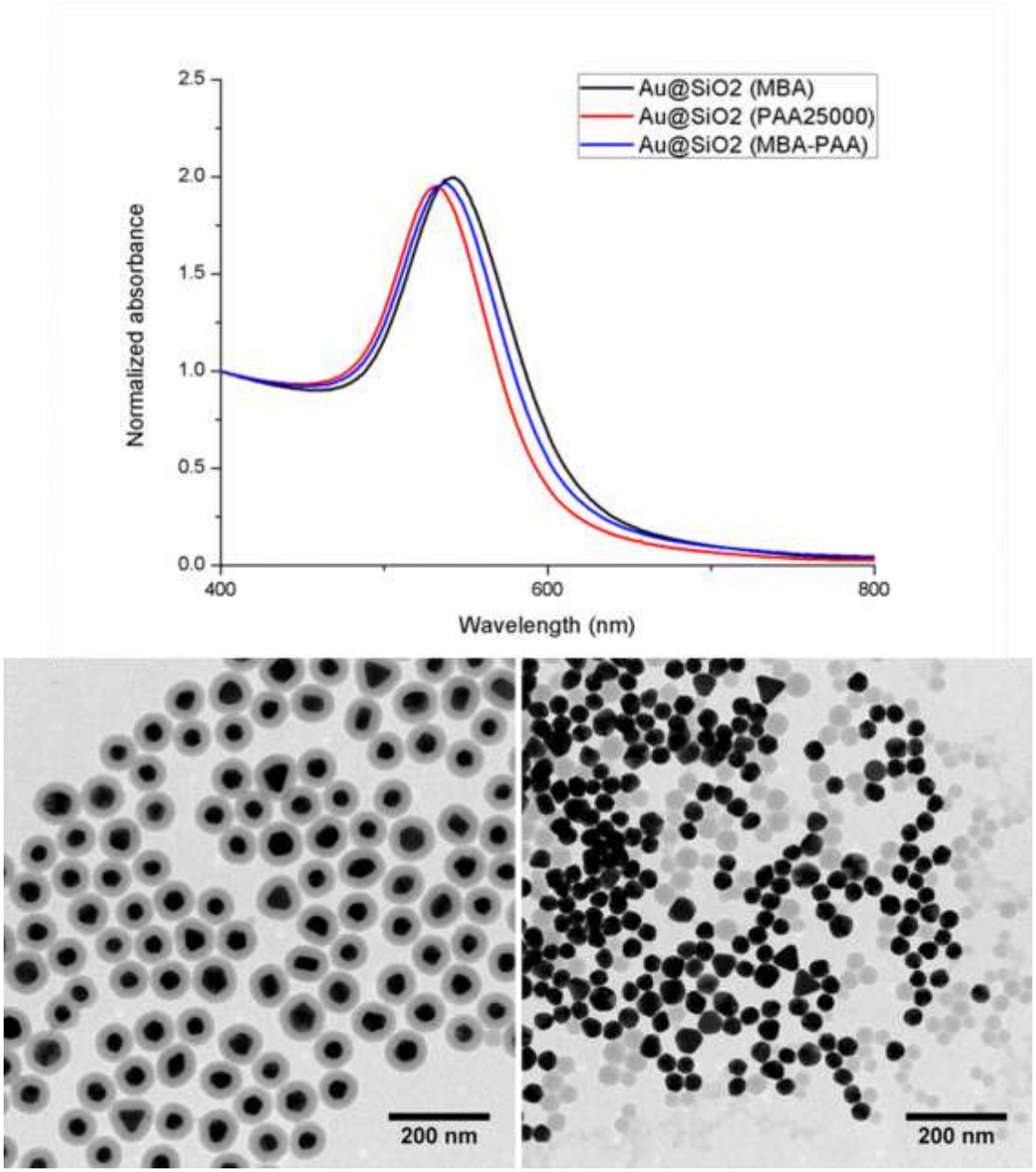

Figure S5. Spectra of the particles obtained when 4-MBA and PAA 25000 were used alone or together during the silica growth. When only 4-MBA was used (redshifted spectrum), core-shell particles were obtained (left TEM picture). In contrast, when using only PAA 25000 (blueshifted spectrum), silica nucleation was observed with no silica coating over the metal (right TEM picture). The appropriate mixture produces the segregation of ligands over the surface, yielding the desired Janus Au-SiO_2 particles.

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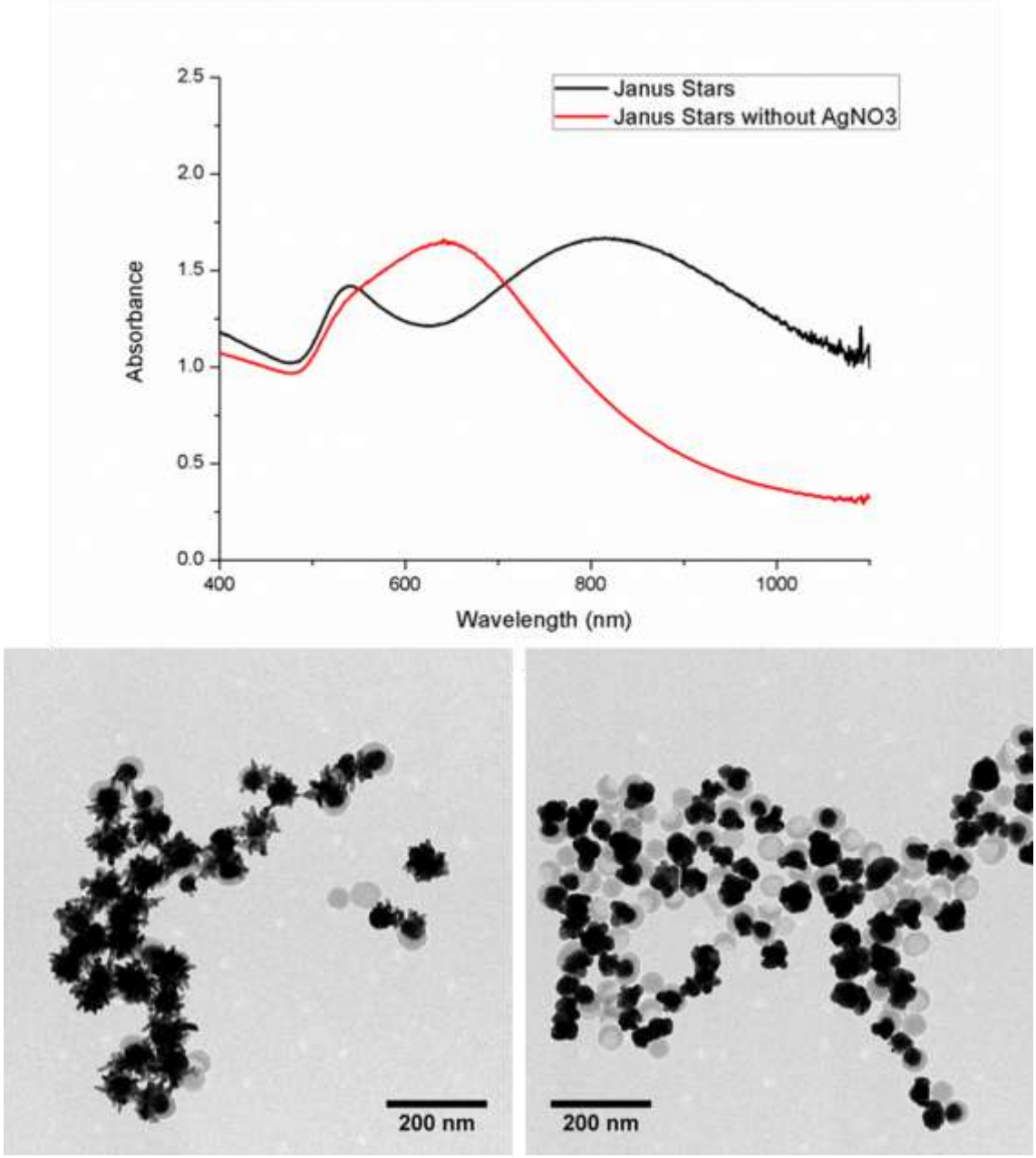

Figure S6. Comparison of the particles obtained when $AgNO_3$ is added or not during gold spikes growth. When added, a strong redshift is observed due to the presence of the tips as can be observed in the left TEM image. When no silver ions are added, a small redshift appears due to overgrowth of gold over the Janus seeds, but no spikes are produced. This indicates that silver ions are responsible for the growth of branches.

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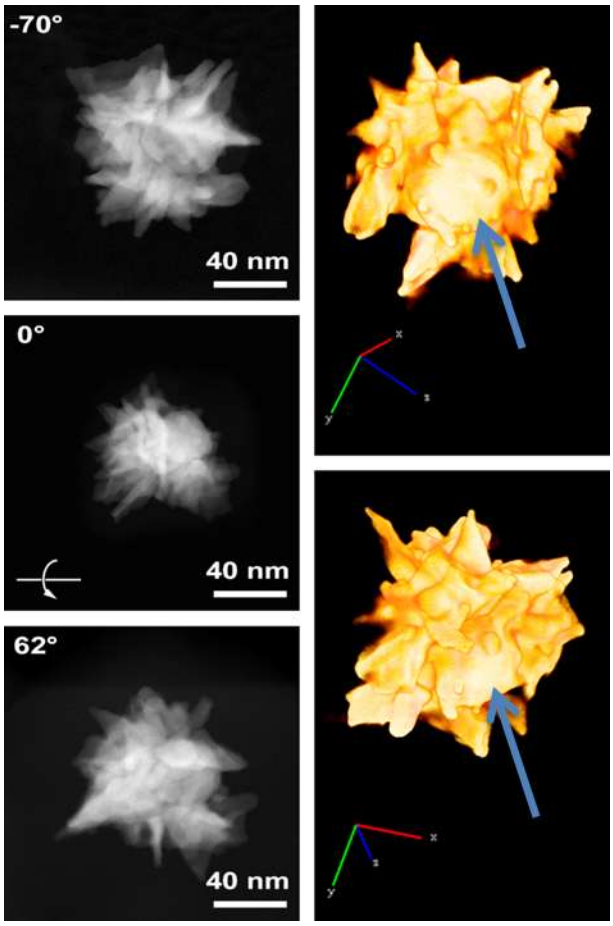

Figure S7. HAADF-STEM micrographs of an Au Janus star, used for tomographic reconstruction acquired at different angles. On the right the corresponding rendered 3D reconstruction is shown along different viewing directions, showing the Au part in yellow and the position where the SiO_2 was located indicated with arrows.

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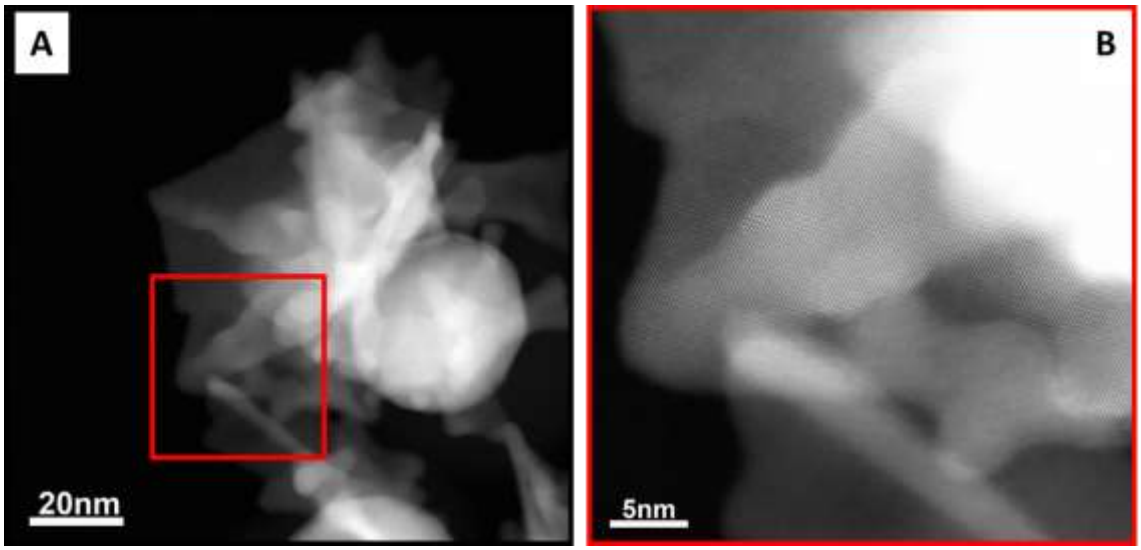

Figure S8. A. HAADF-STEM image of a single Au Janus nanostar with long spikes, revealing the presence of a central core with branches. **B.** HRSTEM image of the same particle showing the starting point of a monocrystalline spike.