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Electronic Supplementary Information

Growth and Branching of Gold nanoparticles Through Mesoporous Silica Thin Films

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Table S1. Size of the particles (nuclei and tips) after different reaction times for S_{60}@SF sample growth with a solution of CTAB, AA and Au with 60:16:1 molar ratio. The analysis was performed using several TEM images.

Reaction time/hs	Core size/nm	Tips width/nm	Tips length/nm
0	59 ± 4		
2	59 ± 4	10 ± 2	11 ± 4
6	59 ± 4	11 ± 2	13 ± 5

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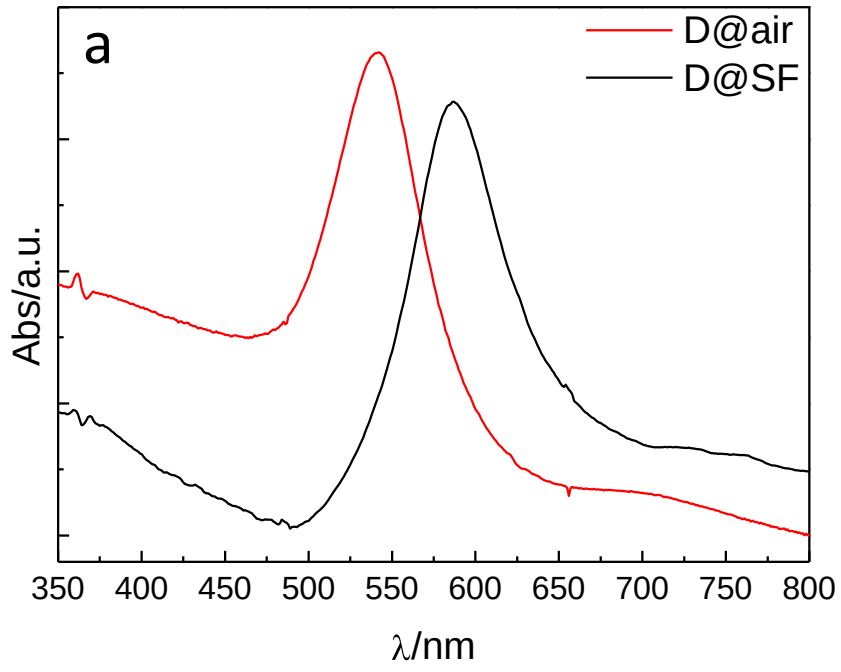

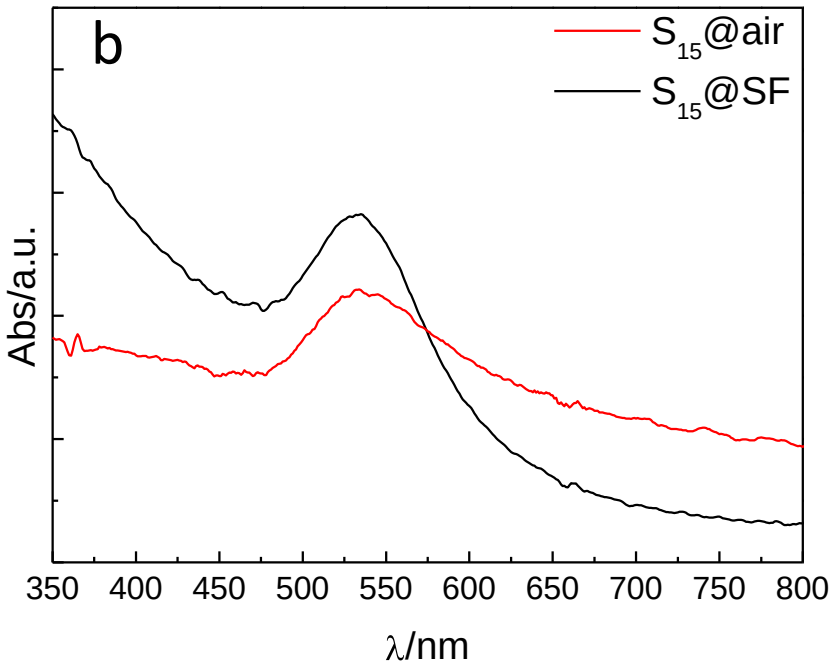

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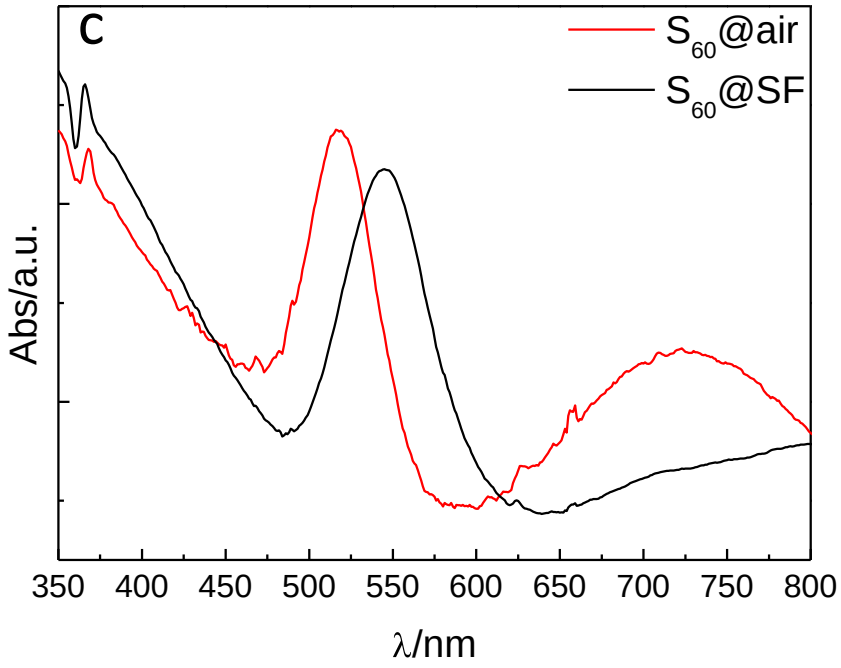

Figure S1. UV-visible spectra of Au decahedra (**a**), spheres of 15 nm diameter (**b**), and spheres of 60 nm diameter (**c**) deposited on top of a glass before and after coverage with mesoporous silica thin films.

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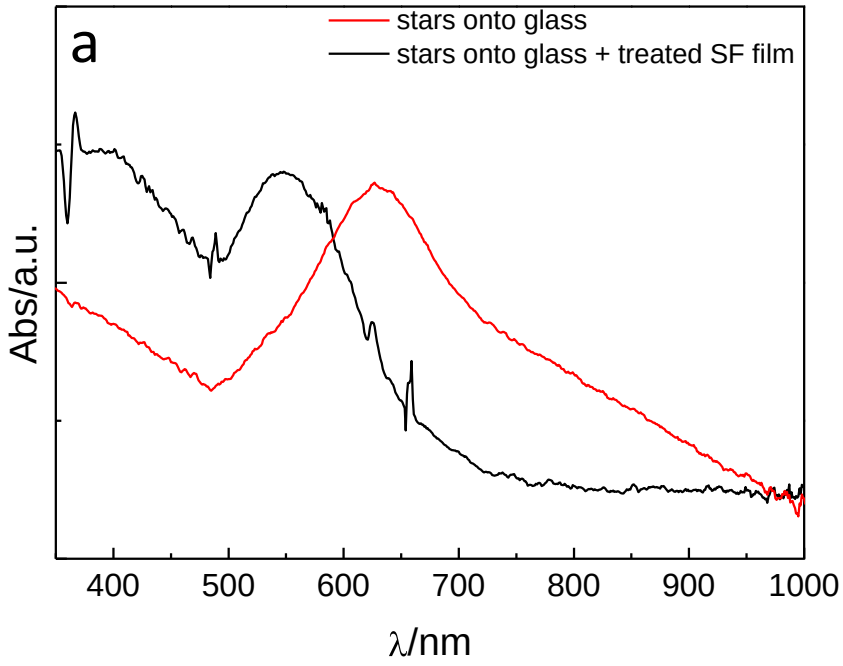

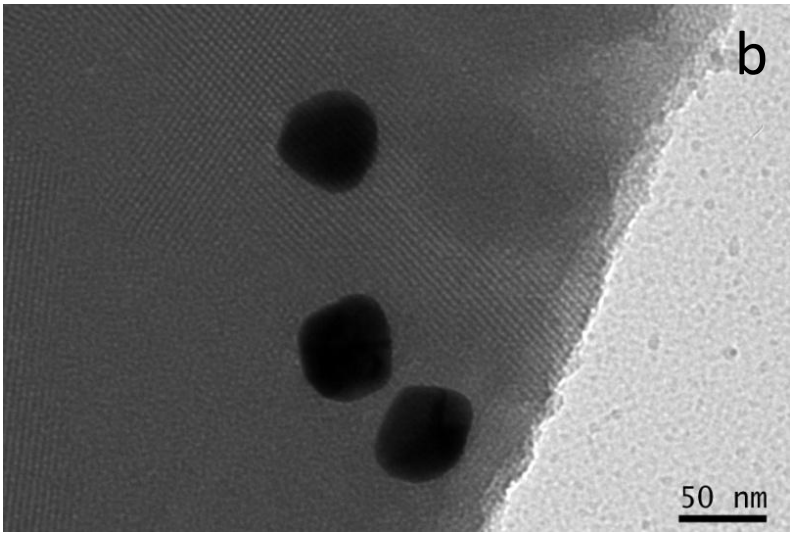

Figure S2. UV-visible-NIR spectra of St@SC sample before the film deposition and after thermal treatment of the film (**a**) and TEM picture after thermal treatment (**b**). Loss of tips is evident in TEM and reflected in the blue-shift of the UV-visible spectrum.

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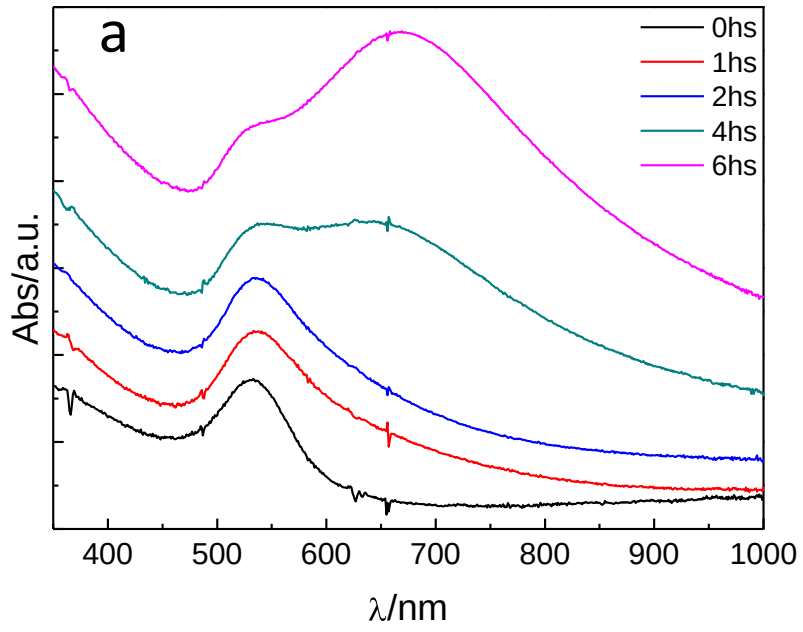

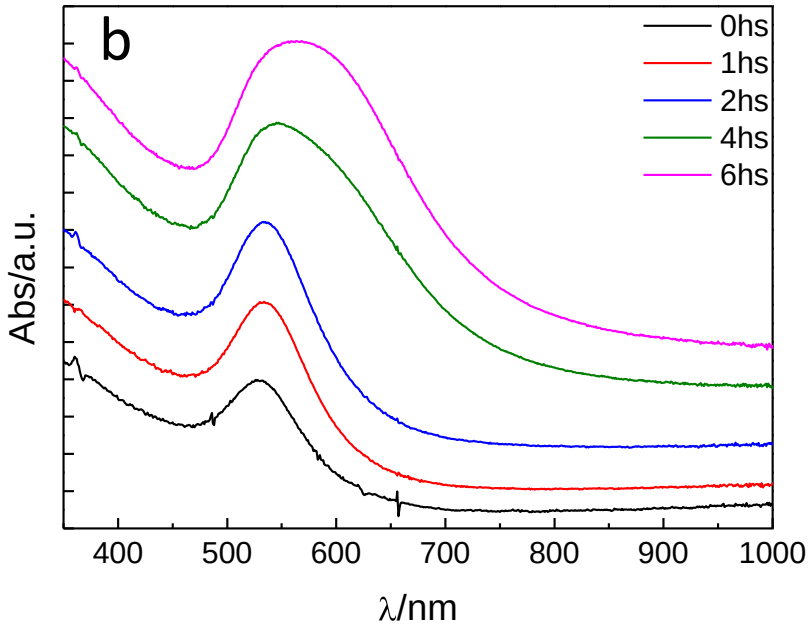

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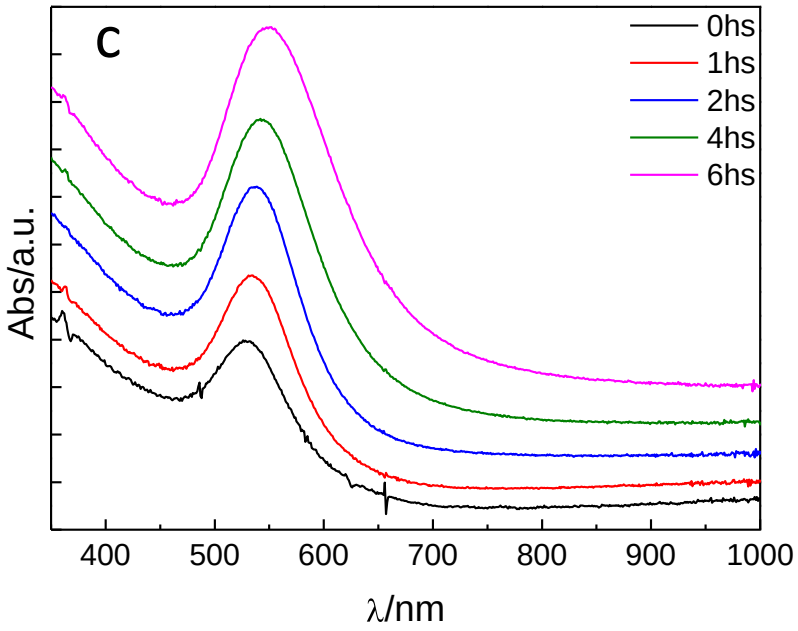

Figure S3. UV-visible-NIR spectra as a function of reaction time for different CTAB:Au molar ratios: 30 (**a**), 240 (**b**) and 800 (**c**). In all the cases, AA:Au = 16. The spectra were shifted vertically to improve visualization.

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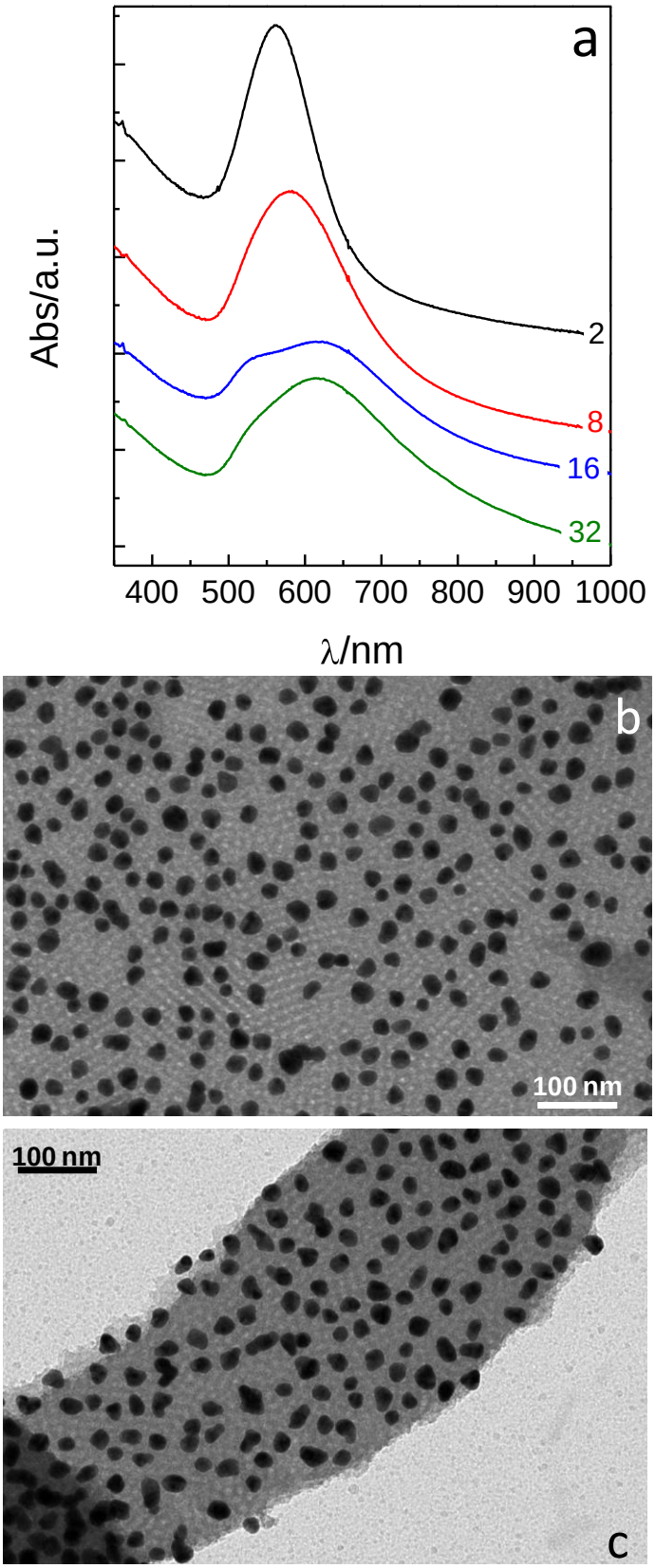

Figure S4. Effect of [AA] variation on the growth of S_{15}@SF with CTAB:Au = 60. (**a**) UV-visible-NIR spectra as a function of AA:Au molar ratio (as indicated in the labels) after 6h of reaction; the spectra were shifted to improve visualization. Representative TEM pictures for the lowest (**b**) and the highest (**c**) [AA].

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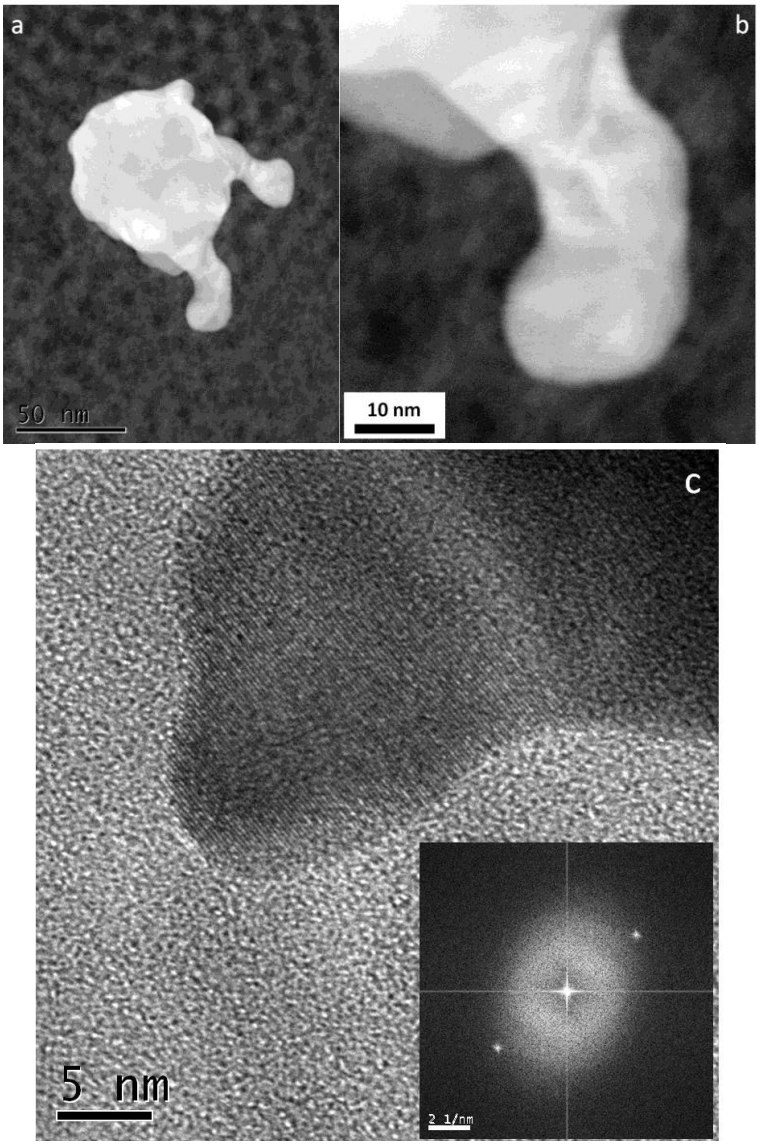

Figure S5. (**a**) STEM DF Image of a GNP from sample S_{60}@SF with particles attached by polyelectrolytes and after 6hs of reaction, (**b**) close up view of the polycrystalline 15 nm wide tip in (**a**). (**c**) HRTEM image of one single-crystal tip showing the Au lattice image. The Fourier transform in the inset confirms the single-crystalline nature of the tip and displays spots with a d_{hkl} of 2.32 Å assigned to (111) Au reflections.

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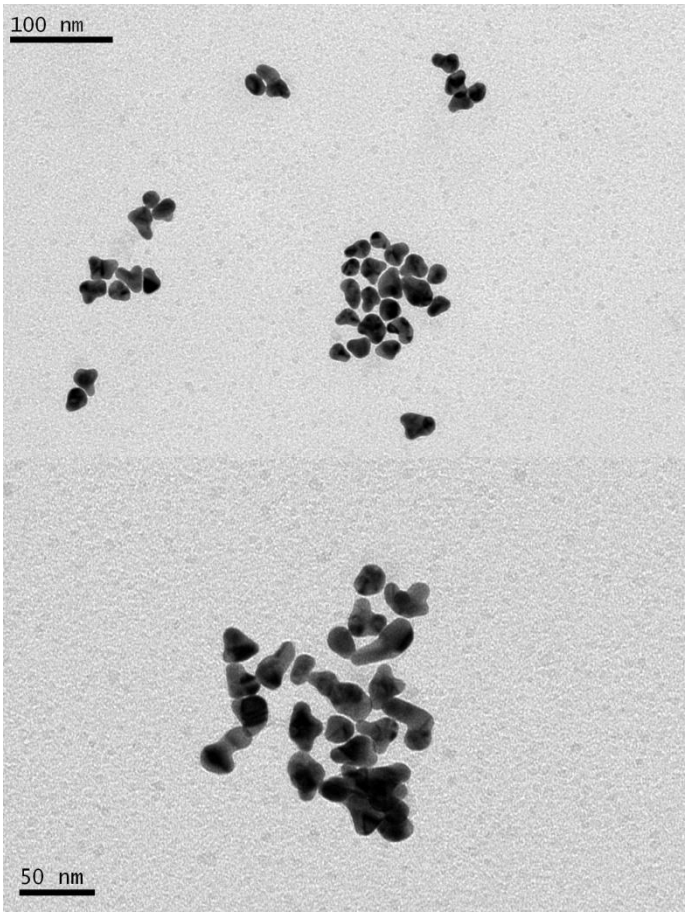

Figure S6. TEM image of particles obtained by dissolution of the SiO_2 matrix (with NaOH solution under sonication) of the sample S_{15}@SF grown for 6h in an Au:CTAB:AA solution with molar ratio 1:60:16.