Controlled Size Manipulation of Free Gold Nanoparticles by Laser Irradiation and Their Facile Bioconjugation.

Vincenzo Amendola and Moreno Meneghetti
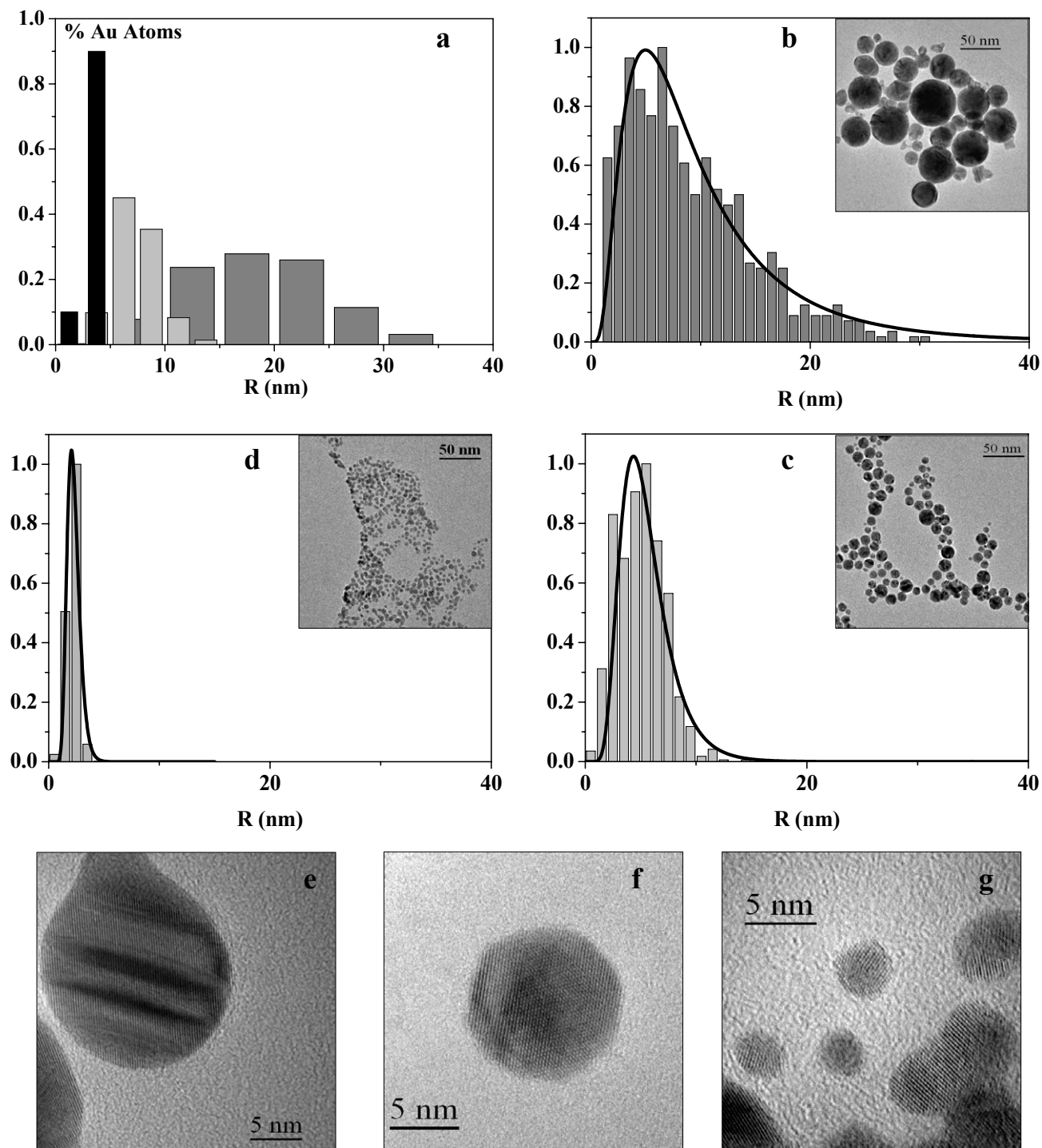
Electronically Supplementary Information

Figure S1. a) Gold *atoms* distributions with respect to particles radii (sample 1: dark grey; sample 2: light grey; sample 3: black) as in fig. 1f but on a linear scale. Gold *nanoparticles* distributions and the relative Log – Normal fittings are reported for sample 1 (b), sample 2 (c) and sample 3 (d). High resolution TEM images are reported for sample 1 (e), sample 2 (f) and sample 3 (g). Further details are reported in Table S1.

Table S1: Average radii (R) with relative root mean square distribution, radii corresponding to average volumes (R_V), the center R_{LN} and the width w of the Log – Normal curves used for fitting the size distribution of the AuNP samples (see fig. S1 b, c, d).

AuNP Sample	*R (R_V)/nm*	*Standard deviation*	R_{LN}/nm	*w*
Sample 1 (Size Reduction)	9 (12)	64 %	8	0.7
Sample 2 (Size Reduction)	5 (6)	41 %	5	0.4
Sample 3 (Size Reduction)	2.2 (2.3)	22 %	2.2	0.25
AuNP in H_2O before Size Increase	9 (12)	64 %	8	0.7
AuNP in H_2O after Size Increase	13 (19)	76 %	10	0.8
AuNP in DMSO before Size Increase	3 (4)	55%	3	0.4
AuNP in DMSO after Size Increase	15 (25)	88%	10	0.5

Table S2: Solutions for size increase experiments. The AuNP solution used for the experiments had an SPA absorbance of 0.53 in a 2 mm cell. Aggregation parameter was defined as the ratio of the absorbance at 750 nm over that of the SPA.

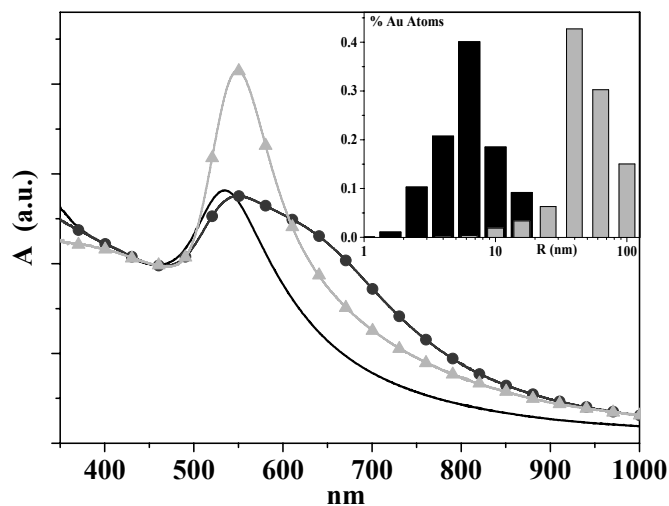| AuNP in H_2O	THF	KCl 0.19 M in H_2O	AGGREGATION PARAMETER
0.80 ml	0.00 ml	75 µl	0.07
0.80 ml	0.15 ml	35 µl	0.27
0.80 ml	0.30 ml	35 µl	0.33
0.80 ml	0.40 ml	35 µl	0.42
0.80 ml	0.15 ml	50 µl	0.50
0.80 ml	0.40 ml	50 µl	0.58
0.80 ml	0.30 ml	75 µl	0.66
0.80 ml	0.40 ml	75 µl	0.71

Figure S2. UV – Vis spectra of the AuNP solution in DMSO as synthesized (black line), after 48 hours ageing (black circles) and after 90 minutes of laser irradiation at 532 nm (grey triangles). Inset shows the gold atoms distributions with respect to particles radii for the as synthesized solution (black) and the irradiated solution (grey). All UV – Vis spectra are normalized at 450 nm for clarity of visualization and the initial solution showed an SPA absorbance of 0.085 in a 2 mm cell.
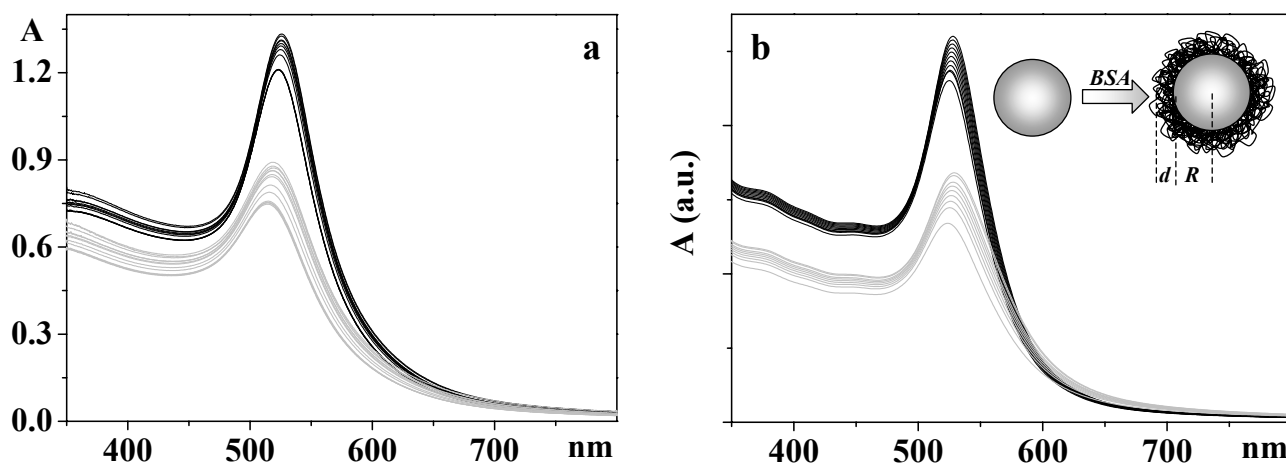

Figure S3. a) UV – Vis spectra of solution 1 (grey lines) and solution 2 (black lines) for different BSA:AuNP ratio. The red shift of SPA and the increase of SPA absorbance with increasing BSA:AuNP ratio are clearly visible for the two solutions. b) Simulation within the Mie theory for core@shell Au@BSA particles in water. Grey lines: gold core radius 4.5 nm; black lines: gold core radius 14.6 nm. Shell thickness d variable between 0 and 2 nm (0.2 nm steps) and with a refraction index n = 1.5.