Supplementary Information (SI) for Soft Matter.

Supporting information

Nanoparticle Superlattice with C14 Frank-Kasper Structure Formed by Highly Monodisperse One-Size Gold Nanoparticles in Suspension

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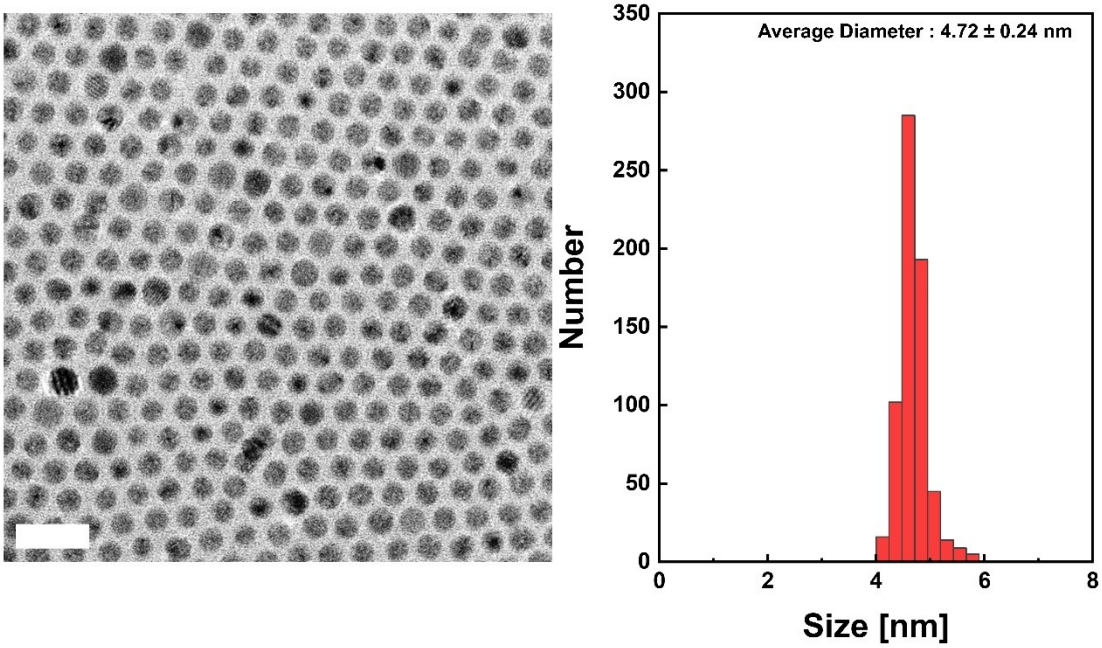

Figure. S1. TEM image (left) and size distribution (right) of 4.7 nm AuNPs. The scale bar in TEM image is 10 nm.

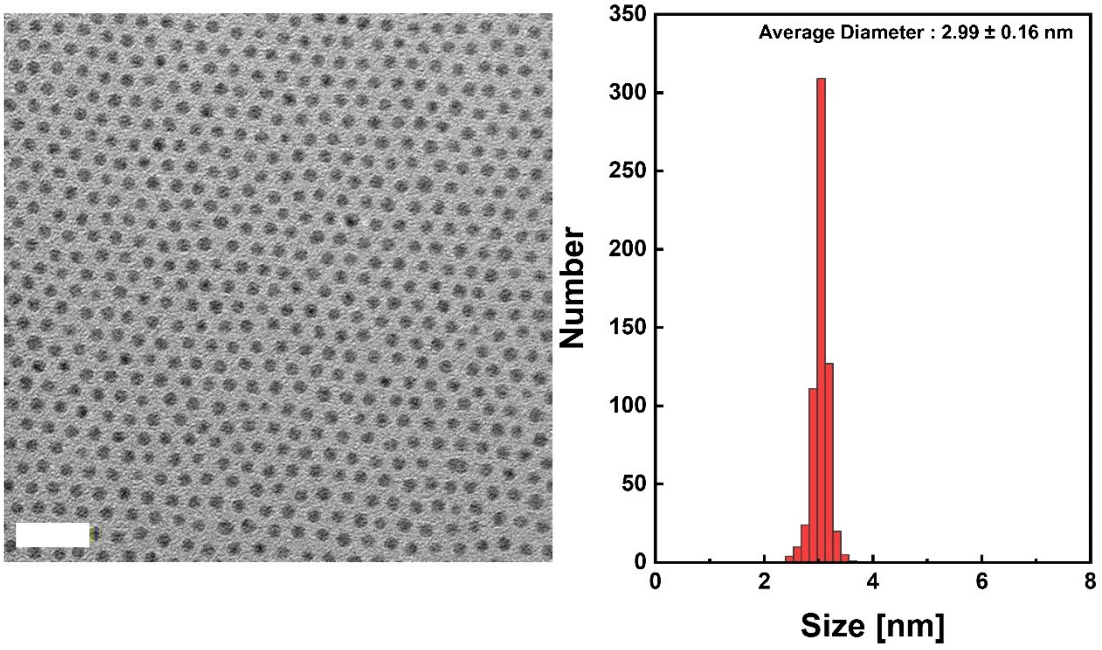

Figure. S2. TEM image (left) and size distribution (right) of 3.0 nm AuNPs. The scale bar in TEM image is 10 nm.

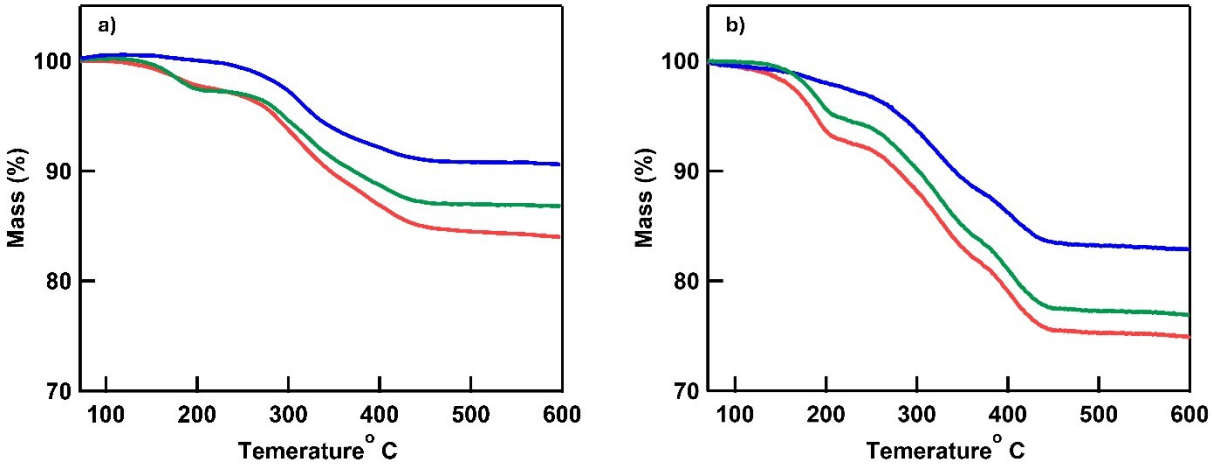

Figure. S3. TGA measurements of AuNPs for different ligand coverage. Mass loss % of (a) 4.7 nm AuNPs and (b) 3.0 nm AuNPs for which the ligand coverage is high (red), medium (green), and low (blue).

The step-like decrease in mass at around 200 °C for AuNPs with high and medium ligand coverage may be due to the presence of free or loosely bound OAm. Similar behavior of the TGA curve was observed for oleic acid-capped iron oxide nanoparticles (Fe_3O_4), which was attributed to the presence of free or loosely bound oleic acid molecules.[1] Recently, it has been reported that when excessive free OAm molecules are present, bilayers of OAm are formed on the surface of Au nanowires (dispersed in n-hexane and OAm mixture), resulting in the surface-to-surface distance between the nanowires which is three to four times the OAm length.[2–4] In our case, however, the surface-to-surface distance between AuNPs is similar to or less than twice the length of OAm molecules, as shown in Tables S1 and S2. This indicates that the monolayers of OAm are formed on the surface of AuNPs, suggesting that excessive free OAm molecules are not present in our system (with high and medium ligand coverage). Therefore, the step-like decrease in mass at around 200 °C for AuNPs with high and medium ligand coverage may be due to the presence of loosely bound OAm. This may also explain the relatively high ligand coverage of AuNPs (up to 7.2 nm^{-2}) which were washed one time. When AuNPs are washed three times, the loosely bound OAm are removed and the step-like decrease in mass at around 200 °C disappears.

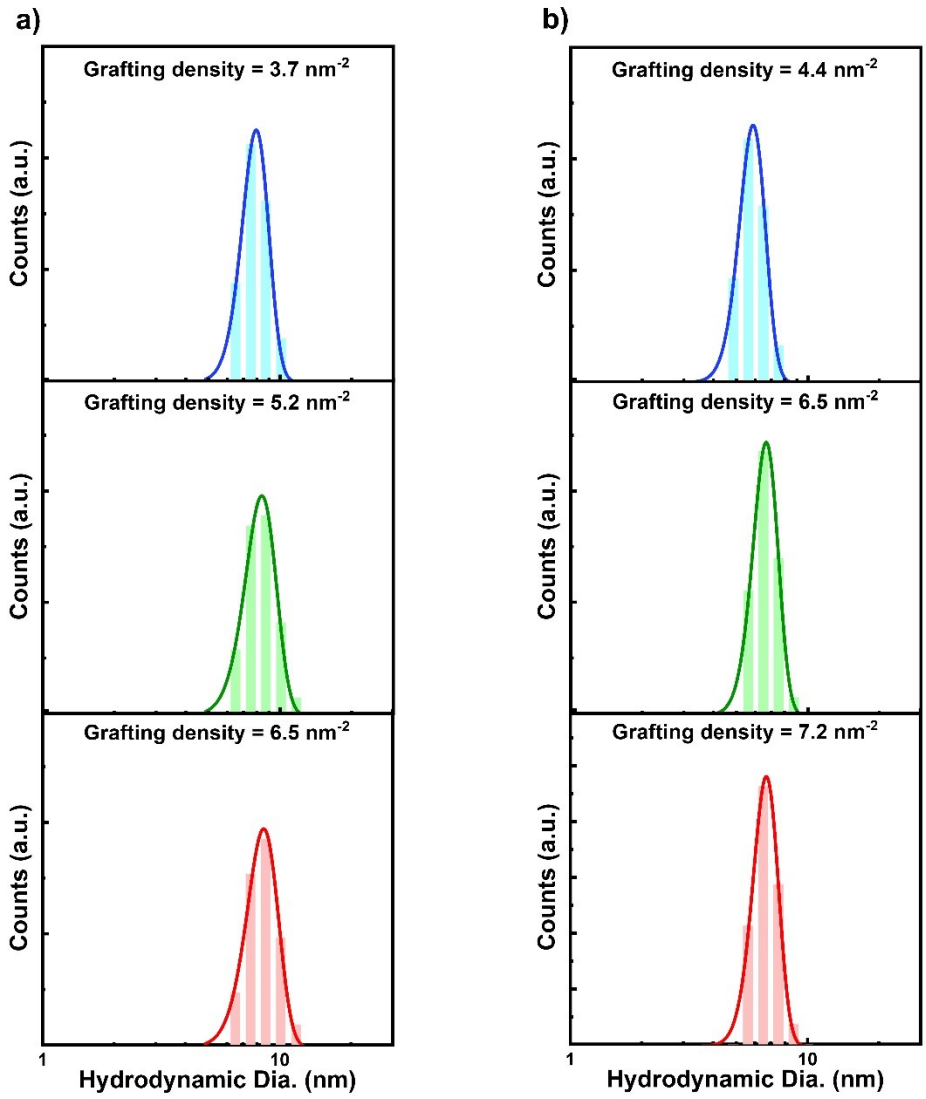

Figure. S4. DLS measurements of Hydrodynamic diameters for AuNPs with different ligand grafting densities for (a) 4.7 nm and (b) 3.0 nm AuNPs

Table S1. SAXS measurements summary of lattice parameters and domain sizes of NPSLs made of 4.7 nm AuNPs at different volume fractions.

Volume fraction	**20 v.v%**		**30 v.v%**	
Space group	$P6_3/mmc$	$Fm\bar{3}m$	$P6_3/mmc$	$Fm\bar{3}m$
Superlattice symmetry	hcp	fcc	hcp	fcc
Lattice parameter a [nm]	8.53	11.32	8.42	11.12
Lattice parameter c [nm]	13.79		13.53	
Lattice parameter ratio c/a	1.62		1.61	
Interparticle distance ***d*** [nm]	8.53	8.00	8.42	7.86
Surface-to-surface distance ***S*** [nm]	3.83	3.30	3.72	3.16
Domain size [μm]	1.37	1.23	1.61	1.17

Table S2. SAXS measurements summary of lattice parameters and domain sizes of NPSLs made of 3.0 nm AuNPs at different volume fractions.

Volume fraction	**20 v.v%**		**30 v.v%**	
Space group	$P6_3/mmc$	$Fm\bar{3}m$	$P6_3/mmc$	$Fm\bar{3}m$
Superlattice symmetry	C14	fcc	C14	fcc
Lattice parameter a [nm]	10.90	8.47	10.96	8.49
Lattice parameter c [nm]	17.92		17.83	
Lattice parameter ratio c/a	1.64		1.63	
Interparticle distance ***d*** [nm]	5.45	5.99	5.48	6.00
Surface-to-surface distance ***S*** [nm]	2.45	2.99	2.48	3.00
Domain size [μm]	1.66	1.56	2.02	2.22

Table S3. TGA measurements results of 4.7 nm AuNPs and 3.0 nm AuNPs at different ligand coverage conditions.

Ligand coverage	Mass loss (wt%)		Ligand grafting density [nm^{-2}]	
	4.7nm	**3.0nm**	**4.7nm**	**3.0nm**
High	16.1	25.0	6.5	7.2
Medium	13.3	23.1	5.2	6.5
Low	9.7	16.9	3.7	4.4

Table S4. Lattice constants and interparticle distances of NPSL with fcc symmetry made of 4.7 and 3.0 nm AuNPs at 30 v.v% with different ligand grafting densities.

Diameter of AuNP [nm]	Ligand grafting density [nm^{-2}]	fcc lattice parameter (a) [nm]	fcc interparticle distance (d) [nm]
4.7	6.5	11.12	7.86
	5.2	11.00	7.78
	3.7	10.51	7.43
3.0	7.2	8.49	6.00
	6.5	8.09	5.72
	4.4	7.96	5.63

Table S5. DLS measurements of Hydrodynamic diameters for 4.7 nm and 3.0 nm AuNPs with different grafting densities

Diameter of AuNP [nm]	Ligand grafting density [nm^{-2}]	Hydrodynamic diameter [nm]
4.7	6.5	8.5
	5.2	8.3
	3.7	7.9
3.0	7.2	6.7
	6.5	6.5
	4.4	5.9

References

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