**Electronic Supplementary Information** 

## Rational design and observation of the tight interface between graphene and ligand protected nanocrystals

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**Text S1. Density Functional Theory (DFT) Calculation of Amine-Stabilized Ag Nanocrystals** In colloidal nanocrystal synthesis, different types of surface ligands are used to stabilize reactive particle surfaces. Lewis basic oxygen in 1-ethyl-2-pyrrolidone is well-known functional group that shows a strong binding affinity to metal surfaces.<sup>1</sup> Another example is amine functionalized organic surface ligands.<sup>2–5</sup> We calculate the surface binding energy between methylamine and Ag surface (blue triangles in Fig. 1a and Fig. S1), and compare the energy with the binding energy between graphene and Ag surface (the optimized surface geometries of methylamine on Ag surface can be found in Fig. S2). Notably, we observe the similar behavior in the binding energy of methylamine to Ag(111) surface as a function of surface coverage. Likewise, the crossover by the binding energy of the graphene occurs at the surface coverage of  $0.012 / Å^2$  which coincides with the critical value calculated from PVP monomers. Our theoretical results suggest that it is worth evaluating binding energies of various types of surface ligands commonly used in nanocrystal synthesis before designing heterostructures to accomplish rational control of the interface between constituent materials.



**Fig. S1** DFT calculation on the binding energy of surface ligand and graphene to Ag nanocrystal surface. Calculated surface binding energy of the functional groups on (100) and (111) facets of an Ag nanocrystal as a function of the density of surface binding groups from LDA+D2 calculations. (black square: PVP on Ag(100); red circle: PVP on Ag(111); blue triangle: methylamine on Ag(111); black dash: graphene on Ag)



**Fig. S2** Optimized geometries of methylamine on (111) facets of an Ag nanocrystal. Tilted view of multiple binding groups and magnified projection view on (111) Ag surfaces are shown on top and bottom images, respectively.



**Fig. S3** Structure of graphene. (a) An aberration-corrected high-resolution TEM image of the multi-layer graphene. (b) Electron diffraction pattern of the graphene.



**Fig. S4** TEM image of the interface between  $SiO_2$  particles and the graphene sheet. Since  $SiO_2$  particle possess no surface capping ligands, the graphene sheet readily forms the tight interface.



**Fig. S5** Low magnification TEM image of a PVP-passivated Ag nanocrystal with graphene in the presence of high concentration of PVP ligands.



**Fig. S6** Low magnification TEM image of graphene blister formed by covering graphene sheet with 4 to 5 layers over the adsorbed Ag nanocrystal.

## References

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