Aqueous supracolloidal assembly of gold nanoparticles guided by hydrophilic triblock copolymers

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Well-defined clusters of gold nanoparticles (AuNPs) have attracted considerable interest due to their remarkable plasmonic, optical and electronic properties. However, unlike conventional 3D colloidal assemblies, controlling the assembling of a limited number of isotropic AuNPs into anisotropic 1D or 2D structures in aqueous suspension remains highly challenging [1] . Such assemblies are particularly attractive for biomedical applications, including sensing, imaging, photothermal therapy or as SERS enhancer... While molecular recognition strategies [2] and approaches based on multivalent ions [3] have been explored, simple and efficient methods to precisely control assembly dimensionality, morphology, and interparticle distance are still lacking.
Here, we introduce a versatile strategy based on the surface functionalization of AuNPs with fully hydrophilic triblock copolymers. These copolymers consist of a central poly(acrylic acid) block that electrostatically adsorbs onto the cationic surface of AuNPs and two external neutral blocks (a poly(ethylene oxide) (PEO) derivative block, and a polyacrylamide (PAM)) that form a stabilizing corona around AuNPs. Importantly, the intrinsic incompatibility between the neutral blocks induces nanoscale phase segregation whithin the corona. This feature is exploited to trigger controlled self-assembly of nanoparticles via selective insolubilization of one of the neutral blocks under external *stimuli* . Specifically, the PEO-based block is selectively insolubilized through non-covalent cross-linking with silica [4] , while the PAM block is selectively collapsed upon addition of a poor solvent. These orthogonal triggers enable precise control over nanoparticle assembly pathways.
The resulting colloidal assemblies were characterized by DLS, UV-visible spectroscopy, cryo-TEM and SAXS. TEM also allowed observing the assembly morphologies on surface after solvent evaporation. A strong dependence of the assembly process morphology was observed on both the copolymer architecture and the AuNPs intrinsic properties. Notably, anisotropic particles (nanorods) exhibit enhanced assembly in suspension, forming either tip-to-tip or side-by-side structures, depending on the applied *stimulus* [figure]. Furthermore, the presence of negatively charged chain ends enables additional control through complexation with multivalent cations, yielding assemblies with increased interparticle spacing.
Overall, this approach provides a simple and modular route to tune the structure of AuNP assemblies in aqueous media, opening new opportunities for plasmonic and biomedical applications.

Keywords:
stimuli-responsive assemblies, steric stabilization by copolymer adsorption, plasmonic properties

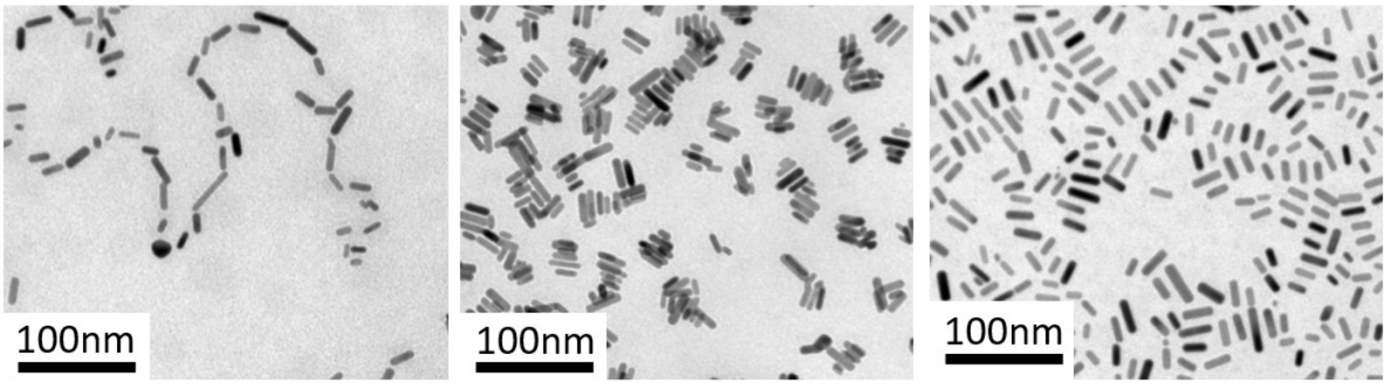

Figure: TEM images of different directional assemblies of AuNP@copolymer suspensions

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