Self-assembly of PEGylated Gold Nanoparticles with Satellite Structures as Seeds†

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We report a very simple method for the self-assembly of spherical gold nanoparticles (AuNPs), coated with poly(ethylene glycol) (PEG), through a slow evaporation process at room temperature. Clusters of particles forming satellite structures may act as seeds for the self-assembly in a crystallization-like process. Based on the transmission electron microscopy (TEM) images obtained a mechanism for the self-assembly was suggested.

The investigation of nanocrystal superlattices has become a rapidly developing field,^{1, 2} leading to a wide range of applications, such as conductive coatings,³ electronic devices,⁴ and sensors.⁵ Ordered assemblies of AuNPs, one of the most studied metallic nanomaterials with applications in electronics, catalysis and medicine,⁶ are no exception. Self-organization of NPs generates a variety of structures in one,⁷ two,⁸ or three dimensions,⁹ and can be achieved via different strategies,¹⁰ including: (i) solution-based self-assembly of heterogeneous NPs¹¹; (ii) self-assembly using templates;¹² (iii) assisted self-assembly with an electric¹³ or magnetic¹⁴ field or light;¹⁵ (iv) self-assembly at an interface.^{3, 16} Some biomolecules such as DNA has been extensively used to functionalize AuNPs and drive their assembly in solution via hybridization of complementary strands.^{17, 18} Unfortunately, its use is expensive and not readily accessible. Polymer grafting is a common alternative.¹⁹ Lately, the solvent evaporation method has drawn a considerable attention as an easy process to create self-assembled nanostructures.¹¹ Herein we report a very simple method to self-assemble PEGylated AuNPs (AuNPs@PEG) via a slow evaporation process. To our knowledge, this is the first time that PEG alone is used to manipulate the self-assembly of NPs. PEG is one of the most common polymers. Its structure is quite simple and controllable. Thanks to its advantageous properties such as

Fig. 1. TEM images of (a) AuNPs@PEG0.8k, (b) AuNPs@PEG2k and (c) AuNPs@PEG6k (scale bar 100 nm) with one representative satellite structure shown in their respective insets (scale bar 20 nm). (d) Particle size distribution of the satellite structures in AuNPs@PEG6k via TEM image analysis.

particle stabilization and degradability it is used for various applications in industries and research for paints formulations,²⁰ polymeric membranes²¹ and also in biomedical fields for its known biocompatibility and serum stability.²²

AuNPs@PEG were obtained via citrate reduction of gold salts followed by functionalization with thiolated PEG (see ESI). All the AuNPs@PEG displayed an absorption band around 522–524 nm, slightly higher than the unmodified AuNPs of this diameter.²³ This red shift suggested the successful functionalisation, which was further confirmed by dynamic light scattering (DLS) results, showing the increase of hydrodynamic diameter from 11.4±2.8 nm for the citrate-coated AuNPs to 38.3±0.8, 44.1±5.0 and 45.2±1.2 nm for the AuNPs@PEG0.8k, AuNPs@PEG2k and AuNPs@PEG6k respectively, and also the increase of zeta potential from -36.6±1.0 mV for the citrate-coated AuNPs to -28.1±1.0, -33.4±1.4 and -21.1±2.0 mV for the AuNPs@PEG0.8k, AuNPs@

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Table 1 Characteristics of the satellites structures and the polymer layer

PEG Mw [g mol ⁻¹]	% Satellite Structures ^[a]	$N_{\text{layer}}/N_{\text{core}}$ ^[b]	$d_{\text{layer}}/d_{\text{core}}$ ^[c]	R_F [nm] ^[d]	L_{DLS} [nm] ^[e]	σ_{Ellman} [chain nm ⁻²] ^[f]	D [nm] ^[g]
0.8k	51	6.4	0.8±0.4	2.0	13.5±2.8	1.54±0.01	0.31±0.43
2k	54	6.0	1.0±0.4	3.4	16.3±3.9	1.07±0.02	1.09±0.00
6k	85	6.8	0.6±0.2	6.6	16.9±1.8	0.55±0.01	1.52±0.01

[a] Percentage of the number of NPs present in all the satellite structures relative to the total number of NPs present in the self-assembly. [b] Ratio of the number of layer NPs and the number of core NPs. [c] Ratio of the diameter of the layer NPs and the diameter of the core NPs. [d] Flory radius. [e] Calculated layer thickness from the DLS and TEM data. [f] PEG grafting density calculated via the Ellman's assay. [g] Calculated distance between PEG attachments on the AuNP surface.

PEG2k, and AuNPs@PEG6k respectively. Fig. 1 shows the AuNPs in approximately spherical shape with a mean diameter of 12.2±2.2, 11.3±2.2, and 12.7±2.6 nm for AuNPs@PEG0.8k, AuNPs@PEG2k, and AuNPs@PEG6k respectively, close to that of AuNPs determined via TEM image analysis (11.4±2.8 nm) (Figs. S1–S2†) and via the Haiss method²⁴ (14.1 nm) (Fig. S3†) since the polymer layer was not easily discernible under TEM due to its relatively low electron density compared to gold. Organized, close-packed structures of AuNPs@PEG were observed with PEGs of three different chain lengths. The most commonly reported self-assembled patterns of nanospheres are hexagonal, nanoring and chain structures.²⁵ Herein, “satellite” structures, composed of a single NP in the center (“core nanoparticle”) and other NPs surrounding it (“layer nanoparticles”), could be reproducibly distinguished in the assemblies (Fig. 1) with a higher proportion for the AuNPs@PEG6k (85%) than for the AuNPs@PEG2k (54%) and the AuNPs@PEG0.8k (51%) (Table 1, Fig. S4†). This was consistently observed in different samples. It was demonstrated that the longer PEG chain could facilitate the more controlled assembly, probably due to its higher flexibility. This hypothesis is validated by the report of Nykypanchuk *et al.* where 3D crystalline assemblies were formed by the AuNPs functionalized with DNA strands with long and flexible spacers, whilst amorphous systems were obtained when rigid spacers were used. The core NPs showed in general, a larger diameter than the layer NPs (Fig. 1d), and there were 6 to 8 layer NPs surrounding every single core NP (Fig. S5†). 6 being the highest number of non-overlapping, equal-diameter spheres that can be arranged such that they all touch a central sphere of the same diameter. Mirkin and co-workers reported the formation of satellite structures of DNA-functionalized AuNPs from binary mixtures of AuNPs: 31-nm core NP surrounded by 8-nm NPs¹⁸. Here the satellite structures were formed by one AuNPs population coated with a single chain-length PEG. There was no significant change in the plasmonic properties of the AuNPs@PEG solutions (Figs. S3 and S6†) indicating that the self-assembly occurred essentially during the evaporation process as previously reported.^{9, 25, 26}

Ming *et al.* reported that a minimum amount of ligand was required for the self-assembly of cetyl trimethylammonium bromide (CTAB)-coated gold nanorods (AuNRs), which was attributed to the amount needed to form a bilayer on the AuNR surface. Furthermore, Xiao *et al.* demonstrated that an excess amount of CTAB led to the crystallization of the surfactant and the inhibition of the self-assembly. Herein, a

Fig. 2. TEM images of (a) AuNPs@PEG2k under defocused conditions (scale bar 50 nm) and (b) representative satellite structure in the AuNPs@PEG2k assembly under defocused conditions (scale bar 20 nm).

specific range of coating densities of PEG is required for self-assembly of the negatively charged AuNPs through the balance between attractive forces (e.g. Van der Waals, hydrodynamic and capillary forces) and repulsive forces (e.g. steric hindrance and electrostatic repulsion). It was found that a low PEG grafting density favored the cluster formation; whereas a high density limited the assembly. The assemblies reported herein concern the AuNPs coated with an amount of PEG below the saturation density but sufficient for stabilization in different buffer solutions at different pHs (Figs. S6–S8† and Table 1). The minimum grafting density required decreases with increasing chain length due to interchain steric interactions.²⁷ TEM images under defocused conditions show that the distribution of the PEG chains was not homogeneous on the NPs surface but organized as “molecular bundles” (Fig. 2), which has been reported for the alkanethiol chains with truncated octahedral silver NPs by Wang *et al.* and with non-perfectly spherical AuNPs by Stoeva *et al.*³³ The average distance between the chains on the surface (Table 1 and ESI) was much smaller than R_F , the Flory radius, (Table 1) indicating that the PEG chains adopted a brush conformation (Table S1, Figs. S9–S10†) possibly since (i) water is a good solvent for PEG and (ii) the single covalent Au–S bond formed enables a stretched conformation²⁷. This implies that the driving force for grafting, the Au–S covalent bond, is superior to the lateral interactions between polymer chains in solution²⁹. The brush conformation can be altered during the assembly process. In the inset of Fig. 1b, the average distance between the AuNPs@PEG2k was about 8 nm between two layer NPs and 6 nm between a core and a layer NP suggesting that the latter had a stronger interaction force. For PEG2k, the Flory radius R_F is 3.4 nm, the PEG chain lengths in helical and zigzag conformations are ~12 and ~16 nm respectively³⁰ and

Fig. 3. Multilayer assembly of the AuNPs@PEG showing apparent (a) chain-like structures in AuNPs@PEG6k (scale bar 50 nm) and (b) a Moiré pattern in AuNPs@PEG2k (scale bar 20 nm).

the chain length L_{DLS} measured via DLS was ~ 16 nm (Table 1). Sau and Murphy²⁵ suggested two types of interactions between the CTAB-coated gold nanocrystals (NCs) depending on the interparticle distance: interdigitation of the hydrophobic CTAB chains from adjacent NCs with distance smaller than two chain lengths, or sharing of a layer of counterions for larger inter-NC spacings. Here, the PEG chains could probably interpenetrate²⁹ causing interchain interactions. However, the spacing between the AuNPs being much lower than the length of an extended PEG chain either in zigzag or helical conformation, the chains should be strongly encompassed and forced to lie on the surface. Similar observations were obtained for the other two PEGs. Thus, PEG greatly influences the assembly process. PEG is flexible, hydrophilic and uncharged; furthermore it can entangle several water molecules per oxyethylene unit via hydrogen bonding. Depending on the number of hydrogen bonds formed per water molecule, linking neighboring oxyethylene units and creating the so-called “water-bridges”, the PEG conformation will change from helical to zigzag³⁰. Hence the evaporation process influences the assembly in two ways: (i) with increasing the AuNPs@PEG concentration the interparticle distance decreases thus increasing the interparticle interaction; and (ii) “breaking the water bridges” within the PEG structure hence modifying the chain conformation and affecting the interchain interaction. The self-assembly did occur not only on the plane (side-by-side) but also on top of the NPs starting to form 3D structures as validated by the formation of apparent “chain-like” structures (Fig. 3a) and Moiré patterns¹ (Fig. 3b) usually observed when two organized self-assembled layers are stacked one on the other with different directions giving a misleading impression of contact, unlikely due to steric interactions.

During the process of evaporation of a droplet of colloidal solution, water is progressively changed into vapor and the concentration of NPs in the solution increases, especially at the gas-liquid-solid interface. Driven by the water evaporation a counter water influx, the pinning force,³¹ brings the NPs in contact with the substrate where the interparticle distance decreases, leading to particle-particle interaction and more creation of ordered self-assemblies. As the evaporation continues more NPs are carried to the edge of the drop until forming a “coffee-ring” pattern³². This simple way to produce

Fig. 4. Schematic of the suggested self-assembly mechanism during the slow evaporation process on a carbon-coated grid.

organized nanostructures is now widely recognized. The factors influencing the assembly include the NP morphology and size, the ligand type and length, and the evaporation rate.²⁶ Here, once a first layer of the NPs was formed around the central core of relatively larger size creating a satellite structure, other NPs came closer around it. This was repeated until reaching the layer NPs of another satellite or until no NP was close enough to be driven by the hydrodynamic forces. Simultaneously a 3D structure can be formed with the attraction of the AuNPs@PEG in the above solution which superimposed to the first layer (Fig. 4). Self-assemblies were observed all over the grid with multilayers in their centers (Figs. 1a-c), suggesting that the self-assembly process did not exactly follow the typical droplet evaporation process. The substrate nature and the interparticle interaction seem to be key factors to counteract the pinning force driving the particles to the contact line. First, the hydrophobicity of the partial carbon film on the TEM grid may play a role since during the evaporation of a droplet of colloidal solution on a hydrophobic surface, agglomerated particles are formed in the center.³³ Second, if the interparticle attraction force is strong enough the assembly far from the contact line is possible. Yunker *et al.* noted that addition of ellipsoids to a sphere suspension could

inhibit the “coffee-ring” effect via alteration of the surface tension. Herein the adsorption of larger, non-perfectly spherical particles with a faceted distribution of ligands could deform the surface and counteract the pinning force. The larger core NPs may act as a nucleus for the self-assembly like a nucleation step during crystallization and the polydispersity of the sample would be compulsory to start the assembly process. Ohara *et al.* studied the crystallization of alkanethiolated AuNPs in hexane and claimed that the larger NPs, even at very low concentration (2%), served as seeds for the further crystallization. They observed size segregation in their TEM images with larger NPs surrounded by smaller NPs and suggested that the self-assembly was driven by size-dependent Van der Waals forces with a final order corresponding to the system with the lowest energy level. The main driven forces of the assembly process are believed to be the hydrodynamic forces during evaporation (pinning force), the capillary forces when the NPs started to protrude from water, the interactions between the PEG coatings of different AuNPs (steric hindrance) or between the PEG chains (interdigitation influence) but also between the remaining citrate molecules (electrostatic repulsion) and between the NP cores (Van der Waals forces) when the AuNPs are close enough according to the DLVO theory. Ming *et al.* reported the formation of the organized assemblies of the CTAB-coated AuNPs within an area of 0.1–0.8 mm², whereas the self-assemblies reported here occupied an area of ~0.1–1 μm². Those short-range assemblies could be optimized for a specific purpose by varying initial sample volumes and/or concentrations and using different substrates. The process of self-assembly would require further studies to obtain more ordered structures. Templates could also be considered to increase the range of assembly.

In summary, the self-assembled AuNPs@PEG were formed reproducibly using a very simple method. Satellite structures were observed with PEGs of three different chain lengths and comprised up to ~85% of the self-assemblies. Acting as seeds their formation enables the further growth of the colloidal crystal, or self-assembly of the functionalized nanoparticles via attachment to the primary seeds, in a crystallization-like process. The particle size heterogeneity and the non-perfectly spherical morphology of the AuNPs, leading to a faceted PEG grafting, as well as the chain length play a major role in the assembly. These self-assemblies could provide interesting features for various potential applications including fabrication of electronic devices.

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