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Disk micelles from amphiphilic Janus gold nanoparticles†

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Janus gold nanoparticles are synthesised *via* a simple preparation method and behave as amphiphiles self-assembling in water into disk-shaped micelles.

Self-assembly of inorganic nanoparticles is of great importance for the construction of nanometre-sized objects with optical and/or electrical functionality.¹ A variety of self-assembly strategies have been reported, however, the controlled aggregation in size and shape by simple methods remains a challenge.² An attractive but nearly unexplored method is the use of amphiphiles, *i.e.* particles that have a hydrophobic as well as a hydrophilic part. Gold nanoparticles containing hydrophobic and hydrophilic ligands have been synthesised and when placed at the toluene–water³ or air–water interface⁴ an amphiphilic distribution of the ligands occurs⁵ resulting in so-called Janus particles. Furthermore, amphiphilic gold nanoparticles containing equal amounts of hydrophobic and hydrophilic ligands, synthesised *via* a so-called interfacial engineering method⁶ or decorated with amphiphilic V-shaped block copolymer ligands,⁷ have been dispersed in water yielding micelle-like aggregates and one-dimensional architectures, respectively. Here we present a simple method, in which the ratio of the hydrophilic and hydrophobic ligands can be varied easily, to synthesise amphiphilic nanoparticles that are able to self-assemble in water forming disk-shaped micelles. Micellar disks have been reported so far for *e.g.* perfluorinated surfactants⁸ and block copolymer micelles⁹ or as a transition between vesicles and micellar rods.¹⁰

The amphiphilic nanoparticles, consisting of a gold core covered with both hydrophobic alkyl (C10) and hydrophilic ethyleneoxide (EO4) ligands *via* dithiol linkages (Fig. 1)^{11,12} were synthesised from tetraoctylammonium bromide-capped gold nanoparticles. Exchange of the organic ligands with different molecular ratios of C10 and EO4, yielding particles with C10 : EO4 ratios of 1 : 0, 3 : 1, 1 : 1, 1 : 3 and 0 : 1.¹³ In all cases absorption measurements showed similar spectra with a broad surface plasmon band around 523 nm (Fig. 1). The size of the gold core was 3.7 ± 0.7 nm,

as determined by transmission electron microscopy (TEM, see Fig. 1), which is consistent with the size approximated from the absorption spectra.¹⁴ H-NMR spectroscopy showed that the ligand ratio after exchange was the same as the fed mixture.¹²

The self-assembly was explored by injecting a concentrated THF solution of the nanoparticles into water. The particles with the ligand ratios 1 : 0, 3 : 1 and 1 : 1 (C10 : EO4) did not dissolve in water, probably due to a too high content of hydrophobic ligands. The fully EO4-covered particles dissolved directly in water and showed the same absorption spectrum as found in toluene.¹² Upon injection of the 1 : 3 C10–EO4–Au Janus particles the solution became opalescent, indicating aggregation of the particles into larger structures. Absorption spectroscopy revealed strong scattering of the light in which the surface plasmon band cannot be discerned (Fig. 1). A critical aggregation concentration (CAC) of approximately 0.02 μ M was determined by using pyrene as a polarity probe.^{12,15}

The aggregates in water were characterised by a variety of techniques. Dark-field optical microscopy on a thin film of solutions between two glass plates revealed the presence of round objects with sizes of approximately 0.5 μ m (Fig. 2a). Interestingly, these aggregates organised along scratches in the glass, yielding one-dimensional arrays of spheres.¹² Scanning electron microscopy (SEM) showed disk-shaped aggregates, lying either flat or on their

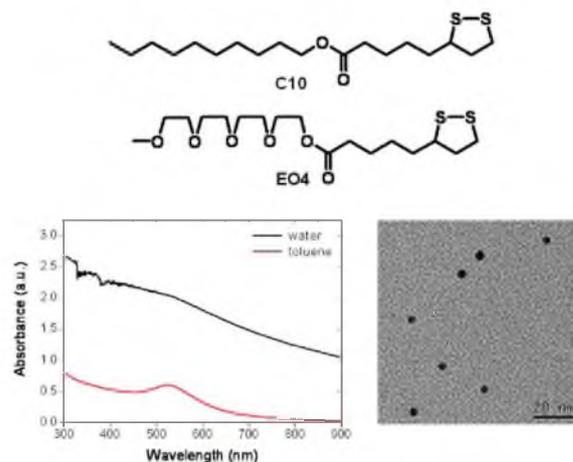


Fig. 1 Top: chemical structure of hydrophobic (C10) and hydrophilic (EO4) sulfur-functionalised ligands for the synthesis of Janus gold nanoparticles. Bottom left: UV-vis absorption spectra of 1 : 3 C10–EO4–Au Janus nanoparticles in toluene (0.6 μ M) and after injection from a tetrahydrofuran solution into water (0.25 μ M). Bottom right: TEM of 1 : 3 C10–EO4–Au Janus nanoparticles deposited from toluene.

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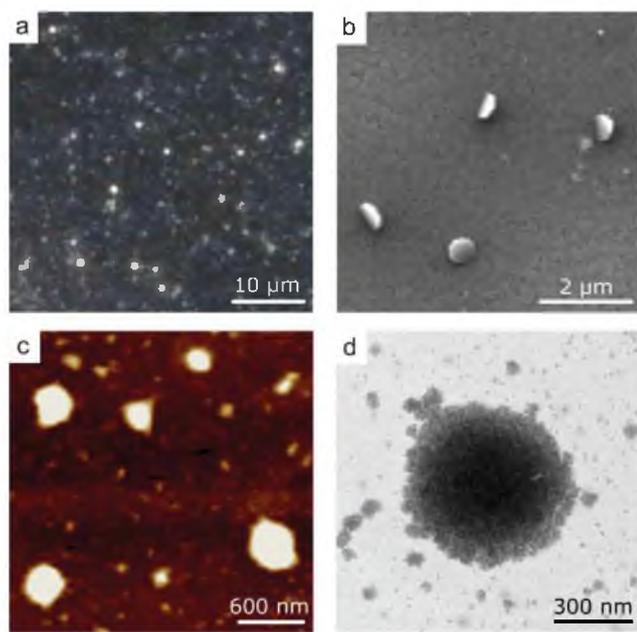


Fig. 2 Microscopy images of disk-shaped aggregates of 1 : 3 **C10-EO4-Au** Janus nanoparticles (0.25 μM in water). (a) Dark-field optical microscopy image of a solution between two glass plates. (b) SEM image of a dried film on indium tin oxide-coated glass. (c) AFM image of a dried film on glass. (d) TEM image of a dried film.

edge on the surface, with an average diameter of $5.3 \pm 0.6 \times 10^2$ nm (Fig. 2b). From atomic force microscopy (AFM) also round objects were identified, which had an average diameter of $4.5 \pm 1.9 \times 10^2$ nm and an average height of 8.5 ± 0.5 nm. Based on the diameter of the gold core (3.7 nm) and the length of the ligands (2.2 nm and 2.5 nm for **C10** and **EO4**, respectively), this indicates that the disks are constructed from bilayers of the Janus particles in which the (folded) ligands are intercalated (Fig. 2c). Additionally, heights of 14.8 ± 1.5 nm and 24 ± 2 nm were observed, which point out that two and three of these bilayered disks were stacked on top of each other, respectively. Also TEM showed the existence of round objects with an average diameter of $5.9 \pm 1.1 \times 10^2$ nm, built up from gold nanoparticles (Fig. 2d). Tilting of the sample holder (70°) revealed that the aggregates are flat.¹²

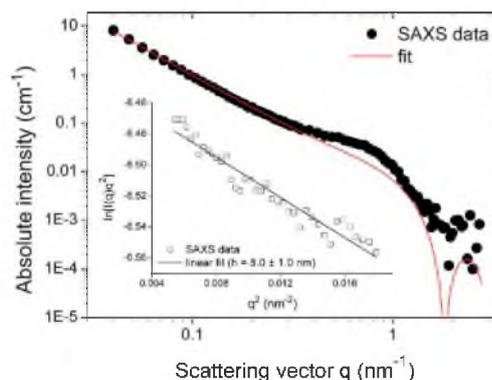
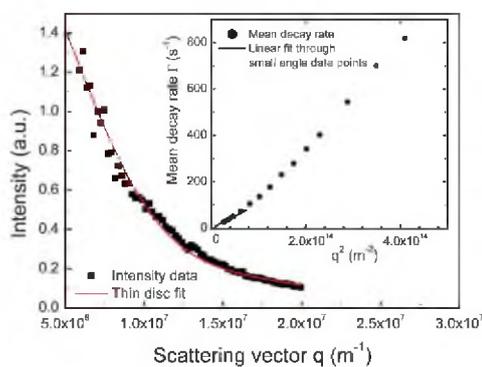


Fig. 3 Scattering studies in solution on disk-shaped aggregates of 1:3 **C10-EO4-Au** Janus nanoparticles (0.25 μM in water). Left: static light scattering (SLS), including the fit for thin disks. Inset: angle dependent dynamic light scattering (DLS), including the fit for the size of the disks. Right: small angle X-ray scattering (SAXS), including the fit. Inset: fit to the SAXS data for the determination of the thickness h of the disk.

To gain more insight into the shape and internal structure of these aggregates in solution scattering studies were carried out. Static light scattering (SLS) revealed a dependence of the scattering intensity as a function of the scattering vector, typical for thin disk-shaped aggregates (Fig. 3a).¹² Small-angle X-ray scattering (SAXS) data, which showed characteristic scattering regions for the shape of the aggregates ($0.035 \text{ nm}^{-1} < q < 0.25 \text{ nm}^{-1}$) and the colloidal subunits ($0.25 \text{ nm}^{-1} < q < 3 \text{ nm}^{-1}$), are consistent with the presence of aggregates built up from colloidal subparticles (Fig. 3b). From simulations of the SAXS data using the expression for a mass fractal consisting of spherical subunits,¹⁶ a fractal dimension (d_f) of 2.3 was obtained. As a d_f value close to 2 is an indication of disk-shaped aggregates, these values point out to the presence of disks with a complex (fractal) internal structure. Furthermore, from the SAXS data a radius of the gold subunits of $R = 2.2$ nm was retrieved, which is in good agreement with the size obtained from TEM. A thickness of 8 nm was calculated for the disks (inset Fig. 3b), which corresponds to a bilayer of gold nanoparticles as was observed earlier by AFM (*vide supra*). Angle dependent dynamic light scattering (DLS) gave similar sizes for the aggregates. Calculations from the small angle region (inset Fig. 3a) yielding disks with a radius of $2.7 \pm 0.3 \times 10^2$ nm and a height of 8 nm.¹²

We propose that during the self-assembly process, phase separation of the ligands on the gold nanoparticles takes place similar as found earlier for nanoparticles on interfaces, yielding Janus particles.^{3,4,17} These Janus particles form a bilayer with a height of 8 nm in which the hydrophobic **C10** molecules are present in the interior, while hydrophilic **EO4** molecules are at the exterior of the micellar disks having an average radius of approximately 270 nm (Fig. 4). Apparently, in case of the 1 : 3 **C10-EO4-Au** Janus particles the balance between the hydrophobic and hydrophilic content is such that these particles self-assemble and stabilise the formed supramolecular aggregate. The fully **EO4**-coated Janus particles are too soluble in water, whereas the 1 : 1 **C10-EO4-Au** Janus particles are too hydrophobic.¹⁸

In summary, *via* a very simple and straightforward procedure amphiphilic nanoparticles have been created by functionalising them with both hydrophobic and hydrophilic ligands. Due to the dynamic character of thiols on gold surfaces, Janus particles are formed that mimic the nature of classical amphiphiles forming disk-shaped micelles in water.

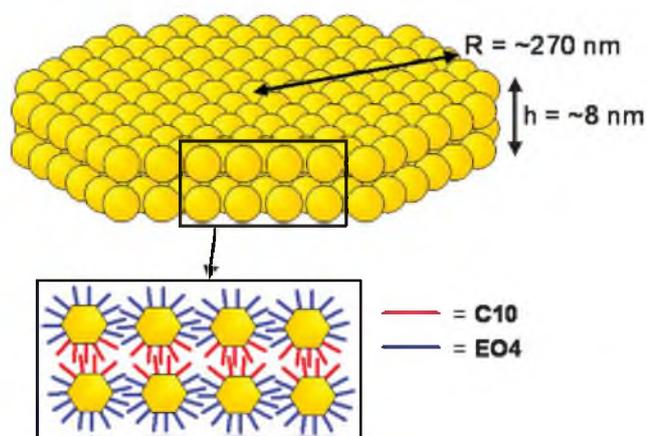


Fig. 4 Schematic representation of a possible structure of the micellar disks self-assembled in water from 1 : 3 C10–EO4–Au Janus nanoparticles.

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