Spontaneous one dimensional arrangement of spherical Au nanoparticles with liquid crystal ligands†

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Spontaneous one dimensional arrangements of spherical Au nanoparticles were accomplished by using a liquid crystalline thiol ligand, 4′-(12-mercaptododecyloxy)biphenyl-4-carbonitrile. Simple thermal treatment of Au nanoparticles with the ligands showed 1D ordering of the Au nanoparticles.

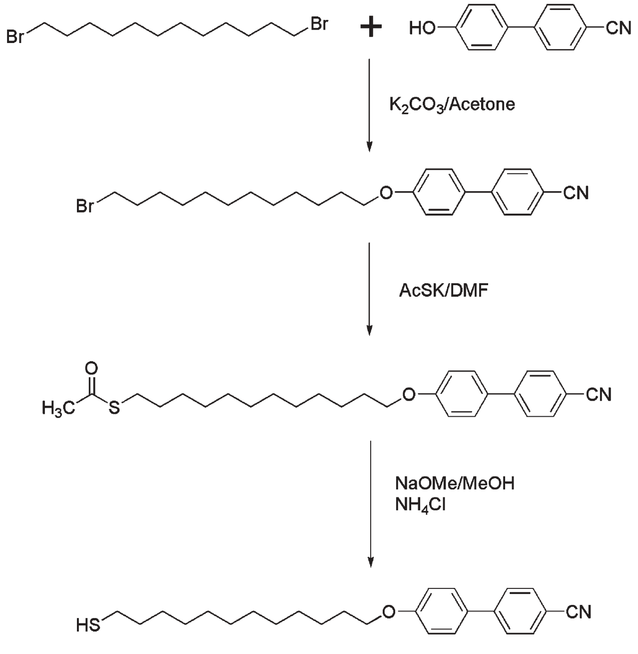
The long-range large scale arrangement of nanoparticles is an important issue in the development of nanostructured materials with new electronic, magnetic, and photonic properties. The two dimensional (2D) and three dimensional (3D) arrangements of spherical nanoparticles have been investigated by many groups, but there is a limited number of reports on the one dimensional (1D) arrangement of nanoparticles.[1] All the previous 1D arrangement attempts involve pre-organized 1D-templates such as patterned surfaces, carbon nanotubes, polysaccharides, block copolymers, liquid crystalline polymers, and DNA. The template-assisted method generally requires the specific attachment or confinement of nanoparticles with the templates that often face difficulties in the full coverage of the templates.[2] Interestingly, two reports describe the 1D arrangement of spherical nanoparticles without templates. One employs genetically engineered viruses and the other uses polymer particles doped with magnetic nanoparticles in the presence of an external magnetic field.[3,4]

In this communication, we describe the spontaneous 1D arrangement of spherical Au nanoparticles with liquid crystalline (LC) ligands. Generally, the shape and symmetry of metal/semiconductor nanoparticles determines the pattern of assembly.[5] Alkane thiol derivatized spherical nanoparticles usually form 2D/3D super lattices due to the close packing.[1] The roles of alkane thiol ligands are the stabilization of assembly by van der Waals force, and the determination of spacing between the neighboring nanoparticles. We found that Au nanoparticles with a ligand consisting of a LC mesogen unit and an alkane thiol unit, spontaneously ordered themselves just by a simple thermal treatment without any templates. The synthesis of LC derivatized spherical gold nanoparticles[6] has been reported, but ordering of the nanoparticles has not been observed. Certainly, the driving force of this 1D arrangement is the LC nature of the thiol ligands because there is no other driving force for the linear assembly of the spherical 'hard' nanoparticles.

The liquid crystalline thiol ligand (LC-SH), 4′-(12-mercaptododecyloxy)biphenyl-4-carbonitrile, was synthesized from 4′-hydroxybiphenyl-4-carbonitrile *via* 3 steps (see Scheme 1).[7] Gold nanoparticles with the LC ligands were synthesized according to the conventional two-phase protocol with $HAuCl_4$, tetraoctylammonium bromide (TOAB), and $NaBH_4$.[8]

The free LC thiol showed typical nematic LC behavior between 50 and 66 °C identified by both differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). DSC analysis of the LC derivatized gold nanoparticle showed the presence of an isotropic melting transition over 130 °C and mesophase between 110 and 130 °C. But distinct texture was not observed with POM. The sample for transmission electron microscopy (TEM) was prepared by dropping a toluene solution of the LC derivatized Au nanoparticles onto a carbon coated copper grid. The average diameter of the gold nanoparticles measured by TEM was 2.7 ± 0.5 nm (see Fig. 1(a)).

After isothermal melting at 140 °C for 3 h, aging at 125 °C for 4 h, and quenching to room temperature, the sample showed a TEM image with a distinct 1D ordering of gold nanoparticles (see Fig. 1(b)). The length of the arrangement was 13∼60 nm and the inter-array distance was about 7 nm. The liquid crystalline ligands play a crucial role in this self-assembly process. The free LC thiol ligand is a nematic liquid crystal but must behave somewhat like a smectic mesogen after binding to a Au nanoparticle for such a 1D arrangement, because of the confinement of neighboring mesogens



Scheme 1 Synthesis of a liquid crystalline thiol ligand.

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† Electronic supplementary information (ESI) available: the DSC curve and POM image of a free LC ligand. The DSC curve and full TEM image of LC derivatized Au nanoparticles after thermal treatment. See http://www.rsc.org/suppdata/cc/b4/b413510e/

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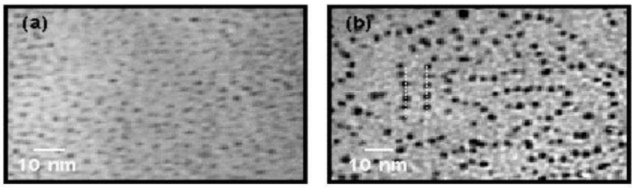

Fig. 1 TEM images of Au nanoparticles with LC ligands (a) before and (b) after thermal treatment.

at the surface of the nanoparticle. A proposed model for this 1D arrangement of spherical nanoparticles is shown in Fig. 2. The inter-array region between the rows is composed of two layers of LC mesogens. The gap distance of about 5.8 nm in the TEM image, which is almost 2 times the size of a mesogen (2.7 nm), supports the proposed model in this study. In the inter-particle region, there are also several mesogen ligands. But in this case, it is supposed that the mesogens are tilted and overlap because the gap distance of 2 nm is much less than the size of a single mesogen (2.7 nm). This situation may cause some defect sites for the longer 1D arrangement. As shown in Fig. 1(b), the 1D arrangement is extended up to about 60 nm and has certain curvatures in some cases.

The structural characteristics of the model were supported by small angle X-ray scattering (SAXS) analysis (see Fig. 3). There are two broad peaks with *d* spacing values of 6.3 and 2.9 nm, which correspond to the inter-array and inter-particle spacing values in both the TEM images and the proposed model.

The above results show that even hard spheres with high symmetry can be assembled spontaneously to the structures with low symmetry. Such an assembly process has not been reported previously. In a previous study by Belcher *et. al.*, the size of individual units (liquid crystalline viruses) is over 800 nm which is much larger than the size of the quantum dots attached to the liquid crystalline virus.[3] So, the assembling units already have the low symmetry that is necessary for smectic or cholesteric mesophase formation. But, in this study, the size of the LC ligand is comparable (2.7 nm) to that of the Au nanoparticles (2.7 nm) and there is no structural motif for the formation of an assembled structure with low symmetry. Obviously, the driving force of the assembly process is the interaction between the numerous neighboring mesogens (inter- or intra-nanoparticle) that seek a more thermodynamically stable state.

In summary, spontaneous 1D arrangements of spherical Au nanoparticles were accomplished with liquid crystalline ligands through a simple thermal treatment. The self ordering behavior of smectic LC-like mesogen is crucial for such an assembly process.

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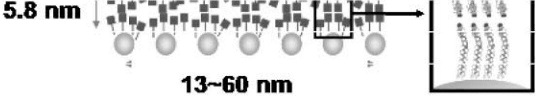

Fig. 2 The proposed model for the 1D assembly of Au nanoparticles with LC ligands.

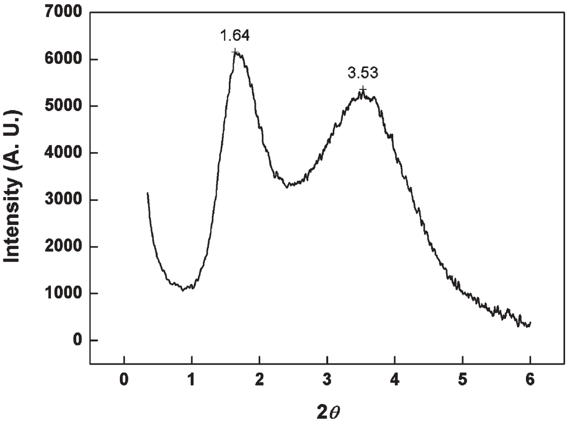

Fig. 3 Small angle X-ray scattering spectrum of Au gold nanoparticles with LC ligands after thermal treatment.

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