Ordered nanocrystal/silica particles self-assembled from nanocrystal micelles and silicate

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Ordered gold nanocrystal/silica particles were synthesized through self-assembly of nanocrystal micelles and silicate. Depending on the use of surfactants, and the kinetic conditions of silica hydrolysis and condensation, well-shaped and irregularly-shaped silica particles were formed, inside which the nanocrystals self-organized in a face-centered cubic mesostructure.

The self-assembly and formation of ordered nanocrystal (NC) arrays have recently received extensive attention due to new physical properties resulting from the coupling of adjacent NCs within the ordered arrays.[1–8] In general, alkane chain-capped monodisperse NCs were mostly used. Consequently, ordered superlattice arrays were formed by the balanced forces of interparticle attraction and steric interaction due to alkane chain interdigitation. Mesoporous silicas have been used as templates to create hybrid silica materials through direct infiltration of either metal or semiconductor nanoparticles or precursor solutions, followed by chemical reactions (*e.g.*, reduction, *etc.*).[9–13] In general, the resulting hybrid materials maintained the morphologies of the original template materials, such as film, powder, *etc*. Recently, we have developed a new method for the synthesis of ordered NC/silica arrays.[3,14,15] In this method, water soluble NC micelles are synthesized through the encapsulation of alkane chain-capped monodisperse NCs within the core of surfactant or block copolymer micelles.[3,14–17] The self-assembly of NC micelles with metal oxide precursors such as tetraethyl orthosilicate (TEOS) in a controlled homogeneous sol–gel process leads to ordered and uniform NC/silica thin films.[3,15] The ordered films exhibit a face-centered cubic (fcc) mesostructure. In this communication, we report a heterogeneous self-assembly process to synthesize ordered NC/silica particles, using NC micelles as building blocks to self-assemble with silicate in a controlled low temperature sol–gel process. Depending on the kinetic conditions of silica condensation and the surfactants used to synthesize the NC micelles, both well-shaped and irregularly-shaped silica particles are formed, inside which the NCs self-organize as a fcc mesostructure.

Gold NC micelles were synthesized using our previously developed surfactant encapsulation techniques *via* an interfacially-driven microemulsion process.[3,14,16,17] 1-Dodecanethiol (DT)-stabilized gold NCs were prepared using the method of Brust *et al.*[18] The NC size distribution was narrowed (<7%) by a

heat treatment and a size selective separation process, according to our previous work.[14,16] Based on the surfactant encapsulation techniques, the gold NC micelles were synthesized using cetyl-trimethyl ammonium bromide (CTAB) and cetyltriethyl ammonium bromide (CTEAB). The extensive van der Waals interactions between the surfactant chains and DT chains leads to an interdigitated "bilayer" structure, stabilizing hydrophobic gold NCs in aqueous solution.[16,19–21] The NC micelles were stable over a wide pH range, from acidic to basic conditions, allowing facile control of the silica hydrolysis and condensation. In a typical synthesis, acid (HCl) was added to an aqueous solution containing monodispersed gold NC micelle building blocks, followed by the addition of TEOS under vigorous stirring. After 10 minutes of stirring at room temperature, the growth of well-shaped gold NC silica arrays was conducted at 0 °C for 4 days. The powder was collected using a filter and dried in a vacuum furnace at 50 °C overnight. X-Ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies were performed on the samples.

From the SEM images, we observed two distinct particle morphologies. As Fig. 1 shows, the particles prepared using CTEB-encapsulated NC micelles exhibit a well-defined external surface morphology; the particle size ranging from 3–10 μm. The XRD pattern in Fig. 2D shows three reflections in the low angle region. The primary peaks can be indexed as (111), (221) and (311), based on a fcc mesostructure; the average measured unit cell $a = 10.8$ nm. The TEM images in Fig. 2A reveal that the gold NCs are organized in an orderly manner inside each particle. The measured unit cell from the [100] orientation (Fig. 2B), a, is 10.6 nm, which is close to that obtained from the XRD results. Under identical experimental conditions, particles with irregular surface morphology were formed when using NC micelles prepared by CTAB, with a smaller surfactant head group than that of CTEAB. Fig. 1B shows the SEM image of particles resulting from the synthesis using CTAB-encapsualted gold NC
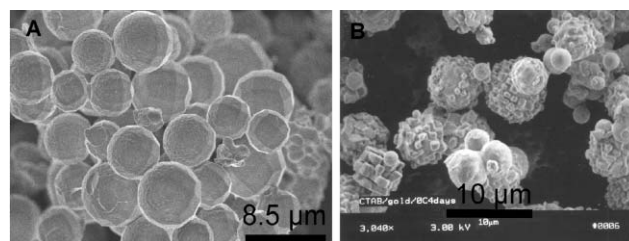
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Fig. 1 SEM images of ordered NC/silica particles. A: Particles prepared using CTEAB-encapsulated NC micelles. B: Particles prepared using CTAB-encapsulated NC micelles.
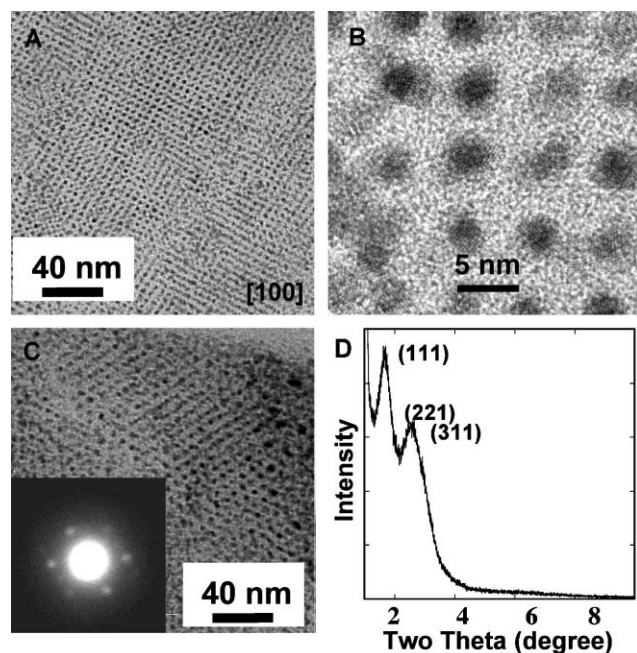
Fig. 2 Representative TEM images and XRD pattern of ordered NC/silica particles. A: [100] orientation of the TEM image of well-shaped and faceted particles in Fig 1A. B: High resolution TEM of image A. C: TEM image of the irregular particles in Fig. 1B. The inset shows the electron diffraction pattern of image C. D: The XRD pattern of the well-shaped particles in Fig. 1A.

micelles. Most of the particles are composed of many smaller subunit particles, with sizes of 1–2 μm and a cubic shape. Despite their irregular topology, the TEM image (Fig. 2C) and electron diffraction pattern (Fig. 2C, inset) indicate that the gold NCs are still organized in an ordered and 3-dimensional fashion inside the particles.

Initial experiments suggest that the formation of faceted gold NC/silica particles is similar to the cooperative self-assembly process to synthesize mesoporous materials.[22–24] The whole NC micelle behaves as a functional building block having a hydrophilic interface with quaternary ammonium surfactant head groups. These provide sites for further self-assembly with silica to form an ordered mesostructure. According to previous work,[4,25–27] the NC size distribution is key to achieving highly ordered and faceted superlattice arrays and solids. In our case, after synthesis using the method reported by Brust et al.,[18] the initial gold NC size distribution was broad. Subsequent heat treatment at 140 °C for 30 minutes extensively narrowed this distribution.[28,29] During heat treatment, Oswald ripening occurred, reorganizing the NC sizes and resulting in much more uniform size distribution.[28,29] In addition, size selective precipitation was carried out using the solvents toluene and ethanol, which made the size distribution less than 7% (size deviation). Encapsulation of such gold NCs within surfactant micelles is driven by an interfacial self-assembly process, in which van der Waals interactions between the hydrophobic alkane carbon chains of CTAB or CTEAB and dodecanethiol stabilize the NC micelle structure through alkane chain interdigitation.[16,19–21] This is a typical physical chemistry process without chemical reactions being involved, and should not affect the NC size and size distribution after encapsulation. TEM studies

suggest the NC micelles maintain the narrow size distribution of the original gold NCs, consistent with our previous observations.[3,16,17] According to our recent studies,[15] slow silica gelation kinetics is the fundamental requirement for the formation of ordered NC/silica arrays. Fast silica gelation kinetics lead to an irregular morphology. Under acidic conditions (pH range 1.0–2.0), TEOS first hydrolyses and then forms silica oligomers.[30] A low pH and low temperature (0 °C) ensured a slow silicate condensation and gelation, which is favorable for the formation of ordered NC/silica arrays. In addition, the balanced hydrogen bonding and charge interactions between the quaternary ammonium groups, silica species and water drive the condensation preferentially at the NC–micelle interface.[22–24,31] Using a long reaction time (4 days), the slow self-assembly process leads to a well-shaped morphology. Our results suggest that the size of the surfactant head group also plays a critical role in controlling the particle morphology. Although the formation mechanism is not yet clear, we hypothesize that the bigger ethyl head groups of CTEAB take up more of the space surrounding the micelles and block direct and strong interactions between charged silicate species and the quaternary ammonium groups. The weak charge interactions between the silicate species and the quaternary ammonium groups result in a slow assembly, and the formation of a well-organized external topology. However, the smaller methyl groups leave more space for silicate species and result in a stronger interaction with the quaternary ammonium groups, resulting in faster assembly and formation of irregular shapes. This has been observed in other self-assembly systems to synthesize mesostructured silica with a well-defined external morphology.[32–36]

Currently, more work is being conducted to gain a deeper understanding of the fundamental factors that underlie morphology control, including variations in pH range, the size and type (ionic or non-ionic) of surfactant head group, temperature and reaction time. By using NC micelles prepared with semiconductor and magnetic NCs,[16,17] we hope that this method can be extended to synthesize similar well-shaped and faceted nanocomposite particles with ordered semiconductor and magnetic NC arrays inside. We expect that these well-shaped NC/silica particles could bring new optical and catalytic properties.

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