

3-Dimensionally Ordered Gold Nanocrystal/Silica Superlattice Thin Films Synthesized via Sol-Gel Self-Assembly **

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Abstract

Nanocrystals and their ordered arrays hold many important applications in fields such as catalysis, Surface-Enhanced Raman Spectroscopy-based sensors, memory storage, and electronic and optical nanodevices. Here we report a simple and general method to synthesize ordered, three-dimensional, transparent gold nanocrystal/silica superlattice thin films through self-assembly of gold NC-micelles with silica or organo-silsesquioxane by spin-coating. The self-assembly process was conducted under an acidic sol-gel condition (pH~2) ensuring spin solution homogeneity and stability, facilitating the formation of ordered and transparent gold nanocrystal/silica films. The monodisperse nanocrystals were organized within inorganic host matrices as a face-centered-cubic mesostructure, characterized by TEM and XRD.

1. Introduction

Nanocrystals (NCs) exhibit unique size-dependent optical, electronic and chemical properties. The ability to adjust properties through control of size, shape, composition, crystallinity, and structure has led to a wide range of potential applications for NCs in areas like optics, electronics, catalysis, magnetic storage, and biological labeling^[1-6]. Furthermore, NC assembly into 2- and 3-dimensional (D) superlattices is of interest for development of ‘artificial solids’ with collective optical and electronic properties that can be further tuned by the NC spacing and arrangement^[7-11]. To date, there have been three approaches to fabricate superlattice solids and thin films. The most commonly used approach involves evaporating a drop of NC organic solution on solid supports (i.e., TEM grid, mica, HOGH, etc), forming face-centered-cubic (*fcc*), body-centered-cubic (*bcc*), or hexagonal-close-packed (*hcp*) superlattice films^[2, 12-14]. Heath *et al*^[9] reported a method to form 2-dimensional *hcp* superlattice films of silver NCs through *Langmuir-Blodgett* deposition. In the third approach, homogenous precipitation of superlattice solids were prepared by slow addition of non-solvents into a NC organic solution^[15, 16]. Over long time aging, well-shaped crystal superlattice solids with *fcc* structure were finally obtained. The common problem in these approaches is that the NCs that have been used are alkane chain stabilized, therefore are hydrophobic and soluble only in organic solvents. The formation of ordered NC superlattice is limited to organic solvents and relies on the van der Waals interactions between interdigitated alkane chains surrounding the NCs. The thermally defined, interdigitated alkane chains result in weak mechanical stability of the superlattice. In such materials, charge transport is conducted through the interdigitated organic media between NCs^[7-11]. Recent results indicate that it is desirable to incorporate NCs in inorganic thin film matrices such as silica or titania for achieving chemical and mechanical robustness and enhanced

device functionality^[17-19]. Earlier efforts have focused on encapsulation of metal nanocrystals inside sol-gel matrices through introduction of metal nanoparticles^[20] or metal precursors followed by either thermally decomposing or reducing them^[21, 22]. Recently, mesoporous materials have been used as templates to create hybrid silica materials infiltrated with metal or semiconducting nanocrystals^[23-27]. Several disadvantages for above methods include: first, the nanocrystal arrays inside the final materials exhibit poor-defined or less ordered structure. This is problematic for the fundamental studies of charge transport to get repeatable/reproducible results. Second, the methods have less control over particle sizes and loading. Finally, it is difficult for above methods to precisely control interparticle spacing that is essential for achieving new physical properties resulting from coupling between neighboring nanoparticles^[9, 11, 28].

In recent work, we reported a facile synthesis of water soluble NC-micelles^[29-31] and their self-assembly into ordered, 3-dimensional gold NC/silica superlattice arrays through in a sol-gel process^[19]. Under basic condition, Fast silica hydrolysis and condensation led to a heterogeneous self-assembly system and ordered arrays in solid/powder form^[19]. For device fabrication, thin film is more desirable than powder. Here we report a detailed synthesis of gold NC/silica arrays in thin film form through slow sol-gel process under acidic conditions. We discovered that silica condensation played important role in formation of ordered 3-D gold NC/silica arrays. Oligo silica species in homogeneous coating solution is essential to form ordered, transparent gold/silica thin films without cracking. Extensive silica condensation leads to less ordered gold/silica mesophase. To this end, the precursor solution was prepared in acidic conditions (pH~2) by addition of aqueous hydrogen chloride to maximize silica gel time, facilitating the self-assembly and formation of ordered nanocrystal/silica thin films^[32, 33]. By using organo-

silsesquioxane, we were able to tune the framework chemistry and dielectrics. The final film consists of monodisperse gold NCs arranged within a silica or organo-silsesquioxane host matrices in an *fcc* mesostructure with precisely controlled interparticle spacing.

2. Results and Discussion

Scheme 1 shows the schematic processes of synthesis of such ordered superlattice thin films. Water-soluble gold NC-micelles were prepared through an interfacially driven micro-emulsion process^[19, 29-31] using cetyltrimethyl ammonium bromide (CTAB) and *n*-dodecanethiol (*n*-DT) derivatized gold NCs. *n*-DT capped gold NCs were prepared according to the method of Brust *et al*^[34] followed by heat treatment to narrow down gold NC size distribution to ~7%^[35]. [See Scheme 1(i)]. The thermodynamically favorable interdigitation between the *n*-DT layer and CTAB layer stabilizes gold NC-micelles in aqueous solution^[30]. Tetraethyl orthosilicate (TEOS) was used as a precursor and added to above solution followed by hydrolysis and condensation under acidic conditions at room temperature for 1 hour. In addition to TEOS, bis(triethoxysilyl) ethane (BTEE) were used to tune the matrix composition within superlattice films. Ordered superlattice thin films were prepared by spin-coating above solution on substrates such as silicon wafer, glass, etc. [See Scheme 1(ii)]. In order to study the siloxane condensation effect on the formation of ordered superlattice, the above solution was aged at room temperature for different periods of time before spin-coating.

The gold/silica superlattice films have an average refractive index of ~1.7 and thicknesses of 100 to 300-nm depending on the spin rate. The film thickness can reach up to 25 μ m when casting. Figure 1d shows an optical micrograph of a film that exhibits reddish color and very good optical transparency. Optical properties of the superlattice film have been characterized

using UV-vis spectroscopy as shown in Figure 1a-c. The superlattice film exhibits a characteristic surface plasmon resonance band at ~518-nm, as expected from gold NCs. In comparison with the spectra of monodisperse DT-stabilized gold NCs, the position and width of the surface plasmon band from gold superlattice film stay unchanged, suggesting that gold NCs inside the film remain monodisperse. This is further confirmed by TEM results (see below). Low-magnification scanning electron micrograph (SEM) imaging (Fig. 2A) shows that the film has a uniform and continuous surface without macroscopic granularity or cracks. Figure 2B shows a high-resolution SEM image of as-prepared film surface. Ordered gold NCs are distributed uniformly on the film surface.

Figure 2-C3 shows a representative low angle x-ray diffraction (XRD) pattern of a superlattice thin film prepared according to pathway i-ii-iii (Scheme 1), using ~3-nm DM-stabilized gold NCs, CTAB, and TEOS. The patterns can be indexed as an *fcc* structure with unit cell $a = \sim 10.5$ -nm. The primary peaks are assigned as (111), (220)/(311), and (222) reflections. Figure 2-C1 shows the XRD pattern of a film prepared using a spin solution aged at room temperature for 24 hours. The film exhibits lower degree of ordering with disappearance of (220)/(311) and intensity decrease of (222). Figure 3A shows a representative cross-sectional TEM image of an ordered superlattice film. Periodically ordered regions are observed throughout the whole film thickness. The sharp, continuous, and uniform air-film and film-substrate interfaces are consistent with SEM results showing no steps, kinks, or cracking that appear in superlattice films prepared by evaporation of NC solution^[14, 36, 37]. A representative plan-view TEM image is shown in Figure 3B. The TEM images are consistent with an *fcc* structure (Fm3m space group) with a measured unit cell $a = \sim 10.8$ -nm and a minimum average interparticle spacing is ~2.3-nm. Note that the gold NC/silica superlattice thin film has a larger unit cell than

that of previous superlattice films and solids^[38]. This is due to that here the gold NCs are arranged within a silica matrix. There exists a thin silica layer between each individual gold NCs. The silica-insulating layer was further confirmed by high-resolution transmission electron micrograph (Fig. 3A inset). As shown in plan-view image (Fig. 3B), regions of ordered gold NC arrays inside silica exhibit no preferred orientation with seamless transition between ordered domains of gold NCs. Within the film, the gold NCs remain monodisperse, which is consistent with UV-vis results (see Fig. 1).

Formation of ordered gold NC/silica thin films is analog to that of self-assembly of surfactant and silica. Charge interaction and hydrogen bonding between hydrolyzed silica and surfactant head groups on NC-micelle surface drive the formation of ordered gold NC/silica mesophase^[39]. However, the two systems exhibit distinct tendency to form mesostructures. Prior work on self-assembly of pure surfactant and silica indicated that a series of mesostructures can be formed including lamellar, 1-d hexagonal, cubic, and 3-d hexagonal periodic symmetries^[39]. In the case of self-assembly of NC-micelles and silica, only *fcc* mesostructure are preferentially formed regardless of basic and acidic catalytic conditions. This is probably due to the fact that the gold NC-micelles are pre-formed in a homogeneous solution and behave rather like a “hard” sphere tending to form *fcc* close packing than “soft” pure surfactant micelles that incline to undergo phase transformation. Vital to the formation of transparent, ordered gold NC/silica superlattice films is the use of stable and homogeneous spinning or casting solution that upon evaporation of water undergoes self-assembly of NC-micelles and soluble silica. For this purpose, we prepared oligomeric silica sols in NC-micelle aqueous solution at a low hydronium ion concentration (pH~2) designed to minimize the siloxane condensation rate, thereby enabling facile silica and NC-micelle self-assembly during spin-coating or casting^[32]. The aging

experiments (Fig. 2, C1 to C5) unambiguously demonstrate that extensive silica condensation, that results in polymeric silica species, does not favor the self-assembly, leading to a less ordered film. The method is flexible and allows tuning of framework composition, thus dielectrics, by using different sol-gel precursors. Organo-bridged silsesquioxane is an ideal low k host, exhibiting chemical and mechanical robustness^[40, 41]. In addition to silica, we have demonstrated the synthesis of ordered gold NC arrays inside organo-silsesquioxane framework. The ordered gold NC/ silsesquioxane was prepared by using ~3-nm DM-stabilized gold NCs, CTAB, and BTEE. The corresponding XRD patterns (Figure 2-C4&5) and TEM image (Figure 3C) reveal that films exhibit ordered *fcc* mesostructure. In addition, we observed from XRD results that the self-assembly when using BTEE is not strongly affected by solution aging unlike that when using TEOS. This is due to that organo-bridged precursor has relatively slower hydrolysis and condensation rate than TEOS^[33]. The ability to form patterned films is essential for device fabrication. The homogeneous solution of gold NC-micelle allows using several soft lithographic techniques such as μ -molding, pen writing, and ink-jet printing, etc to pattern the ordered gold NC/silica superlattice films. We have demonstrated the formation of patterned gold NC/silica superlattice films based on our previous work on patterning surfactant templated silica mesophases. Figure 3D shows the patterned stripes and dots containing ordered gold NC/silica superlattice fabricated using μ -molding techniques^[42]. The pattern sizes are determined by the feature sizes of the PDMS stamps.

In comparison to the previous methods to assemble NC superlattice through evaporation of a colloidal solution of NCs, our method provides several advantageous features. First, unlike previous superlattice films formed through evaporation of organic flammable solutions, the water-soluble gold NC-micelles allow to make superlattice films in water, resulting in enhanced

safety and better compatibility with current semiconductor fabrication processing. Second, by using different sol-gel precursors, our method allows simple tuning of framework composition, thus dielectrics, between gold NCs. This is essential to achieve enhanced collective properties of such three-dimensional superlattice films^[17, 18]. Furthermore, the inorganic framework provides chemical and mechanical robustness, prevents films from cracking, which is important for device fabrication. It is believed that formation of NC superlattice through organic solvent evaporation is an entropy-driven process in which NCs organize in a way to achieve the highest packing density or maximum entropy.^[2, 12, 14, 43] In our method, silica condensation affects ordering during formation of gold NC/silica superlattice film. It is interesting to note that previous methods to assemble NCs during solvent evaporation leads to two-level preferential orientations. First, the ordered NCs pack as *fcc* structure with (111) planes parallel to substrates^[13, 14]. Second, the crystal structure of each individual NCs is also orientated relative to substrates^[13]. In our system, the films consist of ordered “domains” randomly distributed throughout the film. From wide-angle XRD, we observe no preferred orientation of gold crystal structure relative to substrate.

3. Conclusions

We have developed a simple and general method to synthesize ordered, three-dimensional, transparent gold NC/silica superlattice thin films through self-assembly of water-soluble gold NC-micelles and soluble silica by spin-coating. The self-assembly process allows facile tuning of host matrix composition by using different sol-gel precursors, provides compatibility with standard microelectronics processing/patterning, enabling higher temperature operation. Acidic sol-gel chemistry ensures spin solution homogeneity and stability, facilitating

the self-assembly of soluble silica and NC-micelles into ordered and transparent gold NC/silica films. The ease of preparing of semiconducting and magnetic nanocrystal-micelles using interfacially driven μ -emulsion process makes it possible to synthesize ordered quantum dot/metal oxide and magnetic nanocrystal/metal oxide arrays and to integrate them into laser and memory devices^[30, 31]. The robust, 3-D NC/silica superlattice films are of interest for development of collective optical and electronic phenomena, and, importantly, for the integration of NC arrays into device architectures^[8, 44]. Ultimately, the ordered gold/silica superlattice films are ideal platforms for the fabrication of molecule-electronic nanodevices^[45] and SERS based chemical and biosensors^[20, 46].

4. Experimental section:

Synthesis of gold nanocrystals: *n*-dodecanethiol modified gold nanocrystals were synthesized using the method developed by Brust *et al*^[34]. A 60 ml aqueous solution containing 0.7g HAuCl₄ (Aldrich) was mixed with a solution of tetraoctylammonium bromide (4g, Aldrich) in 160ml toluene. The two-phase mixture was vigorously stirred until the tetrachloroaurate was transferred completely into the organic layer (judged by color changes: the aqueous phase became colorless and the organic phase became dark yellow). 0.34g *n*-dodecanethiol (Aldrich) was added to the organic phase. A 40ml freshly prepared aqueous solution of sodium borohydride (0.78g, Aldrich) was slowly added with vigorously stirring and finished during 20mins. After further stirring for 2hrs, the organic phase was separated and evaporated in a rotary evaporator. Heat treatment at 140°C was performed for 30-45 minutes^[35]. The gold nanocrystals were then purified by two cycles of precipitation, followed by size-selective precipitation using the solvent/nonsolvent pair

of toluene/ethanol. In general, the gold nanocrystals were dissolved in 10 ml toluene and precipitated using 50ml ethanol.

Synthesis of gold nanocrystal-micelles: In a general preparation of water soluble gold nanocrystal-micelles, 3ml chloroform gold nanocrystal solution containing 0.35g *n*-dodecaethyl stabilized gold nanocrystals) was added to 8-12g DI-water containing 0.2g cetyltrimethyl ammonium bromide (CTAB) under vigorously stirring. to form solution A. The chloroform was removed by quick heating to transfer hydrophobic gold nanocrystals into aqueous phase through encapsulation. A dark-colored solution (stock solution) was finally obtained and centrifuged at 2000rpm for 5mins to remove precipitates if any.

Gold nanocrystal/silica superlattice thin films: 0.08g tetraethyl orthosilicate (TEOS) or bis(triethoxysilyl) ethane (BTEE) was added to 1ml above stock solution followed by addition of 0.05ml HCl aqueous solution (0.07N or 1N). The mixture was stirred for 1hour at room temperature. Superlattice films were formed through spin-coating using 500-2000rpm speed. Aging studies were performed at room temperature for desired time.

Characterizations: The XRD spectra were used to characterized 3-d ordered arrays (film) and recorded on a Siemens D500 diffractometer using Ni-filter CuK α radiation with $\lambda=1.54\text{\AA}$ in θ - 2θ ($2\theta=1-10^\circ$) scan mode using step size ranging from 0.02 and dwell time of 2. TEM images were taken at JEOL 2010 high-resolution microscope equipped with Gatan slow scan CCD camera and operated at 200 keV. SEM images were taken at Hitachi S-5200 FEG high-resolution microscope.

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Figure captions:

Scheme 1. Formation of water-soluble gold NC-micelles through surfactant/lipid encapsulation

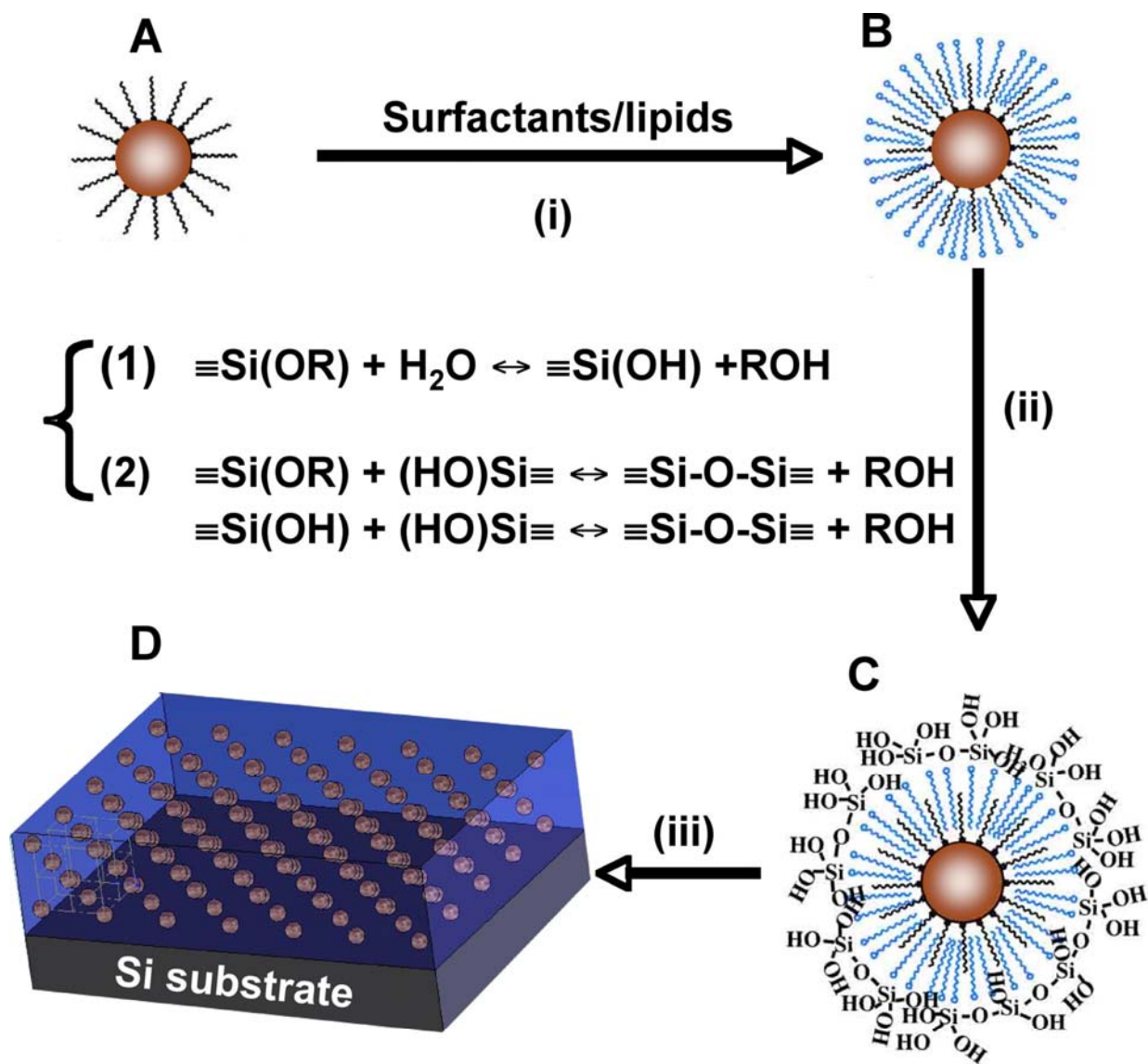
(i) and their self-assembly with soluble silica in a controlled sol-gel process (ii) into ordered gold NC/silica superlattice films through spin coating (iii); A. *n*-Dodecanethiol (DT)-stabilized, hydrophobic gold NCs; B. DT-stabilized gold NCs are encapsulated inside surfactant micelles through interfacially driven oil-in-water micro-emulsion process^[19]; C. Sol-gel self-assembly are conducted in acidic condition, water-soluble oligomeric silica species preferentially interact with gold NC-micelles and further self-assemble into *fcc* gold NC superlattice film (D) upon drying (iii).

Figure 1. Ultraviolet-visible (UV-vis) spectra of DT-stabilized gold NCs (a), gold NC/silica superlattice film prepared by using TEOS (b), and (c) gold/ethyl bridged silsesquioxane film

prepared by using bis(triethoxysilyl) ethane. (d), A optical micrograph of as-prepared ordered gold/silica film on glass substrate that covers on the logo of Sandia National Laboratories.

Figure 2. A. Low-resolution scanning electron microscope (SEM) micrograph of ordered gold NC/silica superlattice thin film. B. High-resolution SEM from same specimen in A. C. X-ray diffraction (XRD) patterns of gold NC/silica superlattice films. C1. Ordered gold/silica film prepared using a coating solution that was aged at ambient condition for 24 hours, and C2 for 5 hours. C3. Ordered gold/silica film prepared using a coating solution without aging. C4. Ordered gold/silsesquioxane film prepared using a solution that was aged at ambient condition for 24 hours. C5. Ordered gold/silsesquioxane film prepared using a solution without aging.

Figure 3. A. Cross-sectional TEM micrograph of ordered gold NC/silica superlattice thin film. B. Representative plan view TEM micrograph of ordered gold NC/silica superlattice films through complete film thickness showing seamless transition among three ordered domains [211] and [111]. Inset, a high resolution TEM micrograph. C. Representative plan view TEM micrograph of ordered gold NC/silsesquioxane superlattice films prepared by using BTEE. D. Patterned gold NC/silica superlattice thin films using μ -molding method^[42].



Scheme 1

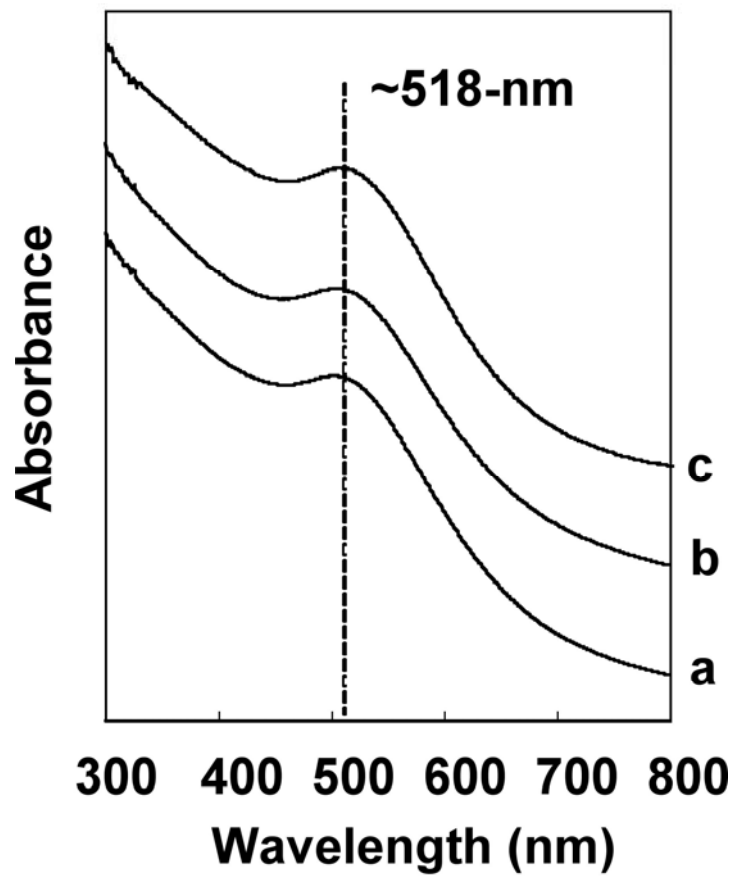


Figure 1

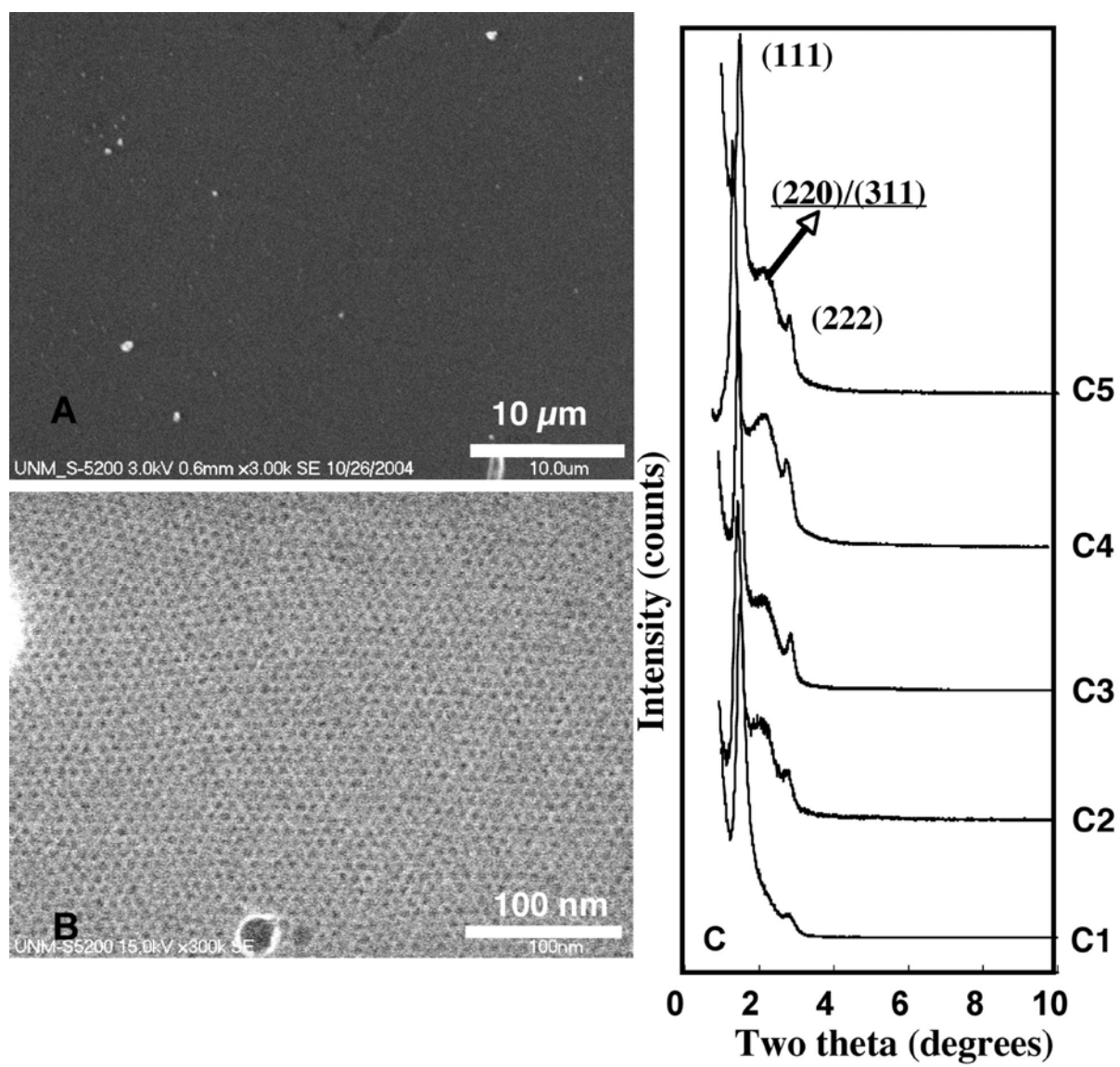


Figure 2

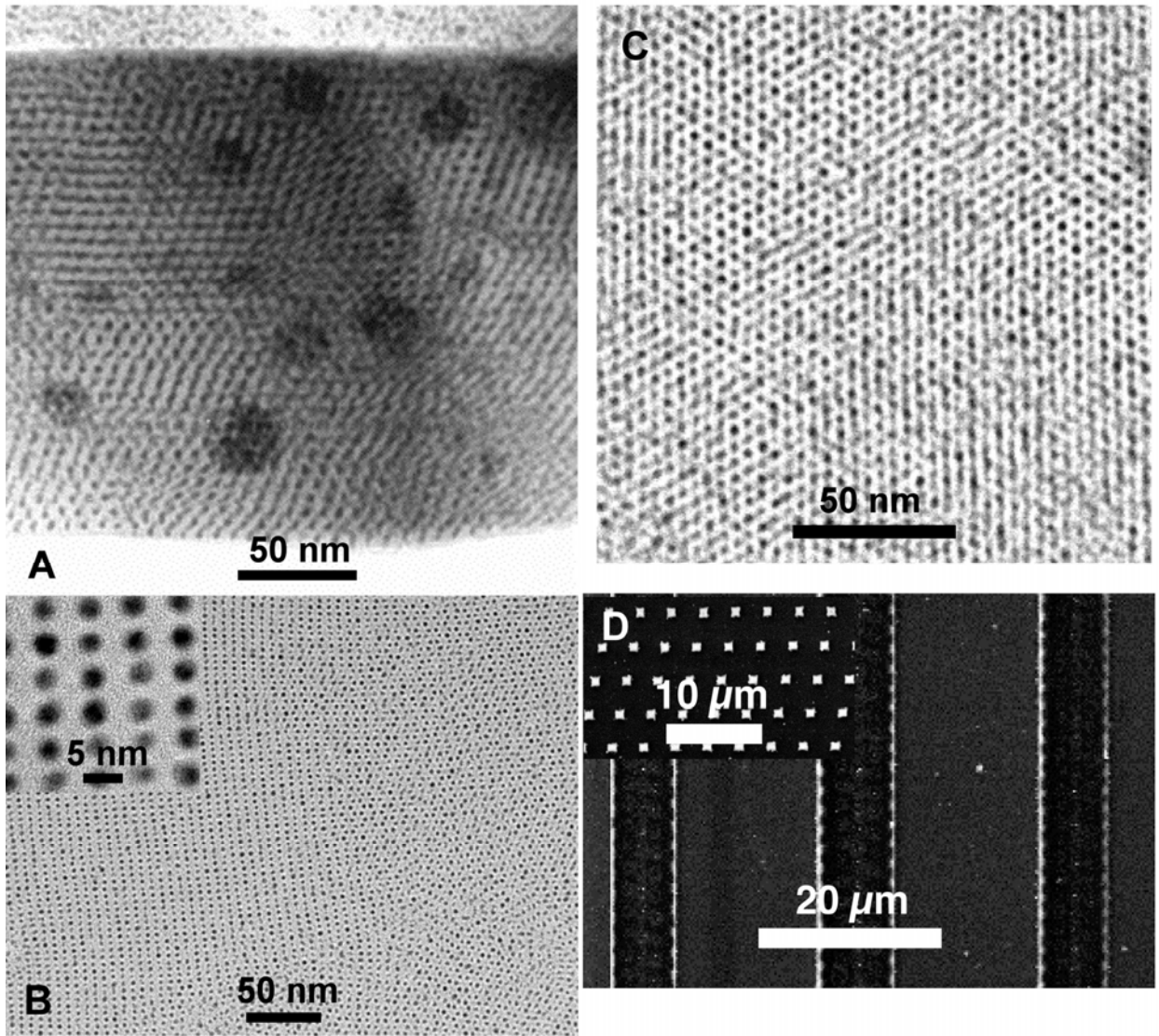


Figure 3

