

## Silver nanocrystal superlattices: Self-assembly and optical emission

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Unique passivated silver nanocrystal superlattices were fabricated via a conventional hydrothermal method. The method is based on a general phase transfer and separation mechanism occurring at the interfaces of the liquid, solid, and solution phases present during the synthesis. A photoluminescence (PL) band centered at 390 nm was recorded from the obtained superlattice samples. Spectral analyses suggest that the PL arises from the radiative recombination of *sp*-band electrons with *d*-band holes in the silver nanocrystals and its intensity enhancement is due to the surface plasmon and an electrostatic enhancement mechanism analogous to that in surface enhanced Raman scattering. © 2006 American Institute of Physics. [DOI: 10.1063/1.2192645]

One of the fastest-developing fields in materials physics and chemistry in the last several years has been the synthesis of two- and three-dimensional ordered arrays of nanoparticles, known as nanocrystal superlattices (NSs) with controllable interparticle distances.<sup>1–3</sup> Such control allows the opportunity to study and apply charge-transport phenomena such as the transition from an insulator to a metallic conductor.<sup>4</sup> Close-packed nanocrystal assemblies are also ideal systems for studying chemical and physical phenomena arising from the collective interaction of the constituting units.<sup>5</sup> Development of synthetic methods that lead to high-quality nanoparticles has enabled the formation of long-range-ordered NSs composed of metals,<sup>2,6,7</sup> semiconductors,<sup>8</sup> and magnetic nanocrystals.<sup>9</sup> In this letter, we present a relatively simple method of fabricating unique passivated silver NSs in bulk quantities via a conventional hydrothermal method which provides a convenient nanotechnology to assemble noble metals with unique structures and functions. A photoluminescence (PL) band at 390 nm was recorded from the obtained superlattices. Spectral analyses suggest that the PL arises from the radiative recombination of *sp*-band electrons with *d*-band holes in the silver nanocrystals.

The hydrothermal method is based on a general phase transfer and separation mechanism occurring at the interfaces of the liquid, solid, and solution phases during the synthesis.<sup>10</sup> The detailed sample fabrication procedures are described as follows: 10 ml of  $1.5 \times 10^{-3}$  M AgNO<sub>3</sub> aqueous solution, 0.8 g sodium linoleate, and a mixture of 1 ml linoleic acid and 5 ml ethanol were added into a 20 ml autoclave tube sequentially. The system was sealed and treated at 150 °C for 10 h. Three phases, liquid (a mixture of ethanol and linoleic acid), solid (sodium linoleate), and solution (a water-ethanol solution containing Ag ions), spontaneously form in this system. A phase transfer process involving the Ag ions occurs across the interface between sodium linoleate and the water-ethanol solution due to ion exchange and it

leads to the formation of silver linoleate and incorporation of sodium ions into the aqueous phases. Afterwards, ethanol in the liquid and solution phases reduces Ag ions at the liquid-solid or solution-solid interfaces, and the *in situ* generated linoleic acid absorbs on the surface of the silver nanocrystals with the alkyl chains on the outside, during which the silver nanocrystals produced hydrophobic surfaces. A spontaneous phase-separation process then occurs because of the weight of the silver nanocrystals and the incompatibility between the hydrophobic surfaces and their hydrophilic surroundings. The products were finally collected at the bottom of the vessel when cooled to room temperature.

The morphology and size distribution of the silver nanocrystals were investigated using transmission electron microscopy (TEM) (Philips, CM20, at 200 kV). The TEM samples were prepared under ambient conditions by depositing droplets of the ethanol solution with the nanocrystals onto carbon films supported by Cu grids. Figure 1 shows the bright-field transmission electron micrographs and corresponding electron diffraction patterns. In Figs. 1(a) and 1(b),

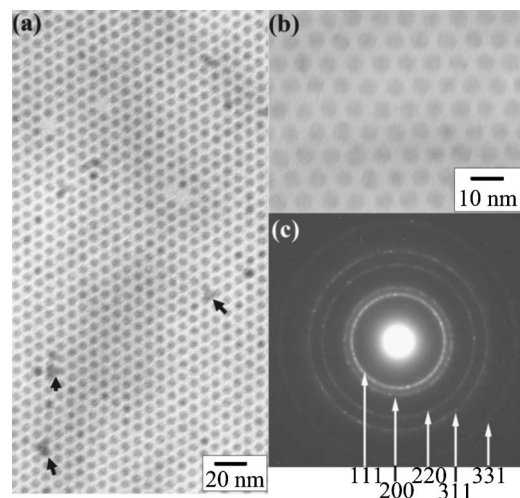


FIG. 1. [(a) and (b)] Bright-field TEM images and (c) the corresponding electron diffraction pattern of a self-assembled monolayer of silver nanocrystals. The arrows point to the self-assembly of adjacent nanoparticles by means of the sodium linoleate tails.

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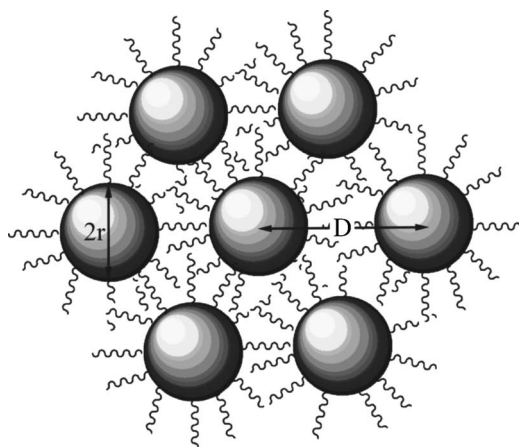


FIG. 2. Schematic illustration of the surface-passivated silver NSs.

the near-complete monolayer silver nanocrystals with a relatively narrow particle size distribution ( $5.0 \pm 0.3$  nm) can clearly be observed. Large quantity and good uniformity are achieved using this approach. The particles have a round shape with smooth surface and self-assemble into highly ordered two-dimensional arrays on the surface of the TEM grid. The smooth morphological structure of the nanocrystal packing indicates that particle diffusion is much faster than the rate of arrival during the drying process. We also used selected area small-angle electron diffraction to probe the structure of the silver nanocrystals. All the diffraction rings can be assigned to face-centered cubic structured silver (JCPDS 04-0783), as shown in Fig. 1(c).

Some interlinking between individual nanocrystals, possibly through the interdigitation of the sodium linoleate tails [see the arrows in Fig. 1(a)] of adjacent micelles, can also be seen.<sup>11</sup> It is known that the high surface energies of metal and semiconductor particles in the nanometer size range make them extremely reactive, and most systems undergo aggregation if their surfaces are not protected or passivated.<sup>1,2,5</sup> To control the particle size and polydispersity, organic capping agents with proper binding strengths to the substrate are often used.<sup>2</sup> In our system, the *in situ* generated linoleic acid absorbed on the surface of the silver nanocrystals with the alkyl chains on the outside (see Fig. 2) not only renders silver nanocrystals hydrophobic but also passivates the crystallite surfaces and quenches the crystallite growth.

Using as-grown passivated silver nanocrystals as the building blocks in conjunction with self-assembly is a promising technique to synthesize superlattice materials with controllable size and shape. The core sizes of the particles can be controlled by the temperature.<sup>10,12</sup> Alkyl chains absorbed on the surface of the silver nanocrystals also provide interparticle bonding. The strength of this bond enhances the structural stability and the maximum temperature the materials can withstand.<sup>1</sup> By controlling the length of the alkyl chains (substitute another fatty acid and sodium stearate for linoleic acid and sodium linoleate),<sup>12</sup> a transition from insulator to semiconductor or conductor can be introduced, resulting in tunable properties.<sup>4</sup>

We measured the PL of the silver NSs on a quartz substrate surface (Jobin Yvon, FluoroMax-2). The silver NSs luminescence under excitation of a 250 nm Xe lamp. The PL band centered at 390 nm is shown in the inset of Fig. 3. Theoretical work has previously demonstrated that the PL of

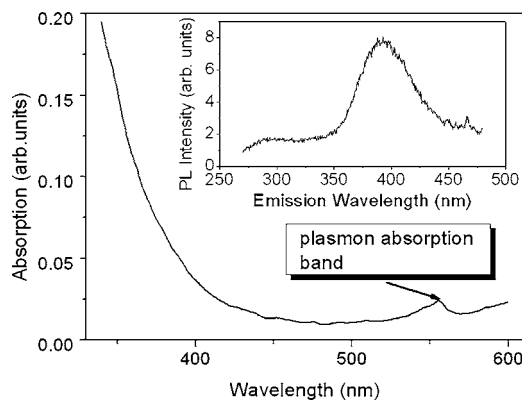


FIG. 3. Optical absorption spectrum of the as-grown silver NSs. The inset shows the PL spectrum of the as-grown silver NSs, taken under excitation with the 250 nm line of a Xe lamp.

noble metals could be viewed as an excitation of electrons from occupied *d* bands into states above the Fermi level.<sup>13</sup> Subsequent electron-phonon and hole-phonon scattering processes lead to energy loss and finally PL recombination of an electron from an occupied *sp* band with a hole. However, optically excited noble metal surfaces show no or very little luminescence. For instance, smooth gold films exhibit PL with very a low efficiency on the order of  $\sim 10^{-10}$  following excitation of electron transitions from the *5d* to the *6sp* bands.<sup>14</sup> One possible reason for this low PL efficiency is that nonradiative energy relaxation processes of photoexcited carriers in metals, such as Coulomb carrier-carrier scattering, are much faster than radiative electron-hole recombination, thus quenching the PL.<sup>15</sup> There is, however, a unique exception from the rule of low PL yields from metals for noble metal nanoparticles. For example, in a previous study, Kokkinakis and Alexopoulos<sup>16</sup> used x rays to excite citrate-ion-stabilized Ag clusters deposited on a surface and embedded in gelatin. They observed PL with a peak wavelength near 390 nm and attributed the PL enhancement to the radiative decay of surface plasmon, which is a commonly accepted origin for the enhanced PL of small-sized noble metal particles.

As noble metals are reduced in size to tens of nanometers, a strong absorption is often observed due to collective oscillation of the electrons in the conduction band from one surface of the particle to the other in response to optical excitation.<sup>5</sup> This oscillation has an absorbing frequency in the visible range, which is called the surface plasmon absorption. This strong absorption, manifesting in vivid characteristic color, has been observed and used. To detect whether there is the surface plasmon in the as-grown silver NSs, we measured the absorption spectrum of the samples (Perkin Elmer, Lambda 2 UV-Vis) and found that the plasmon absorption was very weak, as shown in Fig. 3.<sup>17</sup>

Mie's theory on the surface plasmon resonance<sup>18</sup> and experimental spectra agree well in the size regime of  $>20$  nm until normal incidence absorption no longer shows a plasmon resonance for bulk metals. When the sizes of the nanoparticles are much smaller than the wavelength ( $<20$  nm) of the interacting light, the plasmon band shows a particle size dependence and even disappears.<sup>19,20</sup> For such small particles ( $\sim 5$  nm) only the absorption coefficient contributes to the extinction spectrum, since scattering is quite negligible. This absorption being proportional to the particle

volume, the observation of a weak plasmon band is to be expected.<sup>21,22</sup> On the other hand, a measurement of  $D/2r$  for ordered metal nanoparticle arrays, where  $D$  is the distance between the centers of two adjacent particles and  $2r$  the particle diameter, is necessary in order to describe the classical electronic coupling.<sup>1,4</sup> The  $D/2r$  value of our system is  $\sim 1.75$  which is far beyond the largest calculated result in which a weak electronic coupling occurs (the larger the  $D/2r$  value, the lower the intensity of electronic coupling).<sup>1</sup> Thus, we suggest that the weak plasmon band is not only related to the sizes of the current Ag nanocrystals but also associated with the unique ordered structures.

Comparing previous studies with our present work, a major difference is in the nature of the particle dispersion and average particle separation.<sup>16,23,24</sup> In the previous work, the particles were “painted” onto a substrate, which assured extensive agglomeration leading to a strong plasmon peak. In our samples, we observed weak absorbance maximum from the surface plasmon for the unique structure. Thus, we believe that the surface plasmon mechanism could not be the only one to account for the enhancement in the observed PL.

It is noteworthy that organic molecules adsorbing on noble metal nanoparticles show vast enhancement in their Raman scattering intensities [the surface enhanced Raman scattering (SERS)].<sup>25–27</sup> Angel *et al.*<sup>28</sup> have pointed out that the enhanced PL from roughened and organic-molecule-absorbed small-size metal surfaces is analogous to the SERS effect.<sup>29</sup> Since the 390 nm PL peak can also be attributed to the (1, 0) Mie plasmon,<sup>30</sup> we suggest that the emission of the alkyl chains-passivated NSs arise from radiative recombination of  $sp$ -band electrons with  $d$ -band holes in the silver nanocrystals, while its enhancement, compared to those reported from bulk surfaces and unordered noble metal nanocrystals with extensive agglomeration, is due to the surface plasmon and an electrostatic enhancement mechanism similar to that of the SERS effect.

In summary, a simple method based on general phase transfer and separation has been used to fabricate passivated silver NSs. A PL band is observed at 390 nm. Because a weak plasmon band is found on the absorption spectrum of the as-grown silver nanocrystals, it is believed that the emission arises from the radiative recombination of  $sp$ -band electrons with  $d$ -band holes in the silver nanocrystals, while its enhancement is due to the surface enhancement mechanism of the composite system (metal nanoparticles/surface organic molecules).

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