The remarkable size and shape dependence of physical, optical, and electronic properties of metal and semiconductor nanocrystals make them compelling components of modern materials chemistry.1–3 When spherical metal particles are transformed into nanoscale rods or triangular prisms, the surface plasmon resonances are strongly affected, typically red-shifting and even splitting into distinctive dipole and quadrupole plasmon modes.4 Colloid chemists have recently made much progress in preparing monodispersed spherical nanocrystals via ambient temperature wet-chemical routes or organometallic methods.2 Although the synthesis of spherical nanocrystals is well developed for many materials, systematic manipulation of the shapes of nanocrystals is a significant challenge. Recent work devoted to making nonspherical nanocrystals via anisotropic inorganic nanocrystal growth in liquid media (including electrochemical growth) has yielded Au rods,5 BaCrO 4 rods,6 TiO 2 rods,7 Ag rods,8 Pt cubes and pyramids,9 and rod-, arrow-, teardrop-, and tetrapod-shaped CdSe nanocrystals.10,11 Fabrication of these materials is useful not only for understanding fundamental phenomena such as quantum confinement but also for obtaining “building blocks” featuring optical and electronic properties that are desirable for advanced applications in photovoltaic solar cells, light-emitting diodes, and biological diagnostics.4,12,13

In contrast to nanorods, nanodisks and nanoprisms such as triangles are less well-known. Although a few strategies do exist for synthesizing Co disks,14 Ag disks,15 and Ag triangle nanoparticles,4,16 there is great interest in developing new methods for making nanoparticles with control over shape and size. Herein, we report a new synthesis of disk-shaped Ag nanoparticles using polystyrene spheres as templates.

An aqueous colloidal suspension of carboxylate-functionalized polystyrene (PS) spheres was purchased from Interfacial Dynamics Corporation. Fresh Ag solution containing 10 wt % AgNO 3 and 6% ammonium hydroxide was prepared. Briefly, 160 μL of 110-nm diameter PS spheres and 75 μL of Ag solution were added to 60 mL of somewhat aged N,N-dimethylformamide (DMF). Then, the solution was heated with stirring on a hotplate. Within 8–12 min, the solution color changed from yellow through red to purple, after which the temperature was quickly reduced via a cold-water bath. The product was purified by gradient centrifugation and then kept at 4 °C.

A rich variety of recipes are now available for making Ag nanoparticles in solution. DMF is one of the standard organic compounds used both as solvent and reducing agent. The reduction of Ag + ions in DMF can take place at room temperature, but the reaction rate is markedly increased at higher temperatures. It is also known that DMF slightly decomposes to a more easily oxidized amine upon aging or upon catalytic decomposition with solid base. The availability of the amine evidently accelerates the reduction of silver ions. (We found that dialkylamines are ineffective as additives to fresh DMF but that added hydroxyl-terminated alkylamines do facilitate nanoparticle formation.) Colloidal Ag particles prepared using DMF are usually spherical with a plasmon absorption band centered at 415 nm.17,18 When colloidal polystyrene is included in the preparation, a set of color changes is observed. The final UV–vis spectrum (Figure 1) shows bands at λmax = 340 (weak) and 574 (strong), with other peaks between 430 and 470 nm.

Transmission electron microscopy (TEM, Figure 2A) of a fresh sample shows individual and aggregated polystyrene particles
inherently covered by silver disks that are randomly oriented on the particle surface. The disk shape was verified by tilting the TEM sample plane from $-30^\circ$ through $0^\circ$ to $+30^\circ$ (see Figure 2B), revealing the three-dimensional structure of the nanoparticles. At this stage almost no Ag particles unattached to polystyrene are seen. The geometry of the attached particles suggests that they grow anisotropically on the surface of PS spheres. The presence of edge-oriented disks, appearing as rodlike shapes in the TEM images, allows measurement of their thickness (9.0 $\pm$ 1.0 nm). The average disk diameter is 36 $\pm$ 8 nm.

The TEM image in Figure 3 shows that after one month of aging, most of the PS mesospheres are dissolved, yielding large quantities of unattached Ag nanodisks. The ability to dissolve the template particles without destroying the disk structures could be important for advanced applications. From Figure 3, the fraction of Ag particles present as disks exceeds 90%; only small quantities with other shapes, for example, triangles, have been observed.

It is worth mentioning that, during the initial synthesis of Ag nanodisks, because the reaction requires only several minutes the polystyrene particles are not destroyed. Under surfactant-free conditions, the particles appear to play an essential templating role. We postulate electrostatic binding (adsorption) of Ag ions by surface carboxyl groups of the mesospheres. Upon reduction, the adsorbed Ag atoms presumably serve to nucleate metal-particle formation, a process that is accelerated by temperature elevation. Once nucleation is initiated, the mesospheres may block growth in one direction, effectively templating growth in another (lateral) direction.

The available microscopy also suggests that anisotropic growth occurs between PS mesospheres, leading to aggregation of the particles present as disks exceeds 90%; only small quantities with other shapes, for example, triangles, have been observed. It is worth mentioning that, during the initial synthesis of Ag nanodisks, because the reaction requires only several minutes the polystyrene particles are not destroyed. Under surfactant-free conditions, the particles appear to play an essential templating role. We postulate electrostatic binding (adsorption) of Ag ions by surface carboxyl groups of the mesospheres. Upon reduction, the adsorbed Ag atoms presumably serve to nucleate metal-particle formation, a process that is accelerated by temperature elevation. Once nucleation is initiated, the mesospheres may block growth in one direction, effectively templating growth in another (lateral) direction.

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