Polygonal gold nanoplates in a polymer matrix†

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Polygonal gold nanoplates are generated *in situ* in poly(vinyl alcohol) film through thermal treatment, the polymer serving as the reducing agent and stabilizer for the nanoparticle formation and enforcing preferential orientation of the plates. The rare pentagonal as well as the more commonly observed hexagonal, triangular and square/rectangle shapes are obtained by fine-tuning the Au/PVA ratio and the time and temperature of fabrication.

Properties of nanocrystals are strongly influenced by their size, shape and assembly. Synthesis that enables control over these attributes and generates novel geometries are of fundamental interest. The 'bottom-up' approaches to metal nanoparticles are mostly based on the colloidal route and the size and shape control are often rendered through the choice of capping agents or seeding protocols. We envisaged that the growth of nanoparticles inside anisotropic environments such as thin solid polymer films would be a simple and convenient approach to gain enhanced control of nanoparticle shape. Such *in situ* fabrications offer additional advantages such as the production of free-standing films[1] for device applications and the possibility of further optical and mechanical manipulations.[2] These also avoid potential health hazards of inhalable nanoparticles[3] and a judicious choice of the polymer facilitates environmentally safe synthesis[4] without the requirement of additional reducing/stabilizing agents.

Gold nanoparticles with a range of shapes including triangles,[5] squares/cubes,[6] hexagons,[7] rods[8] and tadpoles[9] are known. Even though there is a report of faceted nanocrystals with a few possessing pentagonal faces,[10] a route to regular pentagonal gold nanoplates is conspicuously absent. Many methods are available for the synthesis of gold nanocrystals,[11] including those carried out inside confined spaces;[12] however, selective formation of several shapes by small variations in a single process are rare.[7] Addressing the latter question, we have explored the *in situ* synthesis of gold nanoparticles in spin-cast poly(vinyl alcohol) (PVA) films through mild thermal treatment. The chemistry involved and the method we have developed[13] are simple, efficient and environmentally safe. It leads to free-standing films with embedded nanoparticles possessing the various advantages listed above. Most significantly, it is shown now to provide facile control on the particle shape leading to triangular, square/rectangular, *pentagonal* and hexagonal nanoplates and several other shapes and patterns. Additionally, the nanoplates show preferential orientation in the thin films.

Aqueous solutions of $HAuCl_4$ and PVA (average MW ~ 20,000, % hydrolysis = 86) were mixed; different Au/PVA weight ratios were investigated.† The solutions were spin-coated on glass or quartz substrates directly or with a pre-coating of polystyrene (PS). Nanoparticles were generated by heating the films; temperatures, 100–170 °C and heating times, 5–60 min were explored. PVA acts simultaneously as the reducing agent, stabilizer for the nanoparticles and the matrix for immobilization and oriented growth; the by-products of the reaction also could play a role in controlling the particle growth. The thickness of the Au-PVA and PS layers are ~1.4 and ~4.0 μm, respectively. The Au-PVA/PS films can be peeled off as free-standing films. Alternately, the PS layer could be dissolved in toluene to release the Au-PVA film which was directly examined in a transmission electron microscope (TEM) without the need for microtoming.† Electronic absorption spectra were recorded using Au-PVA on quartz substrate.

The *in situ* formation of gold nanoparticles in the PVA film is demonstrated by the emergence of the plasmon absorption discussed later. Since no additional reducing agents are employed, PVA alone is available for the reduction of the $AuCl_4^-$ ions. The polyol process is a popular method for the synthesis of metal nanoparticles. Ethylene glycol is often employed for the reduction of metal ions to form the nanoparticles; examples include silver,[14–16] platinum[17] and ruthenium.[18] PVA has been used as the reducing agent in the synthesis of silver[13,19] and gold[20] nanoparticles; reduction of $AuCl_4^-$ to gold nanoparticles has been reported to occur slowly at room temperature.[20] In the spin-cast films we have studied, the heating will enhance the reaction. FT-IR spectra of the films provide insight into this process.† PVA/PS film showed characteristic absorptions at 3347 and 1732 cm^{-1} assignable to hydroxy and carbonyl groups stretching vibrations respectively; the latter arises due to the remnant acetyl groups present in the PVA. The unheated $HAuCl_4$-PVA/PS film shows a considerably reduced carbonyl peak, possibly as a result of the interaction with the acid protons.[21] Most significantly, on heating the film, the carbonyl peak appears with an intensity higher than that in PVA/PS, accompanied by a marked reduction of the hydroxy peak absorption; the aromatic C=C stretch due to the PS layer at 1601 cm^{-1} could be used as a convenient internal standard to monitor peak intensity variations. The IR spectral changes together with the appearance of the gold nanoparticle plasmon absorption indicate that the alcohol groups of the PVA reduce the metal ions, themselves getting oxidized to ketones in the process. HCl is the by-product and the protons are likely to interact with the keto groups; however, their larger population leads to the improved intensity. The mechanism deduced from these observations is similar to that proposed for the formation of metal nanoparticles by ethylene glycol reduction.[14]

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† Electronic supplementary information (ESI) available: Details of synthesis and film fabrication, FT-IR studies, photographs of the nanoparticle-embedded films and TEM and electron diffraction data. See http://www.rsc.org/suppdata/cc/b5/b500536a/

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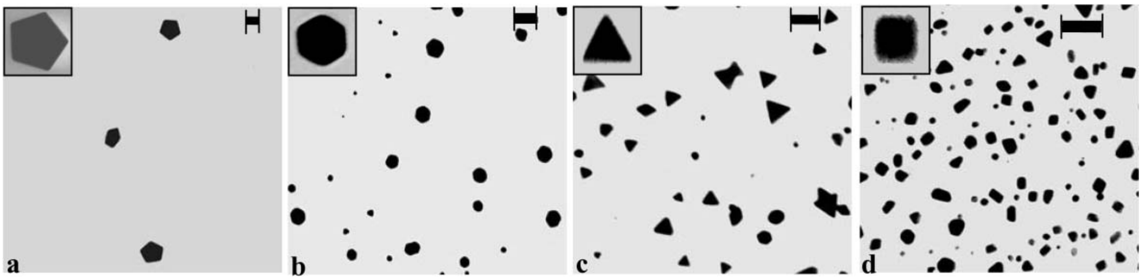

Fig. 1 TEM images of Au-PVA films with polygonal nanoplates generated under different conditions. The Au/PVA ratio, temperature of heating (°C) and time of heating (min) are indicated in that order in parenthesis: (a) pentagons (0.04, 170, 5); (b) hexagons (0.08, 130, 30); (c) triangles (0.12, 100, 60) and (d) squares/rectangles (0.18, 100, 60). Scale bar = 50 nm. Inset shows enlarged view of a single nanoplate with the dominant shape in each case.

The thin film nature of the polymer matrix enforces a plate morphology on all the particles generated, with preferential orientation parallel to the substrate. The shapes and sizes of the nanoplates are found to be sensitive to the Au/PVA ratio and time and temperature of heating. When both the concentration and temperature are low, no particles are formed, whereas when both are high, a mixture of plates with different shapes is obtained. Careful control of these factors led to the enrichment ($\sim$70–80%) of specific polygonal shapes. Fig. 1 illustrates the prominent polygonal nanoplates obtained and the conditions favoring their formation. Regularity is observed in the evolution of the shape; pentagons, hexagons, triangles and squares/rectangles are formed with increasing concentration, decreasing temperature and increasing heating time. The rationale behind the observed sequence is not clear at present. The number of particles is commensurate with the concentration. The perfect regular pentagons deserve special mention. To the best of our knowledge, exclusive formation of pentagonal nanoplates of gold or any other metal has not been reported; pentagonal forms have been found only in mixtures with other morphologies,[22] in twin structures[23] or faceted crystals[10] and as tubes.[24] The restricted growth allowed by the solid polymer matrix appears to be the critical factor promoting pentagonal plate formation in the present case. The size of the polygons shows sequential variation; the sides of the pentagons, hexagons, triangles and squares/rectangles are in the range 70–85, 20–35, 15–45 and 10–25 nm, respectively. These are notably smaller than the sizes of polyhedral gold nanocrystals reported earlier,[5–9] ranging from 200 to 500 nm. The plate morphology of the nanocrystals in the PVA matrix is revealed by the slightly tilted crystals found occasionally in the films (Fig. 2). The thickness of these plates is $\sim$5–8 nm. The aspect ratios range from 15 to 2. Electron diffraction from several single nanoplates were examined. The patterns can be indexed to fcc gold with a dominant (111) face,† indicating effective inhibition of growth along the perpendicular axis. The plasmon resonances recorded for the Au-PVA films are collected in Fig. 3. The peak intensities scale with the quantity of particles (Fig. 1). The absorption maxima are blue-shifted with decreasing size, from pentagons to hexagons to triangles; the red shift with squares/rectangles could be attributed to the admixture of larger size triangles. A weak near-IR absorption is observed in all cases as a consequence of the moderate aspect ratios. Under specific conditions† a range of other shapes and patterns are observed in the gold plates generated in the polymer matrix. Examples illustrated in Fig. 4 show beautiful stress patterns in a truncated triangle and what looks like a conglomerate of polygons. It is likely that the uniform stress imposed by the polymer matrix causes the symmetric buckling of the ultrathin gold plates.[25]

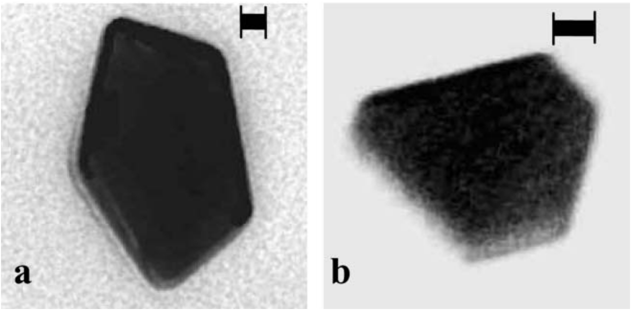

Fig. 2 TEM images of a gold pentagon and a truncated triangle found in tilted orientation in the Au-PVA film. Scale bar = 10 nm.

We have demonstrated the *in situ* generation of nanocrystals in polymer films using the matrix as the only reagent, leading to free-standing films with embedded particles of different shapes. Appreciable orientational ordering of nanoplates is obtained without the help of special templates or linker molecules. Preliminary experiments suggest that factors such as the rate of heating and temperature gradients on the film can lead to further

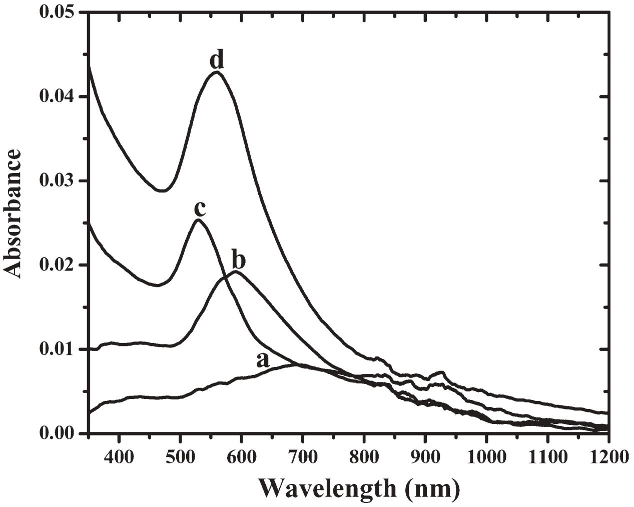

Fig. 3 Electronic absorption spectra of Au-PVA films with polygonal nanoplates: (a) pentagons, (b) hexagons, (c) triangles and (d) squares/rectangles, corresponding to the films in Fig. 1.

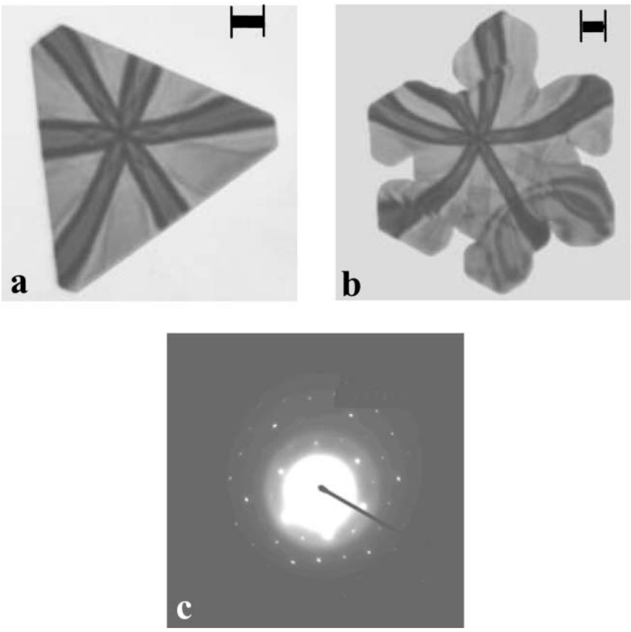

Fig. 4 (a) and (b) TEM images of gold nanoplates in PVA films, formed with stress patterns. Scale bar = 50 nm. (c) Electron diffraction of the nanoplate shown in (a).

variations in the morphology and assembly of nanoparticles. We are currently exploring the potential opto-electronic applications of these nanoparticle-embedded polymer thin films.

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