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Synthesis of gold nanoplates by aspartate reduction of gold chloride†

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Single crystal nanoplates with thickness less than 30 nm, characterized by hexagonal and truncated triangular shapes bounded mainly by {111} facets, were obtained in large quantities by aspartate reduction of gold chloride.

A growing interest is being shown in biomineralization and biomimetic synthesis[1] for the creation of nanoscale materials because environmentally benign, 'green' conditions can be used rather than the extreme conditions needed for conventional chemical synthesis.[2] Crystal morphology and size have often been biologically regulated by biomolecules[3,4] or organisms.[5,6] Some fundamental investigations have revealed that biomolecules and organisms can selectively recognize inorganic surfaces or serve as matrices for inorganic growth and nucleation.[7] Bacteria,[8] silver-binding peptides[9] and silver-tolerant yeast,[10] for example, have been used to fabricate silver nanoparticles, and the morphology of gold crystals has also been influenced by polypeptides.[11] It is natural that constituent units from biomacromolecules or organisms should pose a basis for genuine biological nanofabrication. Therefore, amino acid moieties from an organic matrix may exert an influence on the specific interactions between biomolecules and inorganic materials. Here we show that biologically related small molecules, L-amino acids, can control the size and morphology of the resultant gold nanostructures.

Reactions were carried out at 25 °C under mild stirring in aqueous solution containing 0.01% tetrachloroaurate and 0.5 mg mL^{-1} amino acids for 12 h. No additional reducing agent and surfactant were needed for the synthesis of gold particles. Ultraviolet-visible (UV/Vis) spectroscopy was first used to screen crystals of gold nanostructures (Fig. S1†). The solution incubated with L-tryptophan quickly turned red in color with a very characteristic surface plasmon absorption centered at 560 nm, showing the formation of gold nanoparticles. The solution of aspartate gave two characteristic plasmon peaks centered at 570 nm and 750 nm, indicating special gold nanostructures. The gold particles prepared using amino acids were further analyzed by transmission electron microscopy (TEM) and electron diffraction. It is very interesting that the aspartate-prepared particles show a distinct shape. From TEM, the product is dominated by nanoplates (Fig. 1). The X-ray photoelectron spectroscopy (XPS) analysis reveals that the prepared nanoplates consist of elemental gold (Fig. 2). The nanoplates mainly assembled in a randomly overlapping fashion when the sample was mounted on carbon-coated copper grids, but the shape of the nanoplates can be clearly distinguished (Fig. 1a). The nanoplates, with thickness less than 30 nm measured by the comparison of the TEM images from simultaneously formed spherical and plate-shape nanoparticles, are of hexagonal and truncated triangular morphology, as clearly shown in Fig. 1b. The nanoplates have very sharp and smooth edges with average edge length 590 nm for hexagonal nanoplates (Fig. 1c) and 840 nm for truncated triangular nanoplates (Fig. 1d). To our knowledge, this is the first report on the production of large planar gold nanostructures based on biologically related small molecules. The continuous and randomly distributed pairs of lines can be seen across the faces of the flat crystals and have also been observed in gold crystals synthesized by repeating polypeptides.[11] These lines, always starting from spots and radiating down to the edges of the flat crystals, may be ascribed to bending of the thin crystals[12] or the presence of multiply twinned structures.[9,11] The insets of Fig. 1c and 1d show the electron diffraction patterns obtained by aligning the electron beam perpendicular to the planar surface of the nanoplates. The hexagonal symmetry of these pattern spots indicates that these nanoplates are single crystals bounded mainly by {111} facets.[13] On the other hand, the X-ray diffraction (XRD)

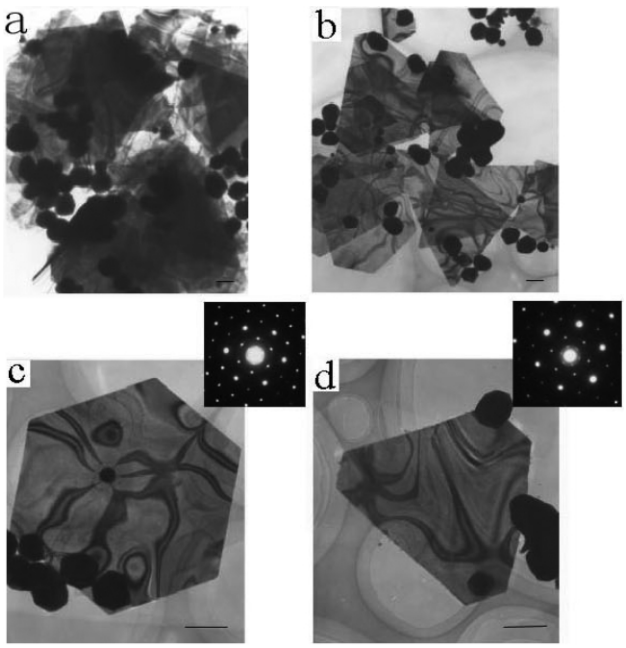

Fig. 1 Typical TEM images of a sample prepared from a reaction solution containing aspartate, showing the high- (a) and slightly lower- (b) degree assembled nanoplates during the evaporation of solvent. The representative images of individual hexagonal and truncated triangular nanoplates are shown in (c) and (d). The insets show the selected-area electron diffraction patterns. The scale bars are 200 nm.

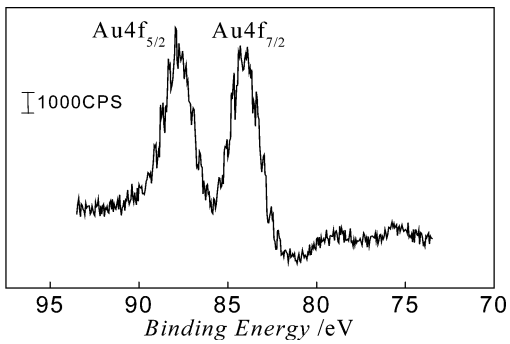

Fig. 2 XPS analysis of Au 4f orbitals of the as-prepared gold nanoplates supported on a glass slide.

† Electronic supplementary information (ESI) available: Fig. S1. UV/Visible-NIR extinction spectra of an aqueous dispersion of gold nanoparticles synthesized by tyrosine (a), phenylalanine (b), lysine (c), aspartate (d) and tryptophan (e). See http://www.rsc.org/suppdata/cc/b3/b315732f/

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pattern recorded from the batch sample is also displayed in Fig. 3, and the peaks are assigned to diffraction from the {111}, {200}, {220}, {311}, and {222} planes of fcc gold, respectively. It is worth noting that the ratio between the intensities of the {200} and {111} diffraction peaks is much lower than the conventional value (0.071 *versus* 0.53). The ratio between the intensities of the {220} and {111} peaks is also much lower than the conventional value (0.034 *versus* 0.33). These observations confirm that our nanoplates are mainly dominated by {111} facets, and thus their {111} planes tend to be preferentially oriented parallel to the surface of the supporting substrate.

However, compared to aspartate, TEM of the lysine-prepared gold particles shows spherical nanoparticles 6 ± 2 nm in diameter (Fig. 4a). Similarly, that of the tryptophan-prepared gold particles shows the presence of spherical nanoparticles 60 ± 5 nm in size with high monodispersity (Fig. 4b). However, the size distribution of the arginine-prepared nanoparticles is very wide with diameter 10 ± 5 nm (Fig. 4c). Examination of the tyrosine-prepared gold particles

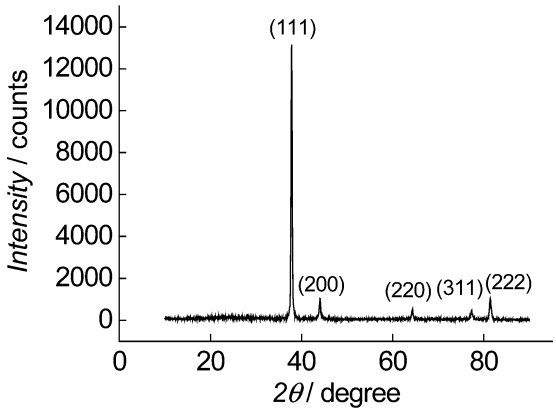

Fig. 3 XRD pattern of a batch sample synthesized by aspartate.

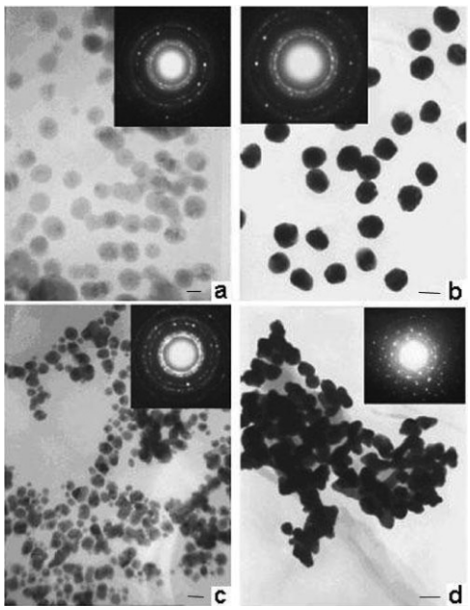

Fig. 4 TEM images of the gold nanoparticles synthesized by lysine (a), tryptophan (b), arginine (c), and tyrosine (d). The scale bars are 5 nm (a), 50 nm (b), 20 nm (c), and 100 nm (d), respectively. The insets show their selected-area-electron-diffraction patterns, respectively.

reveals the presence of spherical and rod-shaped particles (Fig. 4d). In these cases, the polycrystalline natures of the as-prepared nanoparticles are revealed by electron diffraction patterns (Fig. 4, insets). Based on these observations, aspartate may be specific for binding to facets other than {111}. This specific interaction of the amino acid with the crystal lattice structure may not only influence the surface energies but also alter the distribution of surface concentration of this species. The specific-binding amino acid also served as reductant for gold(III) at the growing crystals. The increase in the local concentration of the amino acid at the binding facets should elevate the chemically reducing environment within this local region and must bias accretion onto a face other than {111} thus increasing the area of the {111} facet. Clearly, the amino acid provides both recognition and reduction. But the facet-specific recognition may lose at elevated temperature since under boiling conditions tetrachloroaurate was reduced to yield spherical gold nanoparticles in different sizes depending on the molar ratio of aspartate to tetrachloroaurate and no other morphologies were found.[14] Nevertheless, amino acids other than aspartate show an unspecific binding to gold facets. The fact that aspartate does show such distinct shape control over the crystal growth reflects that these biologically related small molecules also have a profound influence on the gold crystal growth as macromolecules.[11]

In summary, L-amino acid-based one-pot synthesis of gold nanostructures has been described. Some size and shape controls can be exercised by different amino acids. Among natural L-amino acids, aspartate shows a very distinct capability of shape control to produce gold nanoplates. Although not yet optimized for a certain amino acid by altering the concentration ratio to fabricate other special gold nanostructures, the experimental protocols herein serve to emphasize the practical significance of certain amino acid residues from biomacromolecules or organisms in biomimetic construction of nanomaterials. This work provides a further insight into understanding the contribution from these residues for the natural process of biomineralization.

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