Peptide-mediated shape- and size-tunable synthesis of gold nanostructures

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While several biological processes have been shown to be useful for the production of well-designed, inorganic nanostructures, the mechanism(s) controlling the size and shape of nano and micron size particles remains elusive. Here we report on the controlled size- and shape-specific production of gold nanostructures under ambient reaction conditions using a dodecapeptide, Midas-2, originally selected from a phage-displayed combinatorial peptide library. Single amino acid changes in Midas-2 greatly influence the size (a few nanometers to ~100 μm) and shape (nanoparticles, nanoribbons, nanowires and nanoplatelets) of the gold nanostructures produced, and these are controllable by adjusting the solution pH and gold ion concentration. The ability to control the shape and size of the gold nanostructures by changing the peptide structure and reaction conditions will lead to many potential applications, including nanoelectronics, sensors and optoelectronics, because of their unique size- and shape-dependent optical and electrical properties.

1. Introduction

Recent advances in nanotechnology and heightened concern for the environmental impact of nanoscale materials require the development of environmentally benign methods to synthesize nanostructures with controlled morphology and architecture. The size and shape of nanomaterials has a major influence on their physical and chemical properties, and the ability to control these parameters remains a great technological challenge with important implications for nanoscale science and engineering [1].

Over the last 30 years [2] several chemical synthesis methods have been developed to produce semiconducting and metallic nanostructures. These methods, however, have several major drawbacks, including the use of toxic chemicals, extreme synthesis conditions involving high operating temperatures and/or pressures and highly acidic or alkaline reaction conditions. In contrast, several natural biological systems have been shown to produce inorganic materials under physiological conditions, including the zero- and two-dimensional nanostructures of magnetite [3], metal sulfides [4], selenium [5], tellurium [6], gold [7] and silver [8] and the one-dimensional nanostructures found in tellurium nanorods [9] and arsenic sulfide nanotubes [10]. Relative to chemical routes, biological systems appear to be extremely adept at directing the synthesis and assembly of inorganic nanostructures at near ambient conditions, in environmentally compatible solutions and utilizing ecologically friendly reducing and capping agents [11].

Engineered peptides that recognize inorganic surfaces have been shown to be useful for the assembly and synthesis of inorganic nanostructures [12–18]. Brown et al. used gold binding polypeptides (GBP1), initially identified in a cell surface display library, to synthesize micron wide and nanometer thick platelets and nanoparticles of gold [19] and Xie et al. isolated a protein from the green algae Chlorella vulgaris that formed nanometer thick gold platelets at high yield [11]. Nanoplatelets are two-dimensional nanostructures with a large aspect ratio (>100) between the width and thickness (<100 nm) of the platelets. Despite the variety of structures produced by biological systems, most synthesis products do not meet the requirements needed for engineering applications, which frequently require uniformly precise nanomaterials with exacting and specific dimensional characteristics. Until now, however, selectively controlling the size and shape of nano and micron size particles has remained elusive.

In the studies reported here we describe the use of the dodecapeptide Midas-2 (TGTSVLIATPYV), originally selected from a
phage-displayed combinatorial peptide library, to synthesize gold nanostructures in a precise and controllable manner. The size, shape and structural architecture of the resulting nanoparticles, nanoribbons, nanowires and nanometer thick platelets were controlled by manipulating the peptide's primary sequence and solution pH. The size of the nanostructures, which varied from a few nanometers to ~100 μm, was controlled by adjusting the concentration of gold ions.

These newly designed gold nanostructures have many potential applications, including transducers for biological and chemical sensors, contrasting agents for electron microscopic and medical imaging, highly conductive interconnections for single electron transistors and catalysts for carbon monoxide and hydrogen oxidation.

2. Materials and methods

2.1. Chemicals and peptides

HAuCl₄·3H₂O and metallic gold powder were purchased from Aldrich (St Louis, MO). Sodium hydroxide and hydrochloric acid solution were purchased from Fisher Scientific (Pittsburgh, PA). Nanopure water used was prepared using a Milli-Q system from Millipore (Billerica, MA) and autoclaved to avoid microbial contamination. All reagents were used as received with no further purification steps. All peptides used were purchased from Any Gen Co. Ltd. (Gwangju, Korea).

2.2. Isolation of gold binding peptides

A random phage display peptide library was purchased from New England BioLab (Ph.D.-12 phage display peptide library kit, Ipswich, MA). The manufacturer's instructions were followed for all steps to isolate gold binding peptides. However, metallic gold powder in an Eppendorf tube was directly used as the target material for isolation of binding phages instead of a substrate coated with the target material or a solution of phage with a target attached by affinity tags.

2.3. Change in primary structure of gold nanostructure synthesizing peptide

A gold binding and synthesizing peptide, comprising 12 amino acids (TGTSVLATPYV), obtained by the combinatorial peptide phage display techniques, was named Midas-2. In order to investigate the role of each amino acid in Midas-2 in the synthesis of gold nanostructures, 12 different Midas peptides were synthesized substituting each amino acid of Midas-2 with glycine. In addition to glycine scanning of Midas-2, the glycine located at position 11 in the peptide Midas-11 was replaced with each of the other 19 amino acids, termed Midas-11amino acid.

2.4. Synthesis of gold nanostructures by Midas peptides

Midas-2 at 0.2 mg ml⁻¹ was dissolved in phosphate buffer (10 mM, pH 7.5). HAuCl₄ was added to the solution to a final concentration of 0.5 mM and the final reaction volume adjusted to 1 ml, followed by incubation at room temperature in the dark for 3 days. In order to remove any effect of the solute in the phosphate buffer on the formation of gold nanostructures, deionized water was used instead of phosphate buffer with incubation for 3 days at 37 °C and an initial solution pH of 3.0. To investigate the effect of pH on gold nanostructure synthesis by peptide Midas-11 the initial pH condition was adjusted with 5 M NaOH and concentrated HCl prior to addition of the peptide solution to deionized water containing HAuCl₄. The pH values were fixed at 1.0, 3.0, 4.5, 5.7, 8.1 and 9.0 with 0.5 mM HAuCl₄ and 1.0, 1.7, 3.0, 5.0, 5.4 and 7.0 with 30 mM HAuCl₄ for 3 days incubation at 37 °C. The gold ions remaining in the supernatant of the reaction solutions were measured using AAnalyst 800 (PerkinElmer, Waltham, MA) after the supernatant had been centrifuged and diluted with 10% HCl solution.

2.5. Structural characterization of synthesized gold nanostructures

Synthesized gold nanostructures were collected by centrifugation (5415D Centrifuge, Fisher Scientific, Pittsburgh, PA) at 9300 rcf for 10 min at room temperature, washed twice with autoclaved deionized water and resuspended in 1 ml for surface plasmon resonance analysis using a UV–visible spectrophotometer (Shimadzu, Kyoto, Japan). For the structural analyses using scanning electron microscopy (SEM), transmission electron microscopy (TEM)/energy dispersive X-ray spectroscopy (EDS) and atomic force microscopy (AFM) the washed gold nanostructures were dispersed in 100 μl deionized water. The samples for SEM analyses were prepared by placing ~5 μl of the suspension on a silicon wafer followed by drying in air. Secondary SEM images were obtained using a SEM/E-beam lithography system (Leo SUPRA 55, Carl Zeiss, Germany) with the accelerating voltage fixed at 10 keV. The SEM samples were also subjected to AFM analyses. AFM images were obtained using an Innova Scanning Prove Microscope (Veeco, Plainview, NY). TEM analyses were conducted in a FEI CM300 TEM (Philips, Briarcliff Manor, NY) at an accelerating voltage of 300 keV. The samples were prepared by depositing a droplet of a water suspension of the gold crystals on carbon-coated Cu support grids that were subsequently dried in air. Selected area electron diffraction (SAED) and conventional bright field as well as high resolution imaging were utilized to study the size, shape, distribution and crystallographic orientation of the gold particles and their aggregates.

3. Results

3.1. Isolation of gold nanoparticle-forming peptide and substitution of each amino acid in the peptide with glycine

The dodecapeptide Midas-2, which was selected from a M13 phage-displayed, combinatorial, peptide library, formed monodisperse spherical gold nanoparticles after 3 days incubation at room temperature with 0.5 mM HAuCl₄ and 0.2 mg ml⁻¹ Midas-2 peptide in 10 mM phosphate buffer (pH 7.5). The gold nanoparticles, with an average size of 16 nm, showed a surface plasmon resonance (SPR) band at around 532 nm and a red color (Fig. 1) [20]. Midas-2 contained a central hydrophobic tetrapeptide (VLIA) flanked by two polar tetrapeptides (TGTS and TPYV) with a calculated pl of 5.18 (Fig. 2).

To remove any possible interference by phosphate buffer from the reaction, the solution was changed to deionized water with an initial solution pH of 3.0 at 37 °C for 3 days incubation. Interestingly, polyhedral gold nanoparticles with an average width of ~520 nm and a small number of trigonal, truncated trigonal and hexagonal single crystalline gold platelets were produced when Midas-2 peptide was incubated with 0.5 mM HAuCl₄ in deionized water (Fig. 2a and Supporting information Fig. S3). The formation of metallic gold was confirmed using EDS and SAED analyses in TEM (Fig. 3 and Supporting information Fig. S1).

To determine the relationship between the primary sequence of the Midas-2 peptide and the formation of gold nanostructures, each amino acid in Midas-2 was individually substituted with glycine, producing a set of 12 different mutated peptides (Fig. 2 and...
Supporting information Fig. S2). As expected, the calculated pI values of the majority of substituted peptides remained at 5.18, except for Midas-1 and Midas-11, which had pI values of 5.52 and 5.19, respectively. Surprisingly, when incubated at pH 3 at 37°C with 0.5 mM HAuCl₄ the peptide Midas-11, in which the tyrosine at position 11 was replaced by glycine, produced large trigonal, truncated trigonal and hexagonal gold platelets with widths of ~24 μm and heights of 30–150 nm. Under the same conditions the rest of the mutated Midas peptides produced a mixture of trigonal, truncated trigonal and hexagonal gold platelets and polygonal gold nanoparticles with variable shapes and sizes (Fig. 2 and Supporting information Fig. S2), from submicron to a few micrometers in size (Supporting information Fig. S3).

Due to the production of gold nanostructures of different shapes and sizes the reaction solutions showed different SPR band patterns. The SPR band at 520–580 nm was significantly reduced as the ratio of platelets to nanoparticles increased. No significant SPR band was observed in the gold nanostructures produced by Midas-11 (Fig. 2b and Supporting information Fig. S4).

The substitution of each amino acid in the Midas-2 peptide by glycine also resulted in a reduction in the concentration of gold ions in the reaction solution. Moreover, substitution of the
N-terminal amino acid threonine and the conformationally rigid amino acid proline by glycine, present in peptides Midas-1 and Midas-10, respectively, produced a substantially greater quantity of gold nanostructures after 3 days incubation than did the remainder of the Midas peptides tested (Fig. 2c).

3.2. Effect of pH and gold ion concentration on the production of gold nanostructures by Midas-11

The effect of reaction conditions, pH and gold ion concentration on the formation of gold nanostructures by Midas-11 was investigated. The various gold structures synthesized by Midas-11 at different pH values are shown in Figs. 3 and 4, where the concentration of HAuCl₄ was fixed at 0.5 and 30 mM, respectively. Both the solution pH and gold concentration had a dramatic influence on the shapes and sizes of gold nanostructures synthesized by Midas-11. The nanostructures produced were polycrystalline, polyhedral gold nanoparticles (Fig. 3d), peanut-shaped aggregates (Fig. 3e), large hexagonal or trigonal platelets (Figs. 3a and 4b and Supporting information Fig. S6) from ~10 to ~100 μm in width, one-dimensional gold nanowires from 10 to 20 nm in width (Fig. 3c), long single crystalline nanofibers or extended long single crystal nanoribbons consisting of trigonal segments joined together at the vertices and sides (Fig. 4c–e). At pH >7 with 0.5 mM HAuCl₄ Midas-11 formed random aggregates of small iso- metric gold nanoparticles ranging from 5 to 20 nm in diameter with single or double narrow SPR peaks between 500 and 600 nm and pink or purple colored solutions (Fig. 3f and Supporting information Fig. S5). At pH 5.7 with 0.5 mM HAuCl₄ at 37 °C Midas-11 formed one-dimensional gold nanowires of 10–20 nm diameter. In contrast, at pH ~5 and with concentrations of HAuCl₄ ranging from 0.5 to 30 mM Midas-11 formed extended gold nanoribbons consisting of trigonal segments (Fig. 4d) and large trigonal or hexagonal platelet crystals at one end of the ribbon (Figs. 3b and 4c). The SAED patterns of these “kite-shaped” ribbons indicated that the entire structures were composed of single crystals mixed with isolated trigonal or hexagonal platelets crystals. The “kite-shaped” ribbons were elongated parallel to the (2 1 1) direction and the sides of the trigonal or hexagonal facets were parallel to the (1 1 1)-type faces. The ribbons formed with 30 mM HAuCl₄ were tens of microns in length and had widths ranging from 100 nm to a few micrometers (Fig. 4d and e and Supporting information Fig. S7). The hexagonal or trigonal platelets formed were also relatively large, with sides ranging from hundreds of nanometers to tens of microns. The UV–vis spectra of the reaction solution at a HAuCl₄ concentration of 0.5 mM showed broad absorption over the 500 nm range, which was attributed to the anisotropic gold nanowires and ribbon structures produced (Fig. 3b and c) [21]. The color of the solution varied from grey to dark purple (Fig. 3f and Supporting information Fig. S5). At pH ≤3 Midas-11 formed large, nanometer thick gold platelets with hexagonal or trigonal shapes. The width of the platelets varied from several microns to ~100 μm at HAuCl₄ concentrations of 0.5 and 30 mM. The width of the platelets was controllable by adjusting the gold ion concentration; a maximum width of 89 μm was observed with 30 mM HAuCl₄ at pH 1.7 (Supporting information Fig. S6). At pH 3 the trigonal and hexagonal platelet crystals which were produced with Midas-11 in 30 mM HAuCl₄ had well-developed extended flat {1 1 1}-type faces, with minor growth steps. The terrace-like steps were normally formed during spiral growth. Analysis of the surface of hexagonal platelets using AFM indicated that the crystal platelets were likely formed by spiral growth around a screw dislocation (Fig. 5a). The sides of the trigonal or hexagonal plates were defined by (2 1 1)-type faces, and the vertices of the trigons or hexagons were along the {1 1 1} direction and the {1 1 1} zone axis of the platelets, which was normal to the extended flat faces, showed superstructure reflections at 2.5 Å due to twinning on the {1 1 1} planes.
3.3. Influence of amino acid substitutions at position 11 of Midas-11 on the formation of gold nanostructures

Since the Midas-11 peptide produced exceptionally large, nanometer thick gold platelets at pH 3, we also examined the influence of each of the other 19 amino acids at position 11 of Midas-11 (termed Midas-11 amino acid), on the formation of gold nanostructures. After amino acid replacement the pI values of the Midas-11H, Midas-11K and Midas-11R increased noticeably to 6.40, 8.41 and 9.41, respectively, compared to pI 5.19 for Midas-11. In contrast, the calculated pI values of Midas-11D and Midas-11E decreased to 3.8 and 4.0, respectively. Based on the results obtained from the reaction of HAuCl4 with the modified peptides at pH 3 and 37°C (Fig. 6), the general rules controlling the sizes of gold nanostructures synthesized by Midas-11 amino acid could be deduced as follows.

(1) Midas-11 with substitution of glycine 11 by cysteine, tryptophan or methionine, which have previously been shown to bind metallic gold [22], produced substantially greater amounts (46–68 μg) of gold in the reaction solution than did the other amino acids. These peptides formed trigonal, truncated trigonal and hexagonal gold platelets ≤1–2 μm in size, as well as small amounts of irregular polygonal gold nanoparticles (Fig. 6b and Supporting information Figs. S10 and S11).

(2) In contrast, Midas-11G, Midas-11N, Midas-11F and Midas-11D (Fig. 6d and e and Supporting information Fig. S10) formed gold platelets in the 10 μm size class and deposited 10–20 μg of gold in the reaction solutions (Supporting information Fig. S11).

(3) Substitution of glycine 11 in the Midas-11 peptide by the polar and basic amino acids, histidine, lysine and arginine caused the pI to increase to 6.40, 8.41 and 9.41, respectively. These substitutions produced relatively lower quantities of gold than did the other amino acids and resulted in the formation of gold platelet-like structures with irregular shapes and uncontrolled sizes (Fig. 6f and Supporting information Fig. S10).

4. Discussion

In the studies reported here we have shown that the dodecapeptide Midas-2 formed monodispersed, spherical gold nanoparticles after 3 days incubation at pH 7.1 with 0.5 mM HAuCl4 in phosphate buffer (pH 7.5). The particles had an SPR band at approximately 532 nm, possibly due to interaction between the gold nanoparticles, where the peak position depends on the diameter of the nanoparticles [23]. Midas-2 did not contain sulfur- or amine-containing amino acid residues, which are known to covalently bind to the surface of gold particles [24], or other motif sequences previously found in gold binding proteins [25]. Moreover, the pI of Midas-2 was 5.18, which was much lower than other reported gold binding peptides [25]. Taken together, these results indicate that Midas-2 represents a new class of gold nanoparticle-forming peptide.
It is worth noting that the trigonal and hexagonal platelet crystals that were produced with 30 mM AuCl₄ had extended flat \{1 1 1\}-type faces, and the SAED patterns along the \{1 1 1\} zone axis of the platelets had superstructure reflections due to twinning on the \{1 1 1\}-type planes. Twinning of large and small trigonal and hexagonal platelets has previously been reported [26]. The development of distinctly different crystal shapes and sizes in the experiments carried out using Midas-11 peptide and solutions with different pH values suggested that the kinetics of nucleation and growth likely control the final size and shape of the gold particles [27]. This hypothesis was supported by the time-dependent studies.

Under alkaline conditions at pH >7 the gold particles developed fine nanometer size crystals and aggregates, suggesting that the nucleation rate was high but subsequent growth was strongly reduced and the particles did not grow significantly beyond their original nucleation size. In contrast, the shape and size of the gold nanostructures at pH <3 were quite different and large, hexagonal or trigonal shaped platelets were formed. At pH <3 the nucleation rate was higher, since more twinned and multiple twinned particles were present. The size and morphology of the synthesized gold particles evolved in relation to time following initial synthesis (Supporting information Fig. S8). Synthesis experiments with incubation times of 6, 12, 24, 48 and 72 h were carried out in deionized water, with fixed conditions of pH 3, 0.5 mM HAuCl₄, 0.2 mg ml⁻¹ Midas-11 and 37 °C. After incubation for 6 h three types of gold particles were formed: (i) rarely produced trigonal and hexagonal platelets with diameters of ~500 nm; (ii) isometric crystals of trigonal and hexagonal platelets ~50–100 nm in size, representing single crystals or multiple twinned crystals; (iii) isolated, 2–5 nm nanoparticles, representing mostly single crystals with rare twinned crystals (Supporting information Fig. S8). The large platelets of trigonal or hexagonal shape became more abundant with increasing incubation time, with the gold platelets increasing in size up to 5 and 20 µm after 24 and 72 h, respectively (Supporting information Fig. S8c).

In contrast, the nanometer size particles decrease in abundance with time of incubation. Small holes were clearly visible inside the...
hexagonal plates, which in most cases had faceted outlines following the hexagonal edges of the platelets (Supporting information Fig. S8b–S8d). These particles also exhibited overlapping hexagonal terraces, suggestive of screw dislocation-assisted growth. As predicted by theoretical consideration [28], and later confirmed by experiments [29,30], screw dislocation growth may cause considerable strain at the core of the dislocation line. The growing crystals will tend to free themselves from the strained part, which for crystals growing in solution results in dissolution of the strained region along the dislocation line and the formation of hollow cylinders. The trigonal and hexagonal thin plate crystals were defined by sides parallel to \{1 \ 2 \ 1\}-type faces, which could be understood in the light of the fact that the growth of the original isometric nuclei took place in an almost two-dimensional environment controlled by the structure of the twins, which can be described as a rotation around an axis normal to the \{1 \ 1 \ 1\} plane. The kinks formed at the edges of the twins are favorable nucleation sites that facilitate subsequent growth of the crystals [26]. In the \{1 \ 1 \ 1\} plane the \{1 \ 1 \ 0\} -type directions are parallel to rows of atoms where the distance between Au atoms is least. Bonding between Au atoms along such close packed rows will require minimum energy. This will induce preferential growth along the \{1 \ 1 \ 0\} direction and, as a consequence, it will cause development of the \{1 \ 2 \ 1\} faces and disappearance of the \{1 \ 1 \ 0\} faces due to their fast growth rate. The growth rate increased compared with the high pH conditions and large platelet crystals were formed that were predominantly controlled by twinned crystals and screw dislocations. Also noteworthy is the fact that the total amount of gold precipitated was low at both low and high pH. The nucleation and growth rates were both high at pH 4.5, and twinning and defect controlled growth again took place. In addition, the peptide chains, which have high reducing activity under these conditions, not only facilitate a fast nucleation process, but also serve as templates to bind the nuclei along the chains, resulting in the formation of extended ribbons.

The time series experiment at pH 4.5 also clearly elucidated the growth mechanism of the gold nanoribbons. After 6 h treatment (Supporting information Fig. S9a) formation of two types of crystals could be observed, the first were small, 2–5 nm, isometric single crystals and the second polycrystalline aggregates in the form of twisted ribbons consisting of single 10–30 nm crystal segments. The aggregates reached lengths of \( \geq 100 \) nm and after 12 h incubation the product consisted of almost uniformly long, up to 1 μm, randomly intergrown, twisted ribbons composed of small, 10–30 nm diameter crystals (Supporting information Fig. S9b). After 24 and 48 h synthesis the ribbons increased in length, but the width did not change significantly (Supporting information Fig. S9c and S9d). At this stage one end of the ribbons usually developed into a region with increased width, which also clearly showed single crystal character. This trend continued during the 72 h experiment and the ribbons become straighter and the length and width of the single crystal region at their tips increased (Fig. 3e and 3f). The tail of the ribbons still showed polycrystalline character, which demonstrates that conversion to the single crystal ribbon was unidirectional from the “head” towards the tail.

From the time series experiments at pH 4.5 it was clear that nucleation starts in the form of small, randomly distributed crystals. Crystal transformation took place during the early process of crystal ripening, where the isometric nuclei were aligned along the peptide chains and formed twisted ribbons of individual crystals that appeared to be randomly joined into a single ribbon. As the reaction progressed the twisted ribbons gradually transformed into more straight chains with single crystal character. Since the ribbons were formed of triangular segments, this suggests that growth of the nuclei was controlled by their twin structures, facilitating development of platelet crystallites, which subsequently interacted at a later stage to arrange themselves into single crystal ribbons by an Ostwald ripening mechanism [21]. The “head” of the ribbons developed in a lateral dimension to a much greater extent compared with the body of the ribbon, most likely due to the spatially restricted supply of Au nuclei and ad-atoms. In addition, it is likely that the development of a platy habit, with exposed fast growing faces, further accelerated crystal growth that led to the formation of large “heads” and thin tails.

The results from the present study also indicate that the primary peptide sequence had a major influence on the structure of the gold nanostructures produced. This is best exemplified by Midas-11, in which the tyrosine at position 11 of Midas-2 was replaced by glycine. Previously, tyrosine was shown to play a fundamental role in the reduction of Au(III) to Au(0) by a number of tyrosine-containing peptides [31]. The fact that Midas-11 formed trigonal, truncated trigonal and hexagonal gold platelets with...
widths of ~24 μm and heights of 30–150 nm at pH 3 indicated that the context of the amino acid sequence, in addition to the role played by each amino acid in the peptide [31], is also an important factor in forming and controlling the gold nanostructures. As shown in Fig. 6 and Supporting information Figs. S10 and S11, a change of glycine at position 11 of Midas-11 for each of the other 19 amino acids also altered the gold nanostructures formed. This may allow control of the size and shape of the gold nanostructures produced and will be useful for application-specific production of precise gold architectures.

There have been only limited reports that peptides can reduce Au(III) to Au(0) and form gold nanoparticles. Brown et al. [25] reprecise gold architectures.

ALTERATION OF THESE PARAMETERS WAS SHOWN TO RESULT IN THE PRODUCTION OF DIFFERENT GOLD NANOSTRUCTURES. AS SHOWN IN Fig. S4, GOLD NANOPLATELETS, SINGLE CRYSTALLINE NANOFIBERS OR EXTENDED LONG SINGLE CRYSTAL NANOribbons consisted of trigonal segments joined together at the vertices and sides. More importantly, the variation in size and shape of the nanostructures produced by Midas-11 was not random, but appeared to be directly controlled by the experimental parameters tested. Therefore, the peptide-mediated synthesis of gold nanostructures described here may provide a versatile and environmentally benign method for the production of shape-specific nanostructures for a variety of applications.

While the shape of the gold particles was controllable by pH, the width of the gold platelets was tunable by adjusting the gold ion concentration. With 30 mM HAuCl₄ at pH 1.7 the Midas peptide produced gold nanostructures with a maximum width of ~89 μm. Previously, gold crystal plates up to 100 μm could only be synthesized using a binary mixture of didodecyldimethylammonium bromide and dibutylamine in a 1:1 M ratio [33].

5. Conclusions

In conclusion, peptide-mediated control of the size and shape of gold nanostructures can be substantially affected by changing the reaction conditions, including pH and the concentration of HAuCl₄. Alteration of these parameters was shown to result in the production of gold nanostructures of diverse shapes (nanostructures, nanowires, nanoribbons, kites and tail structures and nanometer thick platelets) and sizes (from a few nanometers to close to 100 μm). The results from these studies indicate that the synergistic effects of both primary peptide structure and reaction conditions can be used to modulate the size and shape of gold nanostructures, some of which may provide crucial structures for the production of the next generation of nanodevices. The tunability of the gold nanostructures produced via changes in peptide structure and reaction conditions will likely find wide applications for the construction of a variety of nanoarchitectures.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.actbio.2010.01.019.

EDS analysis of the gold nanostructures synthesized by Midas-2 in deionized water (Fig. S1); TEM images synthesized by peptide Midas-1, -4, -7, -8, -9, -10 and -12 (Fig. S2); the average sized of gold nanoplatelets (Fig. S3) and UV–vis spectra of the reaction solution (Fig. S4) of 12 peptides; UV–vis spectra of the reaction solution with 0.5 mM HAuCl₄ at different pH values (Fig. S5); SEM image of the largest gold nanoplate (Fig. S6); SEM images of the gold nanostructures synthesized by peptide Midas-11 in 30 mM HAuCl₄ at different pH values (Fig. S7); TEM images of the gold nanostructures synthesized by peptide Midas-11 with 0.5 mM HAuCl₄ for different incubation times at pH 3 (Fig. S8) and pH 4.5 (Fig. S9); SEM images of the synthesized gold nanostructures (Fig. S10), average size of the nanoplatelets (Fig. S11) and UV–vis spectra of the reaction solution (Fig. S12) for 20 peptides.

Appendix B. Figures with essential colour discrimination

Certain figures in this article, particularly Fig. 5, is difficult to interpret in black and white. The full colour images can be found in the on-line version, at doi:10.1016/j.actbio.2010.01.019.

References


