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Facile synthesis of micrometer-sized gold nanoplates through an aniline-assisted route in ethylene glycol solution

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Abstract

Micrometer-sized edge, polygonal gold plates of several 10 nm thickness, called gold nanoplates, have been synthesized in large quantities through simply introducing aniline to a heated ethylene glycol (EG) solution of hydrogen tetrachloroaurate ($HAuCl_4 \cdot 4H_2O$) without any other capping agents or surfactants. Electron diffraction (ED) and X-ray diffraction (XRD) patterns identified the as-prepared gold nanoplates were single crystals bound primarily by {1 1 1} facets. The study of the optical properties showed these large gold nanoplates had strong absorption in near infrared region (NIR). Investigations suggested the amount of aniline added to the reaction solution played a key role in producing gold nanoplates and the size of the gold nanoplates can be tuned by adjusting the stirring speed. The possible formation mechanism of the as-prepared gold nanoplates was also discussed.
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1. Introduction

Metal nanostructures have attracted extensive interests because of their unique electronic, magnetic, optical, biologic, catalytic and other performances different from their bulk counterparts [1]. It has also been generally acknowledged that the physicochemical properties of nanometer-scaled materials strongly depend on their shape and size besides their inherent chemical constitutions [2]. During the past decades, Researchers have made considerable efforts and well developed the preparation of size-controlled spherical metal nanoparticles along with their assemblies [3]. Despite these, it is still now a challenge to synthetically controlling the shape of metal nanoparticles. Numerous approaches have been attempted so far to obtain anisotropic metal nanoparticles with one-dimensional (1D) or 2D morphologies such as nanowires, nanorods, nanoribbons and nanosheets for promising novel features compared with that of conventional spherical metal nanoparticles [4]. In particularly, strategies based on polymer-mediated EG process have been widely introduced to generate non-spherical metal nanostructures recently [5]. During this thermal-treatment process at higher temperature (generally outclass 100 °C), EG serves as solvent as well as the reducing agent of the metal precursor and poly(vinyl pyrrolidone) (PVP) is commonly used for a capping agent to control the growing rate of different crystal facets leading to anisotropic metal nanoparticles [5,6]. For instance, well-defined cubes and wires of silver in nanometer-scale have been successfully obtained by this polyol process in the presence of PVP [7]. In succession, tetrahedral, icosahedral and cubic gold nanocrystals were also obtained by a similar PVP-EG process [8]. For the preparation of gold nanoplates concerned, however, when adopting the strategy of PVP-EG process, Microwave heating had to be introduced or else the obtained gold nanoplates were of low crystallinity and companied with large spherical particles by single oil-bath heating conditions [9,10]. Up to now, few are reported about a simple method to obtain large gold nanoplates of high crystallinity through a polyol process under conventional heating conditions.

In this work, we developed a facile route to synthesize micrometer-sized edge length (up to 15 µm), single-crystal, polygonal gold plates of several 10 nm thickness in large quantities by simply adding aniline to a solution of $HAuCl_4$ in EG

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at 95 °C without extra addition of any other capping agents or surfactants. The optical spectra of the as-synthesized gold nanoplates showed quite strong absorption in near infrared region. Studies suggested the amount of aniline was crucial to producing gold nanoplates and the size control of the gold nanoplates was also investigated by adjusting the stirring speed. Finally, a possible formation mechanism of the gold nanoplates was presented.

2. Experimental

In our experiments, all chemicals were analytical pure agents and purchased from Shanghai Chemical Reagent Co. Ltd. (China). Aniline was distilled twice at a reduced pressure in the presence of zinc metal powder before use. Hydrogen tetra-chloroaurate ($HAuCl_4 \cdot 4H_2O$), Ethylene glycol (EG), and anhydrous ethanol were used as received. The water used was purified through a Millipore system.

A typical procedure to synthesize the gold naoplates is as follows: 50 ml of EG solution containing 0.036 mmol $HAuCl_4 \cdot 4H_2O$ in a Schlenk flask was heated to 95 °C by a water-bath for 20 min. Then, 0.1 M aniline solution in EG was added to this solution with mild stirring to obtain a 2:1 molar ratio of aniline to gold. The color of the mixture solution changed quickly upon the addition of aniline and the reaction system kept heating for 3 h without any stirring. As a result, we found a large quantity of sand-like precipitates attaching to the interior wall of the flask, which can be easily collected by pouring out the resulting solution. The obtained precipitates were dispersed in anhydrous ethanol under ultrasonication and then were gathered using a suction filter, washed with anhydrous ethanol and water several times to remove the remaining reactants. Finally the purified products were dispersed again in water for further characterization.

Scanning electron microscopy (SEM) images were recorded by using a LEO-1530VP field-emission scanning electron microscope with an accelerating voltage of 5.0 kV and the samples were deposited on silicon substrates, which were also used for elemental analysis conducted by energy-dispersive X-ray spectrograph (EDX) attached to the SEM. Transmission electron microscopy (TEM) photographs were obtained by a JEM-2000EX microscope with an accelerating voltage of 120.0 kV and the samples were prepared on carbon-coated copper grids. Powder X-ray diffraction pattern (XRD, D/Max-RA, Cu Kα, 40 kV, 30 mA) was taken from the sample prepared by dropping 200 ul of the products dispersed in water on a silicon substrate and allowing the solvent to evaporate spontaneously at ambient temperature. The optical properties of the as-prepared gold plates were measured by a SHIMADZU UV–vis-NIR spectrophotometer (UV-3150) and the gold plates were characterized as water dispersions and the thin coatings of the same batch on a glass substrate, respectively.

3. Results and discussion

Fig. 1 shows typical SEM images of the resulting products. The lower magnification image (Fig. 1a) indicates that the pre-
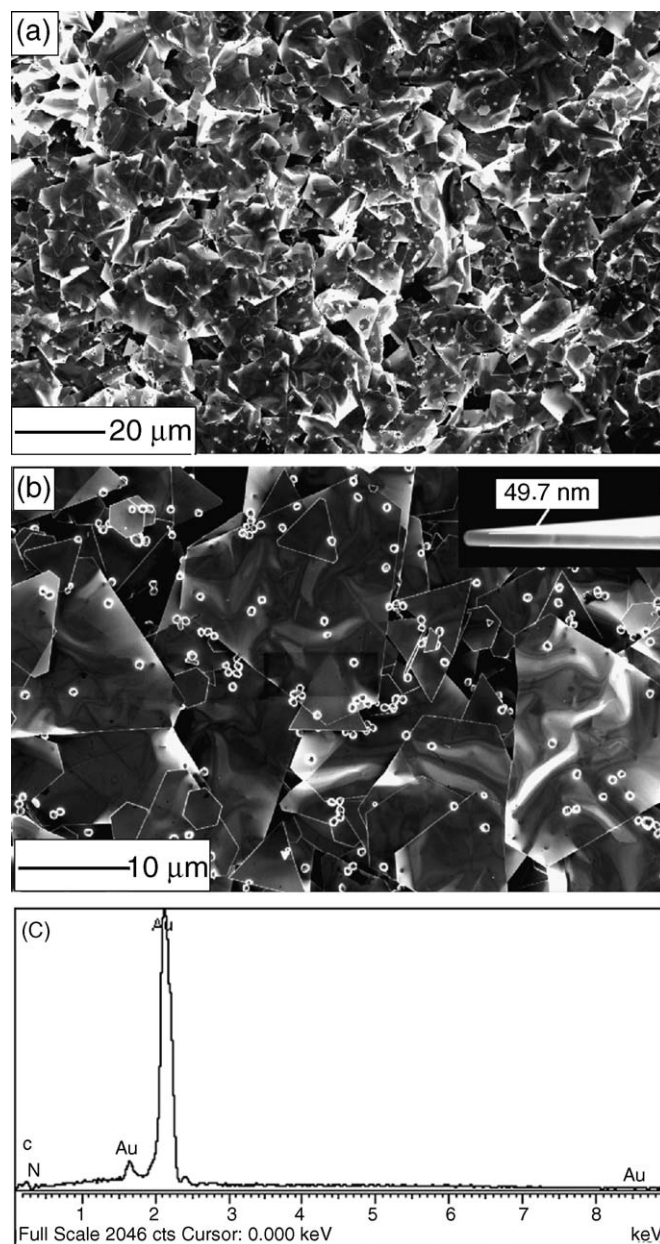

Fig. 1. Typical SEM images of the resulting precipitates of (a) low magnification and (b) high magnification. The inset shows the thickness of a single plate is about 49.7 nm; (c) the EDX pattern of the purified gold nanoplates.

cipitates consist of a mass of plates coexisted with a small quantity of spherical particles as byproduct. The higher magnification image distinctly reveals these large plates with sharp edges are in micrometer-size (up to 15 µm), including hexagonal, truncated triangular and triangular in shapes. To the best of our knowledge, no previous work have been reported about the preparation of micrometer-sized gold plates in an EG system. The inset in Fig. 1b gives the thickness between the two parallel basal planes of one plate protruding from the substrate, which provides the evidence that these plates are nanoplates of several ten nanometers in thickness. The EDX spectrum determined from these purified nanoplates shows strong peaks due to element gold. Weak peaks ascribed to carbon and nitrogen,
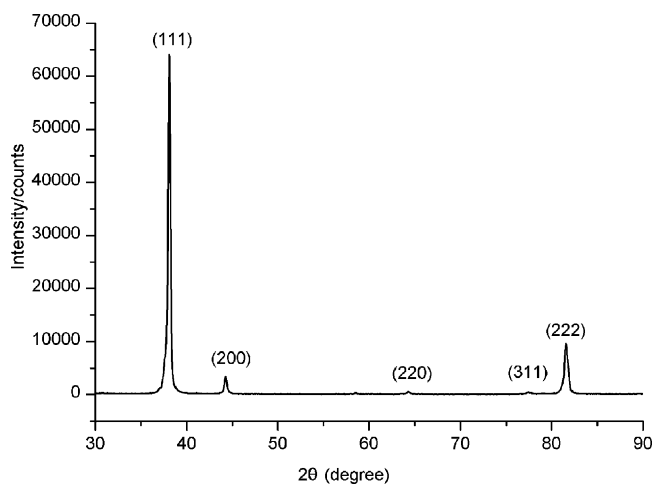
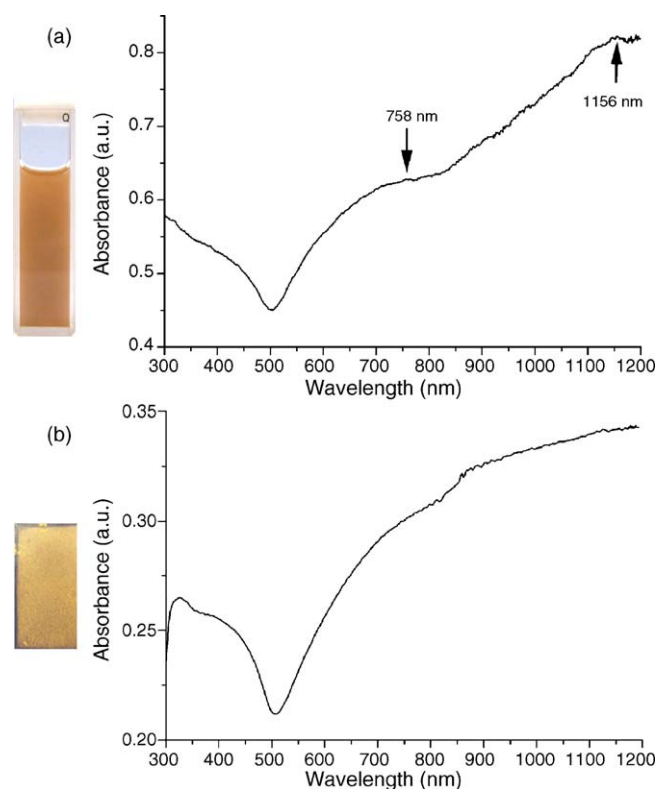Fig. 2. XRD pattern of the as-prepared gold nanoplates.

Fig. 4. (a) The photograph (left) and UV–vis-NIR spectrum of the as-prepared gold nanoplates dispersed in water. (b) The photograph (left) and UV–vis-NIR spectrum of the same batch gold plates forming thin coatings on a glass substrate.

respectively are also observed (Fig. 1c), which reveals these gold plates are covered with aniline resultant.

Fig. 3 gives representative TEM photographs of individual gold nanoplates of different shapes (Fig. 3a–c) and a typical selected area electron diffraction (SAED) pattern (Fig. 3d) obtained by directing the electron beam perpendicular to a single gold nanoplate deposited flat on the TEM grid. The hexagonal symmetrical spots of the SAED pattern reveal clearly that these gold nanoplates are single crystals and the incident electron beam is perpendicular to {1 1 1} facet of the tested plate [11,12].
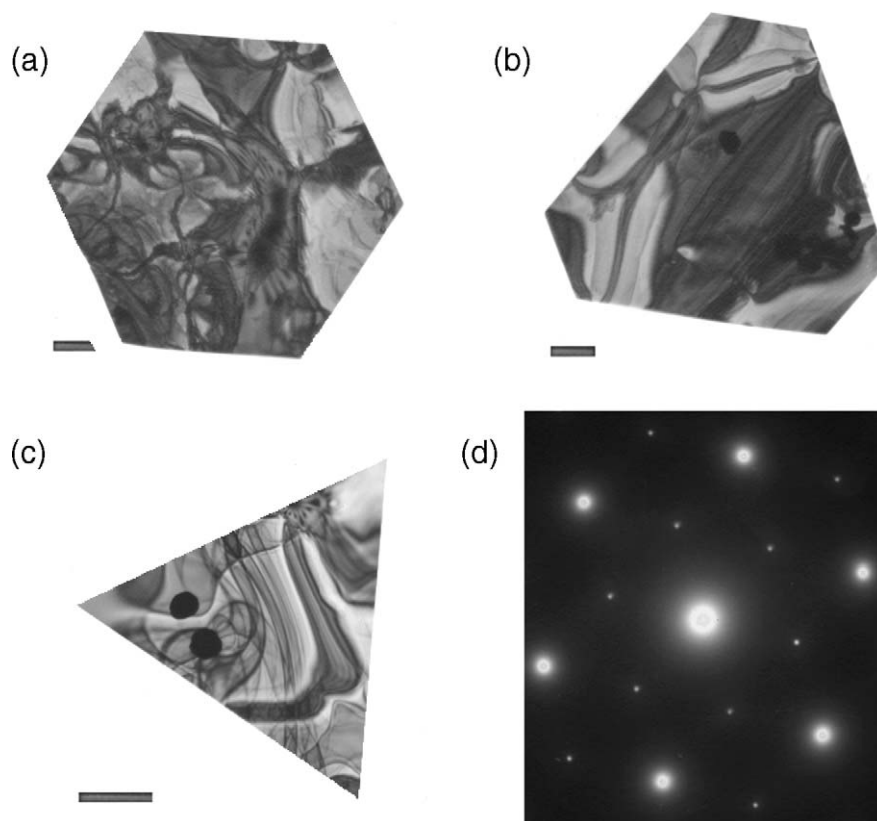

Fig. 3. Typical TEM images of individual gold nanoplates: (a) hexagonal, (b) truncated triangular and (c) triangular. (d) A typical SAED pattern of a gold nanoplate. The scale bars are 1 μm.

The low contrast appearance of these gold plates indicates their thinness feature. The interesting stripes across the {1 1 1} facets of these plates may arise from bending of these thin single crystals [13]. The XRD analysis of the resulting gold nanoplates was carried out to further understand their crystal nature. As shown in Fig. 2, an overwhelmingly strong diffraction peak located at 38.09° is ascribed to the {1 1 1} facets of face-centered cubic metal gold structures (JCPDS, file no. 04-0784), while diffraction peaks of other four facets are much weak. It is worth pointing that the ratio of intensity between the {2 0 0} and {1 1 1} peaks is much lower than the standard value (0.049 versus 0.53). The ratio between the {2 2 0} and {1 1 1} peaks is also even much lower than standard value (0.0065 versus 0.33). These data educe that the as-prepared gold nanoplates are primarily bounded by {1 1 1} facets and their {1 1 1} facets incline to preferentially oriented parallel to the supporting surface [6,11,12].

Optical properties of metal nanomaterials strongly depend on their shape and size [7,14]. Fig. 4a shows a photograph and absorption spectrum of as-prepared nanoplates dispersed in water. These gold nanoplates aqueous dispersion exhibits yellow in color and displays two distinct SPR bands situated at about 758 and 1156 nm owing to the transverse and the longitudinal plasmon resonance [15], which shows notable red shift in contrast with the nanometer-sized gold nanoplates previously reported [10,13,16]. Moreover, another UV–vis-NIR spectrum recorded from a glass substrate covered with thin coatings of the same batch gold plates also exploits very strong absorption in the near infrared region (Fig. 4b). These observations reflect remarkable anisotropic feature of our gold nanoplates.

It has been reported that heating chloroauric acid solution in EG without capping agent only resulted in spherical-like gold particles [10]. Thus, the aniline seems to be important to the formation of gold plates. The effects of the amount of aniline in the solution on the morphologies of gold nanostructures were studied under fixing other parameters of the reaction. As shown in Fig. 5, when the synthesis was conducted under increasing
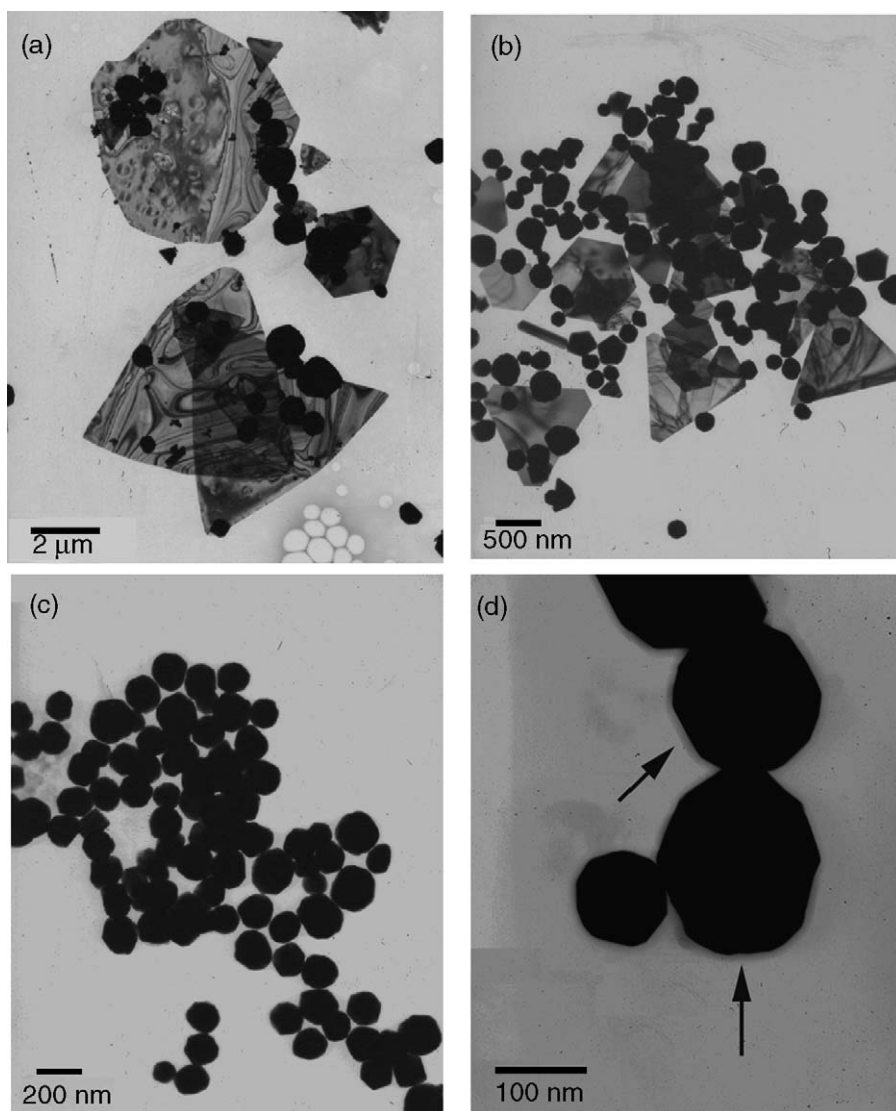

Fig. 5. Typical TEM images of gold nanostructures obtained with an initial molar ratio (aniline to gold) of (a) 1:1; (b) 4:1, (c) 6:1 and (d) 6:1 at a higher magnification. The arrows reveal the particles covered with oxidized aniline.
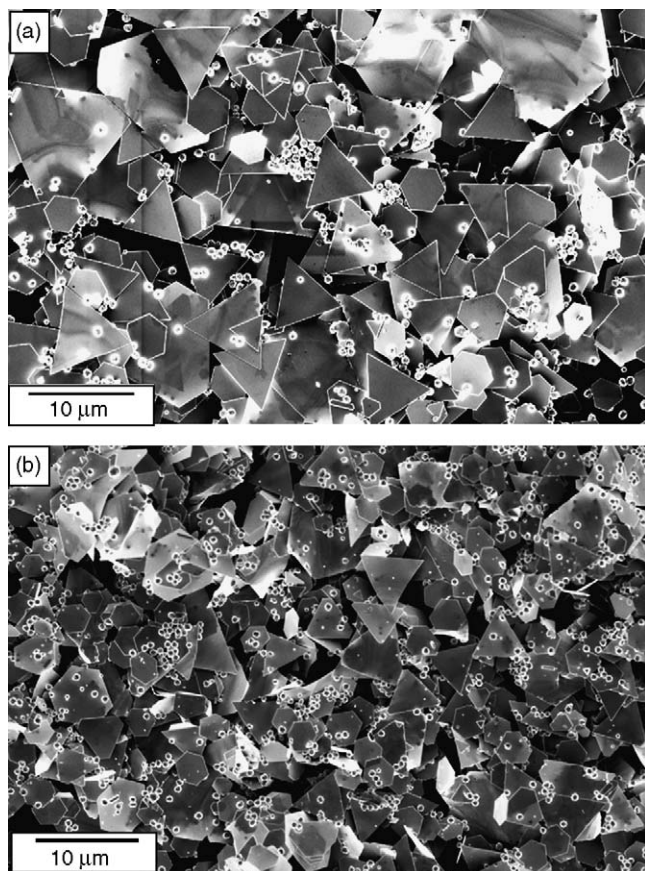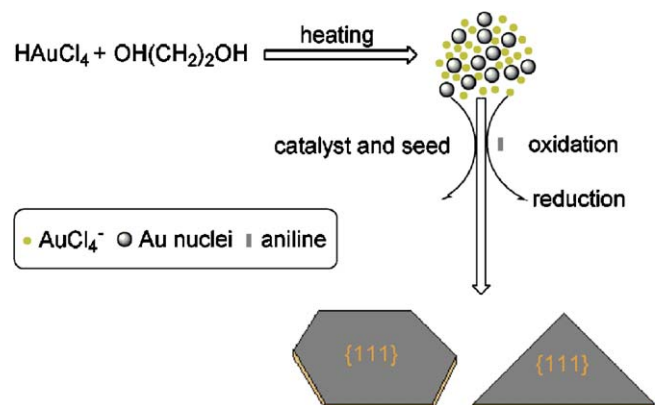
Fig. 6. The SEM images of gold nanoplates resulting from a stirring process instead of keeping stable: (a) stirring speed at 100 rpm; (b) stirring speed at 400 rpm.

Scheme 1. Possible formation mechanism of gold nanoplates through an aniline-assisted polyol process.

molar ratio of aniline to gold, the edge size of the resulting gold plates turned to be sub-micrometer in size and coexisted with lots of quasi-spherical gold particles with diameters of 100–400 nm (Fig. 5b). The gold products were dominated by quasi-spherical particles with diameters of 100–200 nm when the molar ratio rising to 6:1 (Fig. 5c). Furthermore, It is clearly observed at a higher magnification that these particles are covered with thin polymeric layer resulting from the oxidized aniline (Fig. 5d). However, when decreasing the molar ratio to 1:1, the micrometer-sized gold plates with flexural edges due to lower crystallinity were commonly produced (shown in Fig. 5a). It is therefore concluded that the amount of aniline in the solution plays a key role in controlling the morphologies of gold nanostructures.

In addition, it was found adjusting the stirring speed could control the size of the gold nanoplates. When our typical procedure was operated under mild stirring speed at 100 rpm instead of keeping stable after the addition of aniline, the proportions of small edge-sized nanoplates got increased in contrast with that of keeping stable (Fig. 6a). When the stirring speed reached 400 rpm, the edge size of the resulting gold plates were mainly in the range of 3–5 μm (Fig. 6b). Thus, it is believed that we might obtain size-tunable gold nanoplates by carefully adjusting the stirring speed using this way in future work.

Based on the investigations mentioned above, a possible mechanism for the formation of gold nanoplates through our method can be proposed (Scheme 1). At the first step, gold atoms were produced and aggregated to nucleus by heating the EG solution of chloroauric acid owing to the highly temperature-dependent reducing power of EG [7,10,17]. When aniline was added to the solution, each nuclei served as a catalytic reaction centre [18,19] to enhance the reaction between unreacted $AuCl_4^-$ ions and aniline monomers. During this course, $AuCl_4^-$ ions were reduced to form gold atoms rapidly and the oxidation of aniline occurred simultaneously [20,21]. Then, the resulting gold atoms tended to assemble to the gold nucleus to form larger particles and the oxidative products of aniline, including its polymers or oligomers, inclined to adsorbing on the lowest energy {1 1 1} facets of the particles and compress the growing rate of these facets. As a result, other facets adsorbed with fewer molecules of oxidized aniline grew more quickly than {1 1 1} facets and polygonal gold plates bound primarily by {1 1 1} facts were preferentially generated. Higher quantity of aniline leads to a heavy coverage of oxidized aniline on the surfaces of the particles and results in products dominated by spherical-like particles due to the isotropic growth of all facets [10]. Whereas, too lower quantity of aniline leads to an insufficient coverage and the obtained gold plates have lower crystallinity because of the same reason.

4. Conclusions

In summary, we have demonstrated a facile route to synthesize micrometer-sized, single-crystal, polygonal gold nanoplates in large quantities through an aniline-assisted polyol process. This route is carried out at a much lower temperature in contrast with that of conventional PVP-polyol process and with no need of additional capping agents or surfactants. During the reaction process, the added aniline molecules act as a reducer and their oxidative products serve as an effective capping agent or coordinating agent to control the growing rate of different facets of the initial gold particles resulting in the gold nanoplates bound primarily by {1 1 1} facets. Preliminary studies suggest the amount of aniline added to the reaction system is critical to generating gold nanoplates. In particularly, the strong absorption in the near infrared region holds these gold nanoplates for

promising potential applications in medical and architectural fields [22].

Acknowledgements

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