

Morphogenesis of anisotropic gold nanostructures stabilized by the greener ionic liquid 1-butyl-3-methylimidazolium lauryl sulfate

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We report the first synthesis of anisotropic gold nanostructures prepared through hydrothermal citrate reduction of HAuCl_4 in the presence of a greener ionic liquid 1-butyl-3-methylimidazolium lauryl sulfate.

The synthesized nanostructures possess well-defined shape and sharp edges ranging from triangular, truncated triangular and hexagonal geometries with preferred growth along the (111) plane. The morphology of the crystal is conserved except for the occurrence of stacking after prolonged heating emphasizing a preferential growth along the a-b plane. At higher concentration of the ionic liquid, a different geometry, intertwining nanoparticles and nanorods were observed. This elongation was confirmed spectroscopically through the hypsochromic shift of the plasmon band of the nanostructures and evolution of a near-IR peak.

KEYWORDS

crystal growth, nanostructures, ionic liquid, hydrothermal

INTRODUCTION

Controlled morphogenesis of gold nanoparticles has attracted much attention due to their unique properties that are essential to various applications such as catalysis, analytical sensing and in biomedical and optoelectronic devices [Bi and Lou 2008, Xiong et al. 2006, Kundu, et al. 2007, Kerman and Tamiya 2008, Kim et al. 2008]. To date, various methods for the controlled morphogenesis of gold nanoparticles have been reported. However, the reduction of gold precursors in solution is the generally preferred route [Luo 2006] and this can be categorized into: (i) reduction of aqueous chloroaurate ions by a variety of reducing agents such as citric acid [Turkevich et al. 1954], sodium borohydride [Duff et al. 1993], and alkaline tetrakis(hydroxymethyl)phosphonium chloride [Henglein 1999], (ii) radiation induced reduction of Au ions [Henglein 1999, Gachard 1998], and (iii) sonochemical reduction of Au ions [Mizukoshi 2000]. The most popular method of preparing Au nanospheres dispersed in water is the reduction of HAuCl_4 in a boiling sodium citrate solution [Turkevich 1951, Frens 1973]. The average nanoparticle diameter can be tuned over quite a wide range (~10-100 nm) by varying the concentration ratio between the Au salt and the sodium citrate solutions. Another procedure that has also become extremely popular for Au nanoparticle synthesis is the two-phase reduction method developed by Brust and co-workers [1994, 1995]. Basically, HAuCl_4 is dissolved in water and subsequently transported into toluene by means of tetraoctylammonium bromide (TOAB), which acts as a phase transfer agent. The toluene solution is

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mixed with the aqueous solution of sodium borohydride (a strong reducing agent), in the presence of thioalkanes or aminoalkanes, which readily bind to the Au nanoparticles formed. The particle size can be tuned between ~1 nm and ~10 nm by varying the ratio of Au salt and capping agent (thiol/amine). The use of capping agents ranging from simple molecules with compatible functional group, to polymers has been employed to improve the stability of nanostructures in solution [Tomczak et al. 2009].

An emerging strategy in the synthesis of nanoparticles utilizes ionic liquids. Ionic liquids have the potential to make ideal green solvents as they have negligible vapor pressure, making them more environmentally responsible materials than traditional organic solvents. A limited number of syntheses of Au nanoparticles with imidazolium ionic liquid moieties have been reported. Kim and co-workers [2004] were first to report on the one-phase synthesis of Au nanoparticles functionalized with new thiol-containing ionic liquids. They found out that the thiol-containing ILs can act as a highly effective stabilizing agent of Au nanoparticles. Itoh and co-workers [2004] have also reported on the synthesis of Au nanoparticles functionalized with sulfur containing ILs; the Au nanoparticles functionalized with 3, 3'-[disulfanyl bis(hexane-1,6-diyl)]-bis(1-methyl-1H-imidazol-3-ium) dichloride were demonstrated to be useful as optical sensors. The preparation of Au nanoparticles functionalized with a zwitterionic liquid (zwitter-Au) based on imidazolium sulfonate was reported by Tatumi and Fujihara [2005]. Result showed that zwitter-Au has great stability in aqueous solutions with high concentrations of electrolytes, ionic liquids, and protein as the particle size remained the same throughout the process. The interest in these studies is driven by the observation that the interactions of imidazolium-based ionic liquids with metal nanoparticles produce novel properties and enhanced stabilization in these nanoparticles. [Dupont et al. 2002, Scheeren et al. 2003, Huang et al. 2003, Kim et al. 2004]. It is worth noting that some of the ILs used in the above syntheses of Au nanoparticles consist of halide-based anions. However the presence of halides may cause serious concerns if the hydrolysis stability of the anion is poor (e.g., for AlCl_4^- and PF_6^-) or when thermal treatment of the utilized ILs is desired [Wasserscheid et al. 2002].

We report herewith the synthesis of anisotropic gold nanostructures prepared through hydrothermal citrate reduction of HAuCl_4 in the presence of a halogen-free ionic liquid, based on 1-butyl-3-methylimidazolium cation and lauryl sulfate as halogen-free anion. Plates with lateral sizes of 1-2 microns and thickness of 50-70 nm were produced having various well-defined geometries. Under conditions of high ionic liquid concentration networks of polycrystalline nanoparticles and nanorods of 10-20 nm were formed.

MATERIALS AND METHODS

Instrumentation

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra taken in $d_6\text{-DMSO}$ solvent were recorded on a Varian Mercury 400 and 500 MHz, respectively. FT-IR spectra were measured on a Perkin Elmer Spectrum RX I spectrometer, mass spectra were recorded on a liquid chromatograph mass spectrometer (JEOL JMS-SX102A) and UV-Vis absorption spectra were recorded on spectrophotometer (JASCO V-570). The morphology and electron diffraction pattern of the nanocrystals were examined using transmission electron microscopes, Philips Tecnai 20 and JOEL 2000 FX operated at 200 kV and 160 kV, respectively. PXRD patterns were acquired using a Rigaku MXP^3 diffractometer with a $\text{Cu K}\alpha$ radiation at $\lambda=1.5418 \text{ \AA}$. SEM images were taken with a scanning electron microscope (JEOL JSM-6330F).

Synthesis of 1-butyl-3-methylimidazolium bromide.

The synthesis of the precursor ionic liquid follows an established method previously reported by our group [Obliosca et al. 2007]. In a two-necked round-bottom flask, a stirred solution of 1-methylimidazole (79.7 mL, 1 mol) and 1-bromobutane (107.4 mL, 1 mol) was heated to 70°C for 48 hours under N_2 atmosphere. The resulting viscous solution was cooled to room temperature, washed with ethyl acetate (3x20 mL) to remove unreacted starting material (that is, excess of 1-bromobutane), and then dried under vacuum at $70\text{-}80^\circ\text{C}$ for 5-7 hours to yield 184g (85%) of the product, [BMIM]Br. $^1\text{H-NMR}$ (500 MHz, $d_6\text{-DMSO}$): δ 0.766 (t, $J=7.5 \text{ Hz}$, 3H), 1.148 (sxt, $J=7.5 \text{ Hz}$, 2H), 1.700 (qnt, $J=7.0 \text{ Hz}$, 2H), 3.882 (s, 3H), 4.211 (t, $J=7.5 \text{ Hz}$, 2H), 7.881 (d, $J=1.5 \text{ Hz}$, 1H), 7.984 (d, $J=2.0 \text{ Hz}$, 1H), 9.561 (s, 1H); $^{13}\text{C-NMR}$ (500 MHz, $d_6\text{-DMSO}$): δ 13.111, 18.549, 31.286, 35.739, 48.211, 122.090, 123.279, 136.398; FTIR (neat, cm^{-1}): 3460, 3153, 3091, 2960, 2920, 2853, 1637, 1575, 1472, 1382, 1171; ESI-MS: (ESI⁺) m/e 139.17 $\{[\text{C}_8\text{H}_{15}\text{N}_2]^+\}$, (ESI⁻) 78.82 (Br⁻), 80.81 (Br⁻).

Synthesis of 1-butyl-3-methylimidazolium lauryl sulfate.

The synthesis of the greener ionic liquid follows an established method previously reported by our group [Obliosca et al. 2007]. A mixture of freshly synthesized and dried [BMIM]Br (10.6 g, 48.4 mmol) and sodium lauryl sulfate $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ (12.6 g, 43.6 mmol) were dissolved in hot water (20 mL). After which water was slowly removed under vacuum at $70\text{-}80^\circ\text{C}$ and then white solids precipitated out. The liquid mixture was transferred to a separatory funnel, then CH_2Cl_2 (45 mL) was added to extract the product. The ionic liquid was in the lower layer, while NaBr was in the upper layer. The clear but slightly yellow viscous organic extract was then washed several times with water (4x5 mL) and the white solid (accounted for NaBr as by-product) was separated out. The washing was repeated until it was bromide-free; 2-3 drops of 0.1 M AgNO_3 were added to the washings to confirm the presence/absence of bromide ions. The extract was distilled to get rid of the CH_2Cl_2 solvent and finally dried under N_2 and

vacuum for 5–7 hours to afford 15g (85%) of the product, [BMIM][C₁₂H₂₅OSO₃]: mp = 48°C. ¹H-NMR (400 MHz, d₆-DMSO): δ 0.833 (t, J=6.8 Hz, 3H), 0.882 (t, J=7.6 Hz, 3H), 1.221 (m, J=7.6 Hz, 20H), 1.451 (m, J=6.8 Hz, 2H), 1.752 (qnt, J=6.8 Hz, 2H), 3.692 (t, J=6.0 Hz, 2H), 3.845 (s, 3H), 4.158 (t, J=7.2 Hz, 2H), 7.707 (d, J=1.6 Hz, 1H), 7.776 (d, J=1.2 Hz, 1H), 9.120 (s, 1H); ¹³C-NMR (500 MHz, d₆-DMSO): δ 13.226, 13.892, 18.770, 22.106, 25.538, 28.740, 28.811, 29.051 (3C), 29.086 (2C), 31.313, 31.402, 35.677, 48.468, 65.534, 122.268, 123.589, 136.575; IR (neat, cm⁻¹): 3460, 3153, 3091, 2960, 2920, 2853, 1637, 1575, 1472, 1382, 1274, 1217, 1171, 1069, 990, 814, 762, 723; ESI-MS: (ESI⁺) m/e 139.2 {[C₈H₁₅N₂]⁺}, (ESI⁻) 265.13 {[C₁₂H₂₅OSO₃]⁻}.

Synthesis of gold plates of various geometries

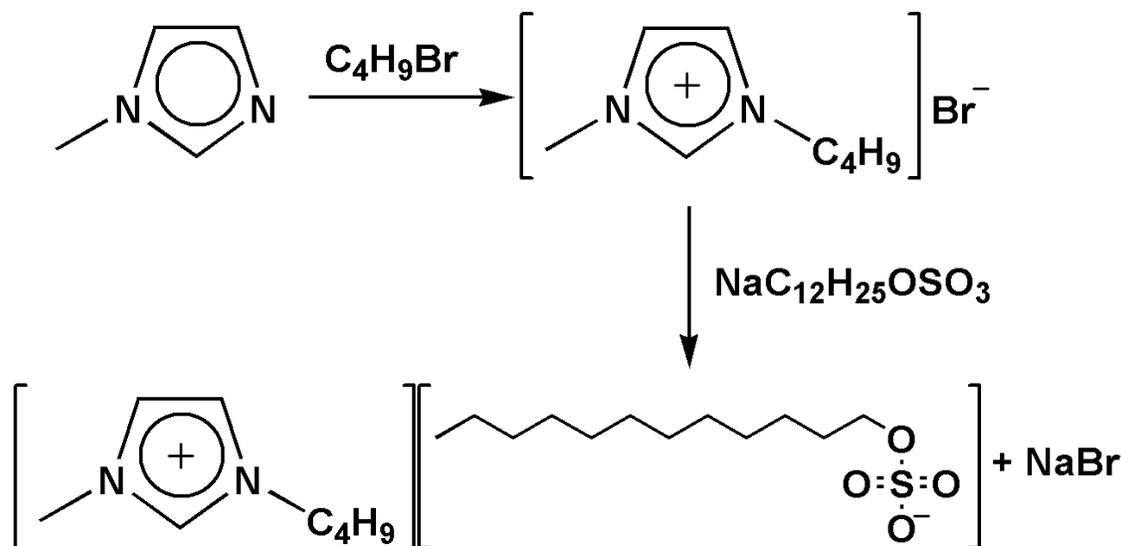
The synthesis of gold plates follows a modification of the procedure described by Chu, et al. [2006]. HAuCl₄ (5.0 mL of 0.01 M) and [BMIM][C₁₂H₂₅OSO₃] (5.0 mL of 0.01 M) were stirred in a round bottom flask and heated at 95°C producing a yellow orange color. In a separate container, trisodium citrate (1.0 mL of 0.025 M) was added to a preheated distilled H₂O (14.0 mL) at 85°C. Immediately thereafter, the citrate solution was added to the gold precursor solution and the resulting mixture was heated under reflux. Gradual color changes from yellow orange to yellow to colorless and finally to brown were observed. The temperature was raised to boiling for 10 and 60 minutes. To assess the effect of the ionic liquid on the morphology of the product, the synthesis was carried in the absence of the ionic liquid. Furthermore, two sets of ionic liquid to AuCl₄⁻ ratio were evaluated namely, 1:1 and 7:1. The resulting mixtures were cooled, centrifuged and analyzed using

transmission electron microscopy, electron diffraction, scanning electron microscopy and powder x-ray diffraction.

RESULTS AND DISCUSSION

In this study, 1-butyl-3-methylimidazolium lauryl sulfate, [BMIM][C₁₂H₂₅OSO₃], was synthesized by reacting 1-methylimidazole with 1-bromobutane and exchanging the bromide ion with sodium lauryl sulfate to afford the ionic liquid. In view of the emerging importance of benign and environment-friendly ILs, the synthesis of greener ILs based on 1-alkyl-3-methylimidazolium cation with lauryl sulfate as the halogen-free anion was explored. Sodium lauryl sulfate (SLS) is of great advantage because unlike other alkyl sulfates which are made from synthetic alcohol, SLS is a naturally derived surfactant made from whole natural coconut. The formation of the product was verified using ¹HNMR, ¹³CNMR-DEPT, FTIR and Mass Spectroscopy. The preparation of [BMIM][C₁₂H₂₅OSO₃] follows the general reaction presented in Scheme 1.

The function of ionic liquid in the synthesis of gold nanostructures, was evaluated through a comparison of the features of these nanostructures formed with and without the ionic liquid. Figure 1a shows the structures formed in the absence of [BMIM][C₁₂H₂₅OSO₃] and it is worth noting that particulates with extended aggregation and no defined geometry were formed. However, in the presence of the ionic liquid, a more ordered growth can be observed as shown in Figure 1b. Triangular, truncated triangular and hexagonal plates of 1-2 μm lateral size were generated. The well-defined geometry of the nanostructures formed in solution highlights the stabilizing



Scheme 1. Synthesis of greener ionic liquid 1-butyl-3-methylimidazolium lauryl sulfate.

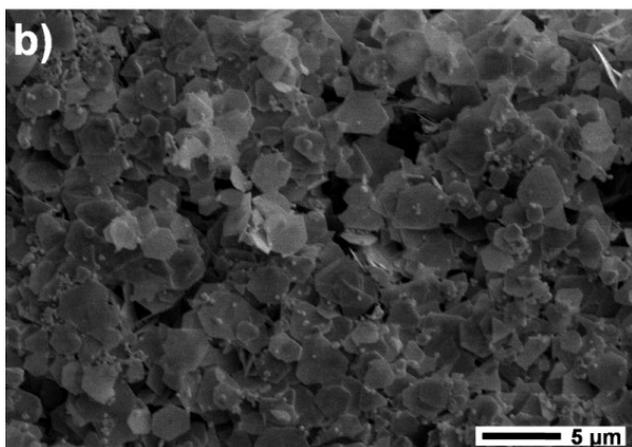
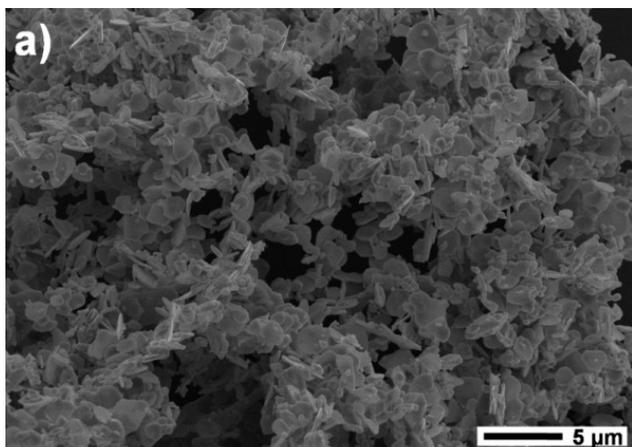


Figure 1. SEM images of structures formed a) without and b) with [BMIM][C₁₂H₂₅OSO₃].

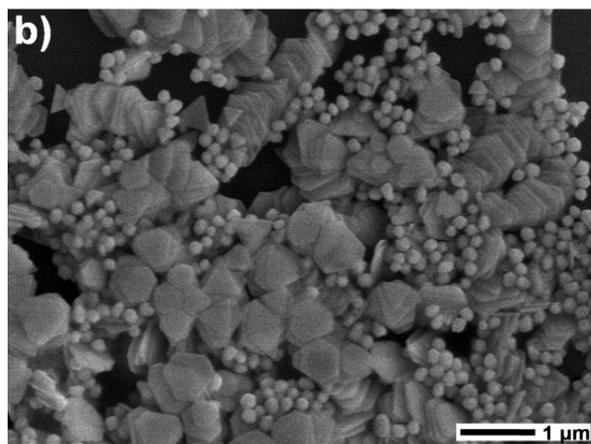
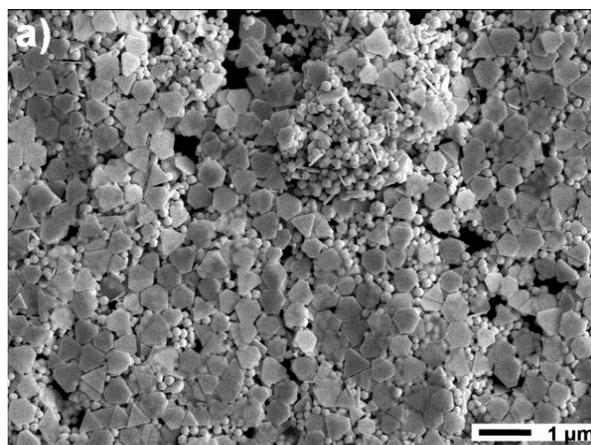


Figure 2. SEM images of nanoplates formed at a reaction time of a) 10 minutes, and b) 60 minutes.

effect of the capping agent used. In the synthetic strategy featured, the ionic liquid acted as a capping agent possibly through the micellar stabilization of the Au nanoparticles, and thus inhibiting their aggregation. The charged imidazole ring of the ionic liquid interacted with the gold precursor through ionic coupling while the alkyl moiety of the ring and the alkyl chain of lauryl sulfate create micellar noncovalent interaction.

The effect of the time of thermal exposure on the morphology of the synthesized Au nanoparticles was evaluated by heating the reaction mixture for 60 minutes under reflux. Figure 2 shows SEM images of Au nanoplates produced at two different reaction times. It was apparent that the mean lateral size was conserved even with prolonged heating. In addition, an extensive stacking of plates was evident after prolonged heating of the reaction mixture showing preferential crystal growth along the a-b plane. This preference is supported by the XRD pattern in Figure 3c.

Representative SEM images of nanoplates with triangular and hexagonal geometries are shown in Figures 3a and 3b, respectively. The lateral size of these structures ranges from 1 –

2 microns with a thickness of 50-70 nm. It is evident from Figure 3b that these structures are very thin such that the outline of the underlying plate is already visible. Figure 3c shows the X-ray diffraction (XRD) pattern of the anisotropic nanostructures. The five peaks show prominent Bragg diffraction that are indexed as (111), (200), (220), (311) and (222) planes of the face-centered cubic gold which agree well with the SAED pattern (inset). The ratio of intensities of the (200) and (111) peaks is 0.25, and is lower than the standard value of 0.53. Likewise, the ratio of (220) and (111) is 0.11, and is only 1/3 of the standard value. These observations indicate that the nanoplates are dominated by the (111) facets which lie parallel to the a-b plane of the substrate surface [Sun et al. 2004].

In addition to the synthesis of Au nanoparticles at a 1:1 ionic liquid to H₂AuCl₄ concentration ratio, a second synthesis at a 7:1 concentration ratio was also carried out. An assessment of the effect of the concentration on the morphology of the nanostructures was made through a comparison of results from the above syntheses. Interestingly, the modification produced nanoparticles and nanorods with size range of 10-20 nm instead of producing nanoplates. Moreover, these structures do not exist

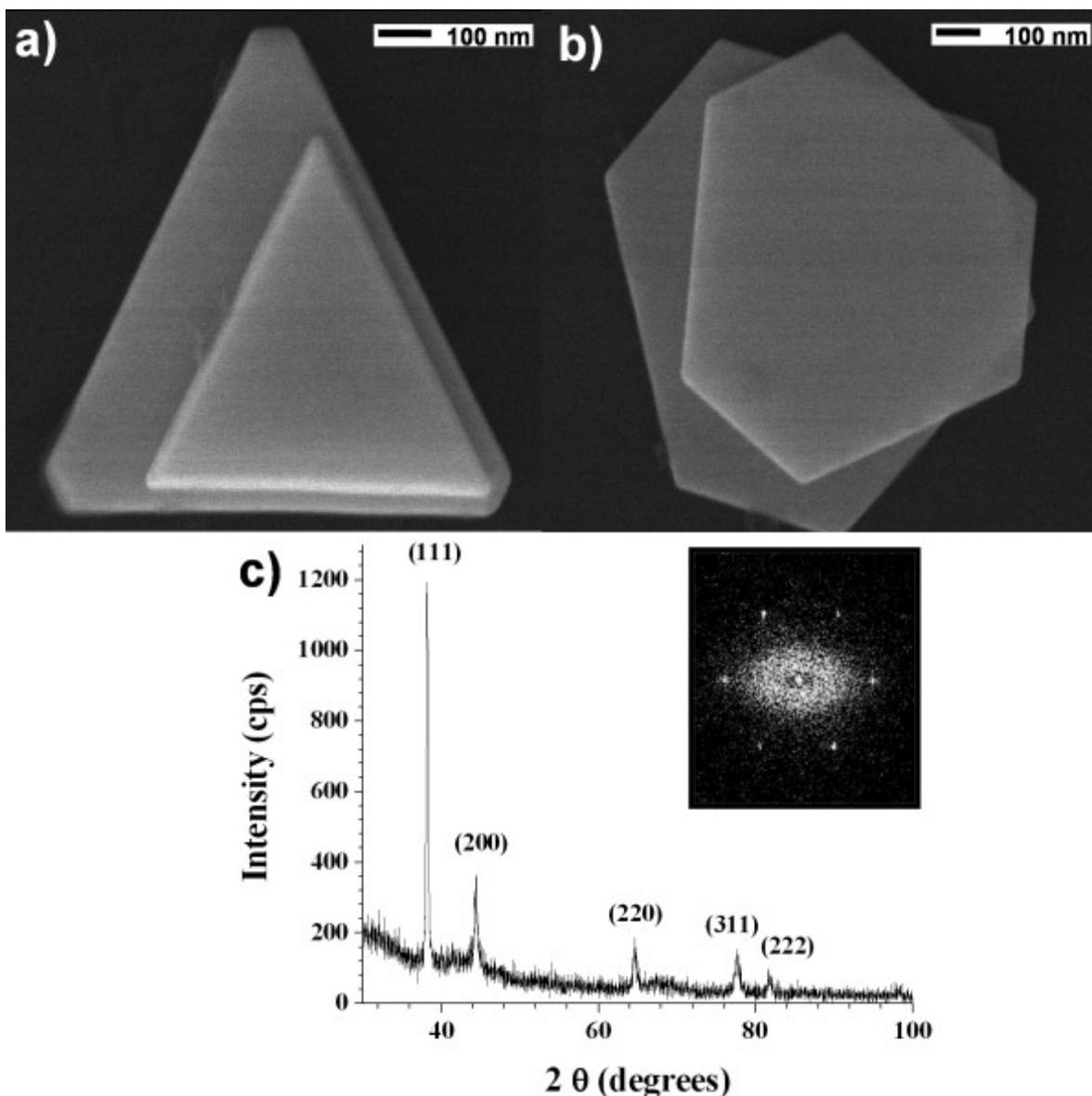


Figure 3. Au nanoplates with 1-2 μm lateral size and 50-70 nm thickness with a) triangular, and b) hexagonal geometries. c) powder XRD pattern (inset: SAED pattern).

as individual particles but are intertwined networks as shown in Figure 4a. This phenomenon may be attributed to the micellar stabilization effected by [BMIM][C₁₂H₂₅OSO₃]. At high concentration of the ionic liquid (7:1/ionic liquid:HAuCl₄), micelles were formed trapping the precursors and inhibiting extensive crystal growth during reduction thus producing very small anisotropic particles. Figure 4b shows the SAED pattern indicating a polycrystalline product. The optical property of these nanoparticles was investigated by means of uv-visible spectroscopy as shown in Figure 4c. Both spectra show absorption around 520 nm which is attributed to the surface plasmon resonance of spherical gold nanoparticles. The absorption band at the onset of reaction is seen at 525 nm. After 40 minutes, a hypsochromic shift from 525 nm to 516 nm was

observed. In addition, the evolution of near-IR absorption, was observed from which the presence of non-spherical nanoparticles [Chili and Revaprasadu 2008] formed by the twinning/fusion of two or more nanoparticles forming rod-like structure was made apparent.

CONCLUSION

Anisotropic gold nanostructures were synthesized through hydrothermal citrate reduction of HAuCl₄ with 1-butyl-3-methylimidazolium lauryl sulfate. The presence of ionic liquid stabilized the formation of nanoplates of a lateral dimension of 1-2 μm and thickness of 50-70 nm. The morphology of the crystal was conserved except for the occurrence of stacking after

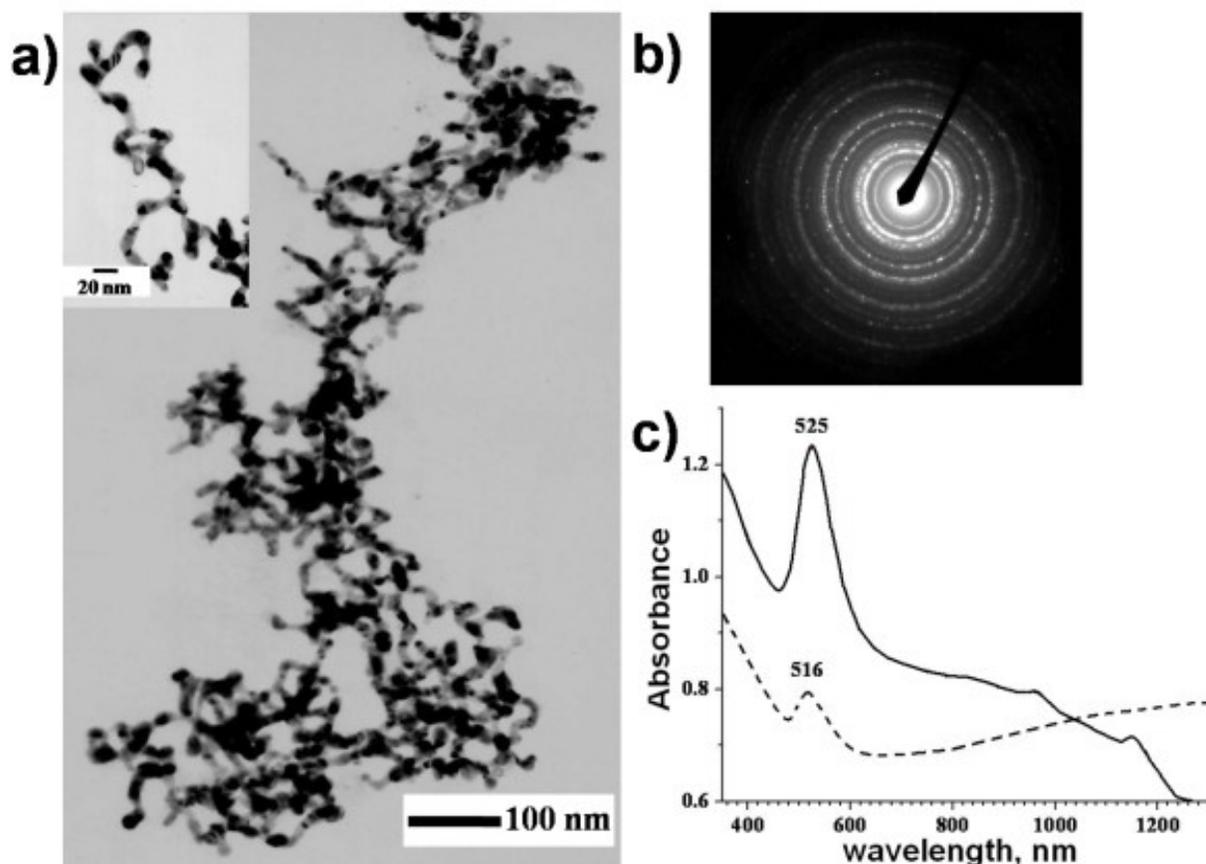


Figure 4. a) TEM image of intertwined Au nanoparticles and nanorods. b) SAED pattern showing polycrystalline morphology, and c) UV-visible spectra demonstrating elongation of nanoparticles (solid, $\lambda = 525$ nm) to nanorods (dashed, $\lambda = 516$ nm, near-IR peak).

prolonged heating emphasizing a preferential growth along the a-b plane. At a high ionic liquid to HAuCl_4 concentration ratio (7:1), formation of intertwined Au nanoparticles and nanorods were observed thereby, exhibiting the effective micellar stabilization of the ionic liquid used in the synthesis.

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