One-step synthesis of photoluminescent catalytic gold nanoclusters using organoselenium compounds

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In this study, a facile and rapid method was developed to synthesize intensely photoluminescent catalytic gold nanoclusters (AuNCs) based on etching small citrate-capped gold nanoparticles using 4,6-dimethyl-2-pyridineselenol-3-carbonitrile as a model for organoselenium compounds. The size and catalytic performance of the as-prepared fluorescent nanoclusters were characterized using suitable transmission electron microscopy (TEM), atomic force microscopy (AFM), electrospray ionization-mass spectrometry (ESI-MS) and photoluminescence techniques. It was shown that Au clusters with an average gold core diameter of 0.78 ± 0.41 nm (in the range of 5–9 atoms) play a catalytic role in the directed growth of gold nanorods with high aspect ratios (a.r. = 18–23). Methylene blue dye was photo-degraded by these photo-responsive gold clusters under UV light (within 40 minutes) and under visible light (within 120 minutes). Furthermore, we demonstrated that the formed nanoclusters display excellent catalytic activity in the photoreduction of toxic compounds, i.e., in the conversion of 4-nitrophenol to 4-aminophenol with high yield (83%) and short reaction time.

Introduction

Development of a wide range of synthesis techniques for gold nanoparticles has been achieved in recent years with the objective of controlling the morphology of the nanoparticles.1–4 Nowadays, it is recognized that stable subnanometric metal clusters display interesting catalytic properties and act as semiconductors because of their bandgap, giving rise to the appearance of new properties, such as photoluminescence.5–7 It has been shown that sub-nm silver and copper clusters can catalyse the anisotropic growth of gold nanorods.7 There are two ways to synthesize metal clusters: top-down and bottom-up techniques. In bottom-up techniques, smaller structures such as single atoms or ions are used to build metal clusters. Depending on the size of the clusters to be synthesized, the most commonly used techniques (wet chemical preparation) of clusters, including the chemical reduction of metal salts8–10 and by kinetic control using, e.g., microemulsions,11,12 electrochemical methods,13–15 etc will be differ.

In top-down techniques, clusters are synthesized from larger nanoparticles or bulk metal. Etching of nanoparticles using ligands (such as thiols)16,17 is one of the widely used top-down techniques for the synthesis of metal clusters. Removing the surface atoms or breaking the metal nanoparticles into smaller clusters by using the etching properties of such ligands will lead to the synthesis of stable quantum clusters. For example, Habib et al. have used the etching of mercaptosuccinic acid protected gold nanoparticles with excess glutathione to yield small photoluminescent gold clusters either with 8 or 25 gold atoms.18 Polyethyleneimine as multivalent coordinating polymers can also be used to etch preformed colloidal gold nanocrystals, producing highly fluorescent nanoclusters.19 It has been confirmed that small noble metal nanoclusters display excellent catalytic activities20,21 such as aerobic oxidation of thiophenol,22 epoxidation of propene,23 oxidation of styrene,24 reduction of p-nitrophenol with NaBH425 and the reduction of methylene blue with hydrazine.26

Organoselenium compounds are of considerable interest due to their wide efficiency and applicability in numerous therapeutic applications.23 In addition, the heterocyclic rings in these compounds upgrade their properties to a great extent. Despite the chemical structure of organoselenium compounds being similar to that of their sulfur analogues, the reactivity of selenium is markedly higher than sulfur.27 Organoselenium compounds that contain cyano (CN) group show high charge transfer properties with other compounds.28 The characterization of micro-structural features and molecular structure visualization of organoselenium compounds such as 4,6-dimethyl-3-cyanopyridine-(2H)-selenone,
which is the tautomer of 4,6-dimethyl-2-pyridineselenol-3-caronitrile, was shown by Elsabawy et al. In this study, top-down approaches were used to synthesize gold nanoclusters by etching gold nanoparticles using organo-selenol compounds by taking the high reactivity of (–SeH) relative to (–SH) in consideration and then, the catalytic activity of the as-formed gold clusters were synthesized.

Results and discussion

Gold nanoparticles with 3.5 ± 0.67 nm were prepared using trisodium citrate as capping and reducing agents. Gold nanoclusters were formed after the addition of 4,6-dimethyl-2-pyridineselenol-3-caronitrile (1) to the as-prepared gold nanoparticles. Organoselenium compound (1) can also exist in the form of 4,6-dimethyl-3-cyanopyridine-2H-selenone. The stretching vibration motion of \( \nu(\text{Se–H}) \) is very important for obtaining information about the structure of 4,6-dimethyl-2-pyridineselenol-3-caronitrile (1) [selenone \( \text{C} \equiv \text{Se} \leftrightarrow \text{selenol} (\text{Se–H}) \)]. The N–H bond absorbs in the region of 2300–2280 cm\(^{-1}\). This vibration band is present in the FT-IR spectrum, supporting the existence of the selenol form.

It is known that spherical gold nanoparticles have a characteristic band called the surface plasmon absorption with a maximum at around 520 nm, which could be slightly shifted depending on the size and dielectric constant of the surroundings. This plasmonic band disappeared in a few seconds (1 min) after the addition of an organoselenium compound (1) (Fig. 1a), which indicates the formation of gold nanoclusters. Similar behavior is observed when another organoselenium compound (4-methylquinolineselenol-3-carbonitrile (2)) was added to the gold nanoparticles’ solution.

The first indication of gold nanoclusters formation is the change in photoluminescence properties (Fig. 1b). The formed nanoclusters show two luminescence bands at 381 and 471 nm, respectively. However, selenol compound (1) shows a broad band at 332 nm, which confirms the formation of Au clusters.

Fig. 1d shows the AFM image of the nanoclusters solution after 1 min of organoselenium compound addition to the gold nanoparticles. The estimated size of the formed species is 0.78 ± 0.41 nm. Therefore, the very small size of the formed species and the absence of a plasmon band points to the formation of small Au nanoclusters with less than 12 atoms. The luminescence properties of the formed clusters can also indicate the presence of such clusters, as observed in Fig. 1b. The number of atoms in the cluster can be calculated by assuming the simple spherical jellium model using the simple expression \( N = (E_p/E_F)^3 \), where \( E_p \) and \( E_F \) represent the Fermi level (5.5 eV for bulk Au) and the HOMO–LUMO energy bandgap, respectively. The value of the bandgap can be estimated using the emission peak energy (471 nm, i.e. 2.63 eV and 381 nm, i.e. 3.25 eV), from which \( N \approx 5–9 \) atoms can be obtained. Therefore, we can assume that Au\(_{5–9}\) nanoclusters can be kinetically trapped after 1 min of organoselenium compound addition; this could be confirmed by ESI mass spectrum, which presents peaks attributed to the formation of Au\(_{5–9}\) at \( m/z = 1378 \) (Au\(_5\)C\(_{14}\)N\(_4\)Se\(_3\)H\(_{10}\) and Au\(_6\)C\(_2\)N\(_2\)SeH\(_5\)), 1743 (Au\(_7\)C\(_{12}\)O\(_{13}\)H\(_{10–12}\)) and 1772 (Au\(_8\)), as shown in Fig. 2.

Usually, the clusters produced using thiols are much larger (approx. 25 atoms) than the clusters produced by bottom-up electrochemical and chemical procedures (2 to 20 atoms). The possibility of etching gold nanoparticles with organic compounds such as thiols and in our case selenols can be assumed by taking into consideration the higher reactivity of the selenol group relative to the thiol group; this is the reason for the rapid formation of the clusters. These strong binding ligands break the nanoparticles into clusters with 5–9 atoms (top-down clusters-synthesis). TEM images (Fig. 3) show the etching process of gold nanospheres into gold clusters by using organoselenium compound (1). The compound (1) contains four types of
H-bonding: two are inter-H-bonds in the same molecule (Se···H···N and Se···H···Se), while the other two are intra-H-bonds (Se···H···CN and Se···H···N). The charge transfer due to these four types of hydrogen bonding contributes to the formation of the clusters.29

Catalytic activity of the formed gold clusters

The photocatalytic performance of the formed gold clusters was monitored by degradation of methylene blue dye (MB) in aqueous solution under low power UV and visible irradiation. The photodegradation was followed by measuring the UV-visible absorption spectra as a function of irradiation time, as shown in Fig. 4.

As shown in Fig. 4, the MB dye is stable under UV-light irradiation (Fig. 4a), but it photodegraded within 40 min with a gold cluster photocatalyst under UV-light irradiation (Fig. 4b). However, under visible light, we can observe that MB is photodegraded with longer irradiation time of 120 min (Fig. 4c) in comparison with the photodegradation of MB with citrate-capped gold nanoparticles (3.5 ± 0.67 nm) with an irradiation time of 360 min under visible light. These results indicate that the gold clusters have semiconducting properties (bandgap of 2–4 eV)5,7,33 and can be used as a highly efficient photocatalyst for the degradation of organic pollutants in aquatic environments in a wide range of the solar spectrum. Under UV light, photoinduced electrons and holes are formed due to the excitation of gold clusters. Then, the electrons or holes can be captured by radicals and consequently, the organic dyes will be degraded.34

As we proposed in our previous study,7 Fig. 5 shows that such clusters, which have large stability and can be adsorbed on specific crystal planes, catalyze the growth of such planes giving rise to different particle shapes such as rods with high aspect ratios. When the concentration of the gold clusters increased, the aspect ratios of the formed rods increased from 18 to 23 (Fig. 5b–d), respectively. The longitudinal plasmonic band that is characteristic of gold rods cannot be seen with these high aspect ratios because the position of these bands appears at more than 1200 nm, as shown in Fig. 5a.

The formed clusters could be adsorbed onto particular surfaces of the gold seeds6,7,35 and can then act as a catalyst enhancing the growth of the GNRs (atomic metal clusters are now recognized as efficient catalysts34). The adsorption of these clusters on one of these facets leads to a break in the growth symmetry and enhances the growth of one of these facets much more than the others, which leads to the formation of rod-shaped particles.7

Herein, we used a model reaction, i.e., the reduction of p-nitrophenol (PNP) to p-aminophenol (ANP) to evaluate the catalytic activity of the formed clusters in the organic reaction. Without the addition of clusters as a catalyst, 4-nitrophenol was mixed with NaBH₄ to form a yellow solution that had maximum absorbance at 400 nm. This peak is characteristic of the 4-nitrophenol anion.36 Upon the addition of clusters, the intensity
of the peak at 400 nm started to decrease, while a new peak at 305 nm simultaneously appeared. After the addition of excess amount of NaBH₄ (10 mM) to PNP (0.1 mM) in aqueous solution, the success of the reaction was evaluated by analyzing the eluting solution by monitoring the progress of the chemical reaction using off-line UV-vis spectrophotometer. Fig. 6 shows the ¹H NMR of PNP as the starting material (Fig. 6a) and the ¹H NMR of ANP as a product (Fig. 6b) after the addition of the formed gold clusters. The new peak at 305 nm exhibited an absorbance corresponding to the reaction product 4-aminophenol. The reaction was monitored for 60 min. ANP with a high yield (83%) in short reaction time was obtained at the end of reaction. It has been proposed that there are two steps in the 4-NP reduction: (i) diffusion and adsorption of 4-NP on the Au surfaces and (ii) electron transfer mediated by Au surfaces from BH₄⁻/C⁰ to 4-NP, i.e., the electron transfer occurs from the negatively charged BH₄⁻ to the 4-NP via the Au clusters. After 60 min of reaction, the reaction mixture was diluted with diethyl ether and the organic phase was separated. Then, to remove impurities from the aqueous phase, extraction using ethyl acetate was performed. The aqueous layers were collected, filtrated and concentrated under reduced pressure at 25 °C to obtain pure sample containing Au NCs for recycling. The second and third recycled catalyst was employed in the reduction of p-nitrophenol (PNP) to p-aminophenol (ANP) to produce 79 and 78% isolated yield.

From all of the above results, it can be inferred that stable and efficient catalytic metal clusters can be formed facilely by the etching properties of the selenol group when added to the metal nanoparticles (see Fig. 7).

**Experimental**

**Preparation of gold nanoparticles**

In brief, gold ions were reduced chemically by sodium citrate in aqueous solution. Sodium citrate solution serves as a reducing agent and also as a capping material, preventing the aggregation or further growth of the particles. Then, 1% of sodium citrate solution (5 mL) was added to 40 mL of boiling chloroauric acid (HAuCl₄) solution containing 5 mg of gold ions. The solution was boiled for 30 minutes and left to cool to room temperature.
Preparation of 4,6-dimethyl-2-pyridineselenol-3-caronitrile (1)

The compound 4,6-dimethyl-2-pyridineselenol-3-caronitrile (1), which is the tautomer of 4,6-dimethyl-3-cyanopyridine-(2H)-selenone, was synthesized as previously described:29

A mixture of chloropyridine derivative (1.66 g, 10 mmol), selenium metal (1.0 g, 12 mmol) and sodium borohydride (1.2 g, 32 mmol) was refluxed in ethanol (50 mL) for 5 h. The mixture was cooled and poured into cold HCl solution. The solid precipitate was filtered, dried, and re-crystallized from ethanol. Details of the resulting data were in agreement with literature data.25 The compound was recrystallized from ethanol for characterization. Yield: 86%; mp = 214–216 (dec.); IR spectrum (cm⁻¹) 2217 (CN-group); ¹H NMR (DMSO-d₆); (δ, ppm): 2.41 (s, 3H, CH₃); 2.49 (s, 3H, CH₃); 7.26 (s, 1H-CH-pyridine), 14.12 (s, exchangeable). The mass spectrum of the compound exhibited a molecular ion peak at m/z, (%) 211 (M⁺, 90%). Anal: calc. for C₈H₈N₂Se (211.12).

Preparation of 4-methylquinolineselenol-3-carbonitrile (C₁₁H₈N₂Se) (2)

Compound (2) was prepared according to the method reported by Abdel-Hafez et al.37 A mixture of the corresponding chloroquinoline derivative (2.02 g, 10 mmol), selenium metal (1.0 g, 12 mmol) and sodium borohydride (1.2 g, 32 mmol) was refluxed in ethanol (50 mL) for 5 h. The mixture was cooled and poured into cold HCl solution.

The solid precipitate was filtered, dried, and recrystallized from ethanol. The compound was recrystallized from ethanol for characterization. Yield: 86%; mp = 298–300 °C; IR spectrum (cm⁻¹) 2200 (CN); ¹H NMR (DMSO-d₆); (δ, ppm): 2.41 (s, 3H, CH₃); 2.70 (s, 3H, CH₃); 7.40–8.10 (m, 4H-Ar-H), 14.95 (s, 1H, SeH– exchangeable). The mass spectrum of the compound exhibited a molecular ion peak at m/z, (%) 211 (M⁺, 90%). Anal: calc. for C₁₁H₈N₂Se (211.12).

Preparation of gold clusters

Compound (1) (1 mg) was added to 10 mL of the as-prepared gold nanoparticles and then, the mixture was sonicated for 20 minutes. After the reaction was completed, compound 1 was precipitated and collected by filtration. Then, for removal impurities in the supernatant, extraction using ethyl acetate (5 × 20 mL) was performed. The aqueous layers were collected and concentrated under reduced pressure at 25 °C to obtain pure sample containing Au NCS. After purification, the emission of luminescent clusters was recorded. The formed clusters were characterized in order to study their catalytic properties in gold nanorod preparation and in the photodegradation of methylene blue dye MB.

The obtained clusters (0.5 mL) were mixed with 10 μM of methylene blue (MB) dye under a low-power UV-lamp (Ana-lamp 254 nm) and a halogen lamp (HALOPAR 20 75 W 230 V 30° GU10, Italy). The temperature was kept constant at 28 °C in all the experiments to avoid thermal degradation.

Preparation of gold nanorods7

Seed solution. Initially, 0.2 M CTAB solution (2.5 mL) was mixed with 5 × 10⁻⁴ M HAuCl₄ solution (2.5 mL). To the above solution, 30 μL of ice-cold 0.1 M NaBH₄ was added under stirring, which resulted in the formation of a solution with brownish-yellow color. Vigorous stirring of the seed solution was continued for 2 minutes.

Growth solution. Different amounts (50, 100, and 150 μL) of gold clusters solution were added to 2.5 mL of 0.2 M CTAB. To this solution, 2.5 mL of 10⁻³ M HAuCl₄ was added and after gentle mixing of the solution, 35 μL of 0.0788 M ascorbic acid was added. Ascorbic acid as a reducing agent changed the growth solution from dark yellow to colorless within 10 minutes.

The final step was the addition of 15 μL seed solution to the growth solution. The color of the resultant solution gradually changed within 10–20 minutes.

General procedure for the reduction of aromatic nitro compounds with NaBH₄

A mixture of 30.0 mL of 0.1 mM aromatic nitro compound dissolved in ethanol and 3 mL of an aqueous solution of the formed gold clusters were added into a reaction flask; then, water (30 mL) was added. A freshly prepared 10 mM NaBH₄ ethanolic solution (9 mL) was added subsequently to the reaction mixture solution under continuous stirring. The mixture was stirred at room temperature for 60 min under visible light irradiation using a halogen lamp. The reaction was monitored by TLC and UV-vis spectroscopy. After 60 min, the reaction was diluted with diethyl ether and the organic phase was separated by TLC and UV-vis spectroscopy. After 60 min, the reaction was diluted with diethyl ether and the organic phase was separated and analyzed using a Bruker-Avance DPX 300 MHZ operating at 300 MHZ for ¹H NMR. The chemical data were reported in parts per million (ppm) downfield relative to tetramethylsilane (δ = 0 ppm). Deuterated dimethyl sulfoxide (DMSO-d₆) was used as the solvent (δ = 2.50 ppm for 1H and δ = 77.1 ppm for 13C).

Conclusions

In conclusion, semiconducting gold clusters were synthesized simply by etching or breaking gold nanospheres using organic compounds containing the highly reactive selenol group. The formed clusters were characterized by using TEM, AFM, ESI-MS and photoluminescence techniques. It has been shown that the
sub-nanometric Au clusters catalyze MB dye degradation under UV and visible light and have a catalytic role in the directed growth of gold nanorods with high aspect ratios. Also, the photocatalytic reduction of 4-nitrophenol using the formed gold nano-clusters is reported in this study.

Conflicts of interest
There are no conflicts to declare.

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Notes and references