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Formation of gold nanoparticles via a thiol functionalized polyoxometalate

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ABSTRACT

A useful method for the synthesis of Au nanoparticles is presented. The synthesis of Au nanoparticles with various morphologies was carried out at room temperature using gamma radiolysis and $NaBH_4$ reduction of $HAuCl_4$ in *N*,*N*′-dimethylformamide:water solutions containing polyoxometalate (POM). The results demonstrated that by controlling the rate of reduction and ratio of DMF and water, metal particle size and shape can be further tailored. It is shown that gold nanoparticles with controllable size can be synthesized. In principle, the general finding of this work can be extended to other transition/noble metal nanoparticles.

1. Introduction

Metal nanoparticles have a variety of interesting spectroscopic, electronic, and chemical properties that arise from their small sizes and high surface/volume ratios. Metal nanostructures with well-defined shapes have been the focus of current research in colloid chemistry [1–4]. Nanoparticles of gold and silver in different geometrical forms have been recently synthesized [2–4] as they have vast applications for optical devices such as antireflective surface coatings, optical gratings, DNA detection, and surface-enhanced Raman spectroscopy [5–7]. Nanoparticles can self-assemble into stable and ordered constructs with the assistance of surfactants, ligands, etc. Hydrophobic compounds such as alkanethiols, alkylamines or cationic surfactants have been used to drive the nanoparticles towards self-organization [7]. Recently, Sau et al. have shown that multiple shapes of Au nanoparticles such as hexagons, cubes, and branched structures can be prepared in conditions almost analogs to those used in rod synthesis [8]. Kim et al. have prepared isotropic gold nanostructures of truncated tetrahedra, cubes, and icosahedra termed platonic nanocrystals by a polyol method [9]. The particle shapes are closely related to the crystallographic surfaces that enclose the particles [7].

Biphasic synthesis of gold colloids using long chain thiols has so far been the best method to prepare thiol capped metal nanoparticles [10,11]. Thiols undergo a strong bonding with the surface of gold nanoparticles leading to spatially well-defined organizations. Dithiols have been successfully used for the formation of 3D networks of gold nanoparticles [12]. In such type of organizations, alkane thiols or dithiols act as a spacer to bridge the gold nanoparticles. These alkanethiol modified Au nanoparticles can be stored for a long period of time in both solution and powder form [7].

Recently, polyoxometalates (POMs) have received increasing attention because of their size which is smaller than gold nanoparticles and intermediate between the colloidal and molecular ranges [13–15]. Mostly, α-Keggin- and Dawson-type heteropolyanions of phosphotungstate, silicotungstate, phosphomolybdate and silicomolybdate are used because of their stability and ease of preparation. Hence, a number of studies involving nanoparticles and POMs are reported in literature [13–16]. Hybrid organic–inorganic materials obtained using POMs and the development of ordered assemblies of POMs in such hybrid systems are of great interest [14]. Recently, a nanoscale hybrid system in which Au nanoparticles associated with thiol functionalized POM was reported [15].

Among many methods known for preparation of metal nanoparticles, radiolytic and photolytic methods are considered as clean methods since no reductant is added from outside [17–19]. In this work, we report a facile synthesis of gold nanoparticles using radiolytic method. The synthesized gold nanoparticles were passivated by thiol derivatized polyoxometalate $[POM(SH_2)]^{4-}$ (Scheme 1) which controlled particle growth and stabilized the particles after they formed in various amounts of DMF/water solution. The various parameters affecting the formation of the nanoparticles have been discussed using different techniques such as: UV–visible spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and attenuated total reflectance Fourier transform infrared (ATR-FTIR) studies.

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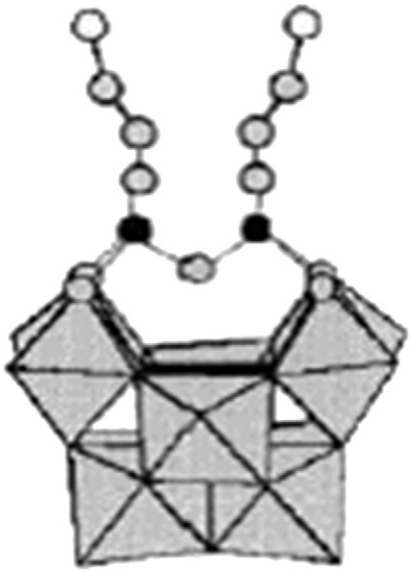

Scheme 1. Schematic representation of thiol functionalized polyoxometalate $[POM(SH)_2]^{4-}$.

2. Materials and methods

2.1. Materials

All the chemicals required for the synthesis of the silane modified polyoxometalate were of analytical grade and purchased from Thomas Baker. $HAuCl_4$ (Aldrich), *N,N′* dimethylformamide (Fluka, Spectroscopic grade) and (3-mercaptopropyl)trimethoxysilane (Aldrich), sodium borohydride (Sigma) were used as received. Water purified by a Millipore system was used for making the solutions.

2.2. Synthesis of thiol functionalized polyoxometalate $[POM(SH_2)]^{4-}$

The lacunary Keggin ion $K_8(\gamma\text{-}SiW_{10}O_{36})$ was synthesized as reported elsewhere [20]. 30.0 g of $K_8SiW_{11}O_{39}$ was dissolved in 300 mL of distilled water and the pH of the solution was adjusted to 9.1 by addition of an aqueous solution of 2.0 mol L^{-1} K_2CO_3. The pH of the solution was kept to 9.1 for 16 min. The potassium salt of the 10-tungstosilicate was precipitated by addition of 40.0 g of solid KCl. During the precipitation, the pH must be maintained at 9.1 by addition of small amount of the carbonate solution. The solid was filtered off and air-dried.

The organosilyl derivative $[\gamma\text{-}SiW_{10}O_{36}(RSi)_2O]^{4-}$ [R = $-C_3H_6SH$], called as $[POM(SH_2)]^{4-}$ was synthesized according to a reported procedure [15]. 0.28 mL (1.33×10^{-3} mol L^{-1}) of (3-mercaptopropyl) trimethoxysilane (HSC_3H_6-Si(Ome)$_3$ is added to a solution of 2 g (6.66×10^{-4} mol L^{-1}) of $K_8(\gamma\text{-}SiW_{10}O_{36})\cdot12H_2O$ and 0.64 g of Bu_4NBr in 40 mL of acetonitrile and 10 mL of water at 0 °C. Then the mixture is acidified by 1.2 mL of a 12.0 mol L^{-1} solution of hydrochloric acid and the solution is stirred overnight. The compound is obtained after evaporation of the organic solution.

2.3. Synthesis of functionalized polyoxometalate capped gold nanoparticles by γ-irradiation

In a typical experiment, 0.0117 g of $HAuCl_4$ is dissolved in 8 mL DMF. To this solution 0.015 g of $[POM(SH_2)]^{4-}$ is added and the solution is made up to 10 mL by addition of water. The ratio of DMF/water is kept at 4:1. Propan-2-ol is added to the solution such that its concentration in the solution is 0.2 mol L^{-1}. The above solution was then irradiated for a period of 60 min in the ^{60}Co γ-source (dose rate 8 Gy/min). Similar experiments were carried out by varying the DMF/water ratio to 3:1, 2:1 and 1:1. Further decrease in the concentration of DMF was avoided as it leads to heavy turbidity in the solution.

2.4. Synthesis of functionalized polyoxometalate capped gold nanoparticles by chemical reduction

In a typical experiment, 0.0117 g of $HAuCl_4$ is dissolved in 8 mL DMF. To this solution, 0.015 g of $[POM(SH_2)]^{4-}$ is added and the solution is made up to 10 mL by addition of water. The ratio of DMF/water is kept at 4:1 and $NaBH_4$ (0.001 g) was added to the solution. The solution was shaken vigorously for 5 min. The resulting gold nanoparticle colloidal solution appeared to be wine red in color. Similar experiments were carried out by varying the DMF/water ratio to 1:1.

2.5. Characterization of gold nanoparticles

Absorption measurements were carried out on a JascoV-530 spectrophotometer. The spectra were recorded at room temperature using a 1 cm quartz cuvette. The FTIR measurement for solid samples was carried out using KBr pellets on a Nicolet Nexus 870 FTIR spectrophotometer. The ATR-FTIR spectra were recorded on a Nicolet Nexus 870 spectrometer equipped with liquid nitrogen-cooled MCT detector and a circle cell (Spectratech Inc.) with horizontal ZnSe crystal rod. The spectra were recorded with a resolution of 4 cm^{-1} and an average of 100 scans. Samples for transmission electron microscopy (TEM) were prepared by putting a drop of the colloidal solution on a copper grid coated with a thin amorphous carbon film. Samples were dried and kept under vacuum in a desiccator before putting them in a specimen holder. TEM characterization was carried out using a PHILIPS CM-200 electron microscope. Particle sizes were measured from the TEM micrographs. The particle size was calculated by taking average of at least 100 particles. Samples for scanning electron microscope (SEM) were prepared by placing a drop of the solution over the Silicon wafer and dried thoroughly. The SEM characterization was carried out on a Leica Stereoscan-440 scanning electron microscope. X-ray diffraction studies were carried out on a Rigaku (D Max III VC) diffractometer.

3. Results and discussion

3.1. Formation of gold nanoparticles covalently attached to the functionalized polyoxometalate

The radiolysis of water gives rise to different radical species in solution as shown in Eq. (1) [21,22](1)

$$H_2O \rightsquigarrow e_{aq}^-, H_3O^+, H^\cdot, H_2, {}^\cdot OH, H_2O_2. \quad (1)$$

Among them, the hydrated electron (e_{aq}^-) and H atom are strong reducing agents. They can easily reduce metal ions to zerovalent state [17,18]. The addition of a small amount of propan-2-ol leads to scavenging of the •OH radical and H atom to alpha-hydroxyalkyl radicals

$$\bullet OH/H\bullet + CH_3CH_2CH_2OH \rightarrow CH_3CH_2\cdot CHOH + H_2O/H_2 \quad (2)$$

$$CH_3CH_2\cdot CHOH + RSH \rightarrow RS\bullet + CH_3CH_2CH_2OH \quad (3)$$

$$2RS\bullet \rightarrow RSSR \quad (4)$$

where, RSH can be considered to be the thiol functionalized polyoxometalate $[POM(SH_2)]^{4-}$. Fig. 1 depicts the UV–visible absorption spectra obtained before and after γ-irradiations of a solution containing $HAuCl_4$, $[POM(SH_2)]^{4-}$ and propan-2-ol at various ratios of DMF/water. At 4:1 ratio, we observed a sharp symmetric curve