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Self-organization of Gold Nanoparticles Protected by 9-(5-Thiopentyl)-carbazole

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Abstract: Through the reduction of $[AuCl_4]^-$ by aqueous sodium borohydride in the presence of 9-(5-thiopentyl)-carbazole, the gold nanoparticles has been prepared and characterized.

Keywords: 9-(5-Thiopentyl)-carbazole, gold nanoparticles.

Introduction

During the past decade, nanometer-sized metal clusters, special the gold clusters, possessing unusual physical and chemical properties have been extensively investigated[1-5]. In recent years, a new effort has been focused on fabricating ordered metal nanoparticles with well-defined two or three dimensions using nanometer-sized metal clusters as building blocks[6-9]. This will provide a new horizon to develop novel optical and nanoelectronic devices. Ordered nanoparticle assemblies are generally achieved by Langmuir-Blodgett techniques[10] or by controlled solvent evaporation on a substrate[11]. However, both the approaches only obtain the relatively simple nanoparticles architectures. In order to solve this problem, one of the strategies is to prepare a nano-particle stabilized by organic ligands with linking sites and the ligands can interact each other by weak interaction[6], such as π-π interactions.

In this paper, we report the synthesis of a novel class gold nanoparticles and the formation of their self-organized superclusters on the carbon-coated copper grid. The designed protective organic ligand, 9-(5-thiopentyl)-carbazole is prepared from 9-(5-bromopentyl)-carbazole[12]. It has two functional groups, a thio group and a carbazole group. The thio group is used to form stable gold nanoparticles and the carbazole group is used to induce the π-π interactions between the ligands. Moreover, the carbazole has special photo-electrical properties and has been used as the functional building block for organic photoconductors, NLO materials, and photorefractive materials[13-15]. This makes the gold nanoparticles protected by ligands containing carbazole unit suitable for fabrication of novel nano-optical and nano-electronic devices. The synthetic route of the gold nanoparticles is sketched in **Scheme 1**.

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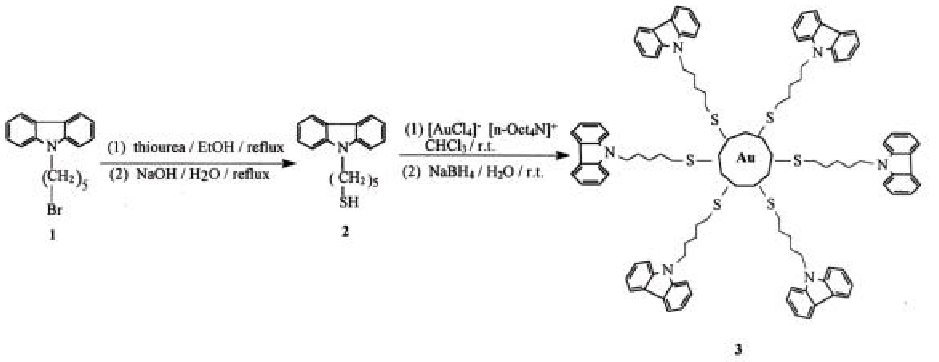
Scheme 1



Results and discussion

The gold nanoparticles were prepared using typical method[1], $[AuCl_4]^-$ was transferred from aqueous solution to chloroform using tetraoctylammonium bromide as the phase-transfer reagent and reduced with aqueous sodium borohydride in the presence of 9-(5-thiopentyl)-carbazole. The $[AuCl_4]^-$ solution turned from orange to purple after the addition of $NaBH_4$ aqueous solution.

The ^1H-NMR spectra of the surface modified nanoparticles in *o*-dichlorobenzene showed that all the resonances assigned to the aromatic and methylene group are significantly broaded, which are characteristics of alkanethiols absorbed at a nanocrystal[16]. The FT-IR spectra of the gold particles are similar with that of 9-(5-thiopentyl)-carbazole. The emission spectra of the gold nanoparticles and 9-(5-thiopentyl)-carbazole are similar, and show the emission peaks at 353 nm and 369 nm. All these results indicate that the 9-(5-thiopentyl)-carbazole is indeed part of the composite.

The absorption spectra of gold nanoparticles in $CHCl_3$ exhibited a little surface plasm absorption band (max. at 546 nm.) which is ascribed to a collection oscillation of conduction electrons in response to optical exicitation[17]. This means the formation of gold nanoparticles. In addition, the characteristic absorption of the carbazole group at 265, 293, 333 and 346 nm are also observed.

The gold nanoparticles are dissolved in chloroform and a drop of the resulting dispersion is placed on a carbon-coated Cu grid and the chloroform allows to evaporate. As the corresponding TEM shown in **Figure 1**, solvent evaporation is accompanied by the self-assembly and the formation of superclusters of nanosize. The diameter of the gold superclusters is in the range of 30 nm to 55 nm. Taking into account of the larger diameters of the gold superclusters, the results suggest that each gold nanoparticle is stabilized by a 9-(5-thiopentyl)-carbazole layer and the interpenetration occurs between adsorbed carbazole by π-π interactions on adjacent particles as shown in **Figure 2**.

Figure 1 The TEM image of 9-(5-thiopentyl)-carbazole—protected gold nanoparticles

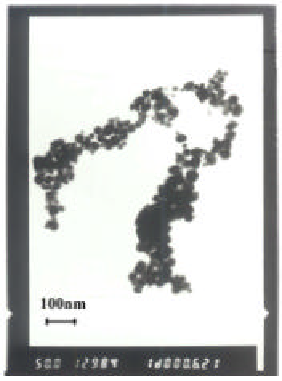
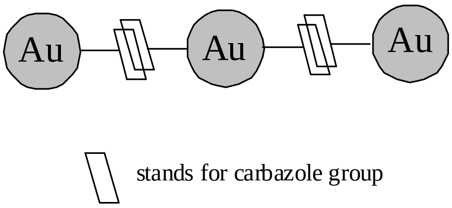


Figure 2 Schematic illustration of the inter-penetration of carbazole group adsorbed on gold nanoparticles



Experimental

Synthesis of 9-(5-thiopentyl)-carbazole

A solution of 9-(5-bromopentyl)-carbazole (315.0 mg, 1.0 mmole) and thiourea (76.0 mg, 1.0 mmole) in 20 mL of 95% EtOH was refluxed for 8 h, and then, NaOH (60.0 mg, 1.5 mmole) was added. The resulting solution was refluxed for 3 h. After the EtOH was evaporated, 0.1 mol/L H_2SO_4 was added. The reacting mixture was extracted with Et_2O (20 mL×3), and the Et_2O extract was dried over Na_2SO_4. After Et_2O was removed, a gum solid was obtained. The crude product was crystallized from $CHCl_3$/hexane to give the product (204.0 mg, 75.8%). IR (KBr, cm^{-1}) 2936, 2856, 1596, 1484, 1452, 1326,750; ^{1}H-NMR($CDCl_3$, ppm) δ 8.11(d, *J*=7.70, 2H), 7.34-7.48 (m, 4H), 7.22 (t, *J*=7.23, 2H), 4.25 (q, *J*=7.06, 7.89, 2H), 2.58 (t, *J*=7.26,1H), 2.38 (t, *J*=6.81,1H), 1.86 (t, *J*=6.81,3H), 1.68 (t, *J*=7.31, 1H), 1.43-1.57 (m, 3H); MS (EI): *m/z* 269 (M).

Synthesis of gold nanoparticles

$HAuCl_4.4H_2O$ (186.5 mg, 0.453 mmole) in deionized H_2O (20 mL) was added to a phase transfer catalyst *n*-Oct_4NBr (1.10 g, 2.02 mmole) in $CHCl_3$ (20 mL), and the resulting mixture was stirred vigorously for 30 min. The organic layer was separated and 9-(5-thiopentyl)-carbazole (29 mg, 0.108 mmole) in $CHCl_3$ (5 mL) and the $NaBH_4$ (190.5 mg, 4.6 mmole) in H_2O (10 mL) were added. The resulting mixture was stirred 12 h at room temperature. The organic layer was separated and evaporated to about 4 mL, and EtOH (20 mL) was added to precipitate the gold nanoparticles. The crude gold nanoparticles obtained by centrifugation were re-dissolved in $CHCl_3$ (5 mL) and re-precipitated by addition of EtOH (20 mL). The gold nanoparticles were obtained by centrifugation and dried 12 h under vacuum.

Conclusions

We have successfully prepared gold nanoparticles protected by 9-(5-thiopentyl)-carbazole. The self-organized gold nanoparticles superclusters are formed on the carbon-coated Cu grid. This presumably due to a π-π interaction between adsorbed species on adjacent particles. These inorganic-organic hybrid materials soluble in common organic solvents are potentially useful for the fabrication of novel optoelectronic nanodevices.

Acknowledgment

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