Micropatterned Film of Silica-coated Gold Nanoparticles Formed by Covalent Bonds

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With well-established surface-chemical properties, monodisperse silica-coated Au nanoparticles (Au@SiO_2) were first functionalized with the silane reagent 3-gylcidoxypropyltrimethoxysilane (GPTS). Then, these epoxy-terminated Au@SiO_2 nanoparticles could be easily assembled onto the silicon surface, which has been patterned with 3-aminopropyltriethoxysilane (APS) SAMs and octadecyltrichlorosilane (OTS) SAMs alternately, to form close-packed two-dimensional nanoparticle arrays by covalent bonding.

Since the pioneering work on the silica-coated gold nanoparticles by Mulvaney and his co-workers in 1996,[1] various works about silica-coated colloidal nanoparticles have been extensively investigated to enhance their colloidal stability.[2–6] Although different methods have been developed to prepare Au@SiO_2 nanoparticles recently, the surface functionalization and the assembly of Au@SiO_2 nanoparticles have not been investigated. However, it is well known that one of the most important developments in nanomaterial is that of the nanostructuring.[7] Nanostructured materials are assembling the nanosized units which display unique, characteristic properties in a microscopic scale. In this paper, we mainly focus on the functionalization of the core–shell Au@SiO_2 nanoparticles and their selective assembly on patterned SAMs by covalent bonding.

In the present work, monodisperse Au@SiO_2 nanoparticles were prepared by homogenous vortex mixing. This method provides more homogenous mixing, avoiding the formation of self-nucleated silica spheres, as well as eliminating the nucleation sites from foreign objects such as stirring bars. Figure 1A shows the typical transmission electron microscopic (TEM) photograph of the gold nanoparticles in 35-nm diameter coated with a uniformly thick silica shell. Obviously, most Au cores have been coated with a 70-nm thick silica shell, and most Au@SiO_2 particles are spherical and have a single Au core.

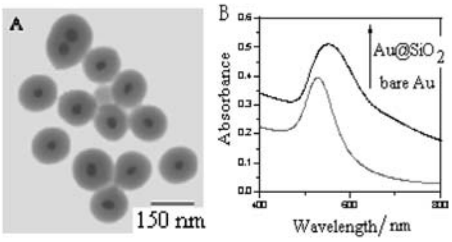


Figure 1. A) the TEM photograph of Au@SiO_2 nanoparticles; B) UV–vis spectra of Au nanoparticles before and after coated with silica.

The UV–vis spectra measured for Au nanoparticles before and after coated with silica show that the optical properties are altered as illustrated in Figure 1B. When the bare Au nanoparticles are coated with a silica shell, there is an increase in the intensity of the plasma adsorption and a red shift in the position of the absorption maximum. This is due to the increase of the local refractive index around the Au nanoparticles and the increase of the particle size based on the bare Au nanoparticles after coated with silica shells, which has been investigated in detail by Liz-Marzán and Mulvaney.[8]

Our modified Stöber process provides a uniform silica surface, which is very important for straightforward surface functionalization of the Au@SiO_2 nanoparticles with different silane reagents. Here, epoxy-terminated Au@SiO_2 nanoparticles were obtained by grafting the silane coupling reagent GPTS on the surfaces of the particles at 50 °C. The FT-IR spectra in Figure 2 give direct evidence that silane reagent GPTS has been successfully bonded onto the surfaces of the Au@SiO_2 nanoparticles. There are two characteristic peaks of methylene ($-CH_2$) at 2935 and 2872 cm^{-1} as marked by circles, which are assigned to the asymmetric and symmetric stretching vibrations of C–H bonds, respectively. In addition, both the Si–OH group and the epoxy ring have absorbing frequencies in the same region of 750–1050 cm^{-1}, these overlapping absorption bands can screen the signal of the epoxy rings, which complicate the interpretation of the results.[9]

One of the most important developments in nanoparticles is the regular assembly. Here, we first structured a supersite-selective micropattern by the ring-opening reaction between the epoxy-terminated Au@SiO_2 nanoparticles and amino-terminated APS SAMs shown in Scheme 1.

Epoxy-group, which is the terminal group of GPTS, is prone to reacting with nucleophilic reagents such as carboxylic acid and amines to form a neutral oxygen–hydrogen bond. Epoxy-functionalized surface has been widely used to immobilize

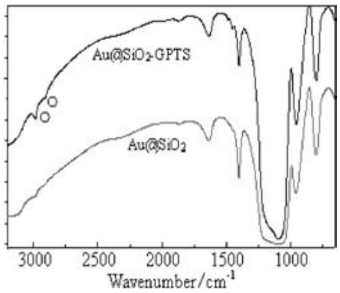
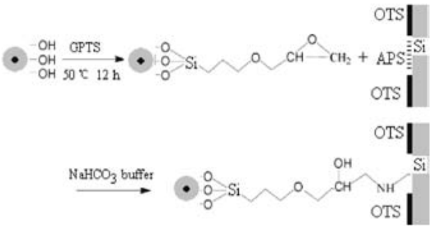


Figure 2. FT-IR spectra of Au@SiO_2 nanoparticles before and after functionalized with silane reagent GPTS.



Scheme 1. Fabrication of Au@SiO_2 pattern with supersite selectivity by covalently bonding.

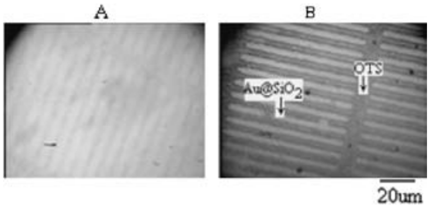


Figure 3. The optical microscope photograph of patterned Au@SiO_2 nanoparticles: A) at pH 7; B) at pH 9.2.

amino-terminated oligonucleotides in the fabrication of biosensors due to the feasible ring-opening reaction.[10,11] Based on this strategy, a micropattern with supersite selectivity has been structured by the interaction of covalent linking. During the experiment, it is found that a strong alkaline condition is favorable for the ring-opening reaction, which can be also testified by the photographs of the patterned film of Au@SiO_2 nanoparticles performed at pH 7 and pH 9.2, respectively, shown in Figure 3. Apparently, under a neutral condition, a blurred image is obtained as shown in Figure 3A. Moreover, the film can be easily peeled off from the silicon substrate. Hence, it can be concluded that the formation of the patterned film is a simple process of physical adsorption at pH 7. However, in a strongly alkaline system, a clear and super selective pattern formed as illustrated in Figure 3B. Clearly, there are no particles deposited on OTS SAMs as a result of the inert property of methyl group. Furthermore, the nucleophilic interaction between the nonbonded electron pairs on the nitrogen of amine group and the carbon atom of the epoxy ring leads to the sequential process of ring opening, electron rearrangement, and the formation of a neutral oxygen–hydrogen bond under alkaline cundition. Hence, the Au@SiO_2 nanoparticles are selectively deposited on the amino-terminated SAMs. In order to further testify whether the particles have been selectively deposited on amino-terminated SAMs, the patterned film has been examined by a SPI-3800N atomic force microscopy (AFM) made by Seiko of Japan. As shown in Figure 4, on the amino-terminated SAM-dominated regions, there exists close film of Au@SiO_2 nanoparticles with a thickness of about 170 nm. However, there are no particles deposited on the methyl-terminated SAMs. In a word, our findings indicate that the epoxy-terminated Au@SiO_2 nanoparticles are believed to be covalently linked to the amino-terminated surface. Due to the limitation of the length, the formation of a covalent linking was not explicitly tested by XPS here.

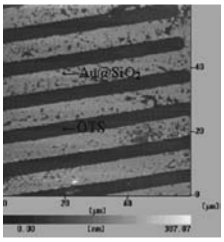


Figure 4. The AFM image of patterned Au@SiO_2 nanoparticles formed at pH 9.2.

In conclusion, the core–shell Au@SiO_2 nanoparticles were first functionalized with the silane coupling reagent GPTS. More interesting, a micropattern with supersite selectivity has been obtained by the strong interaction of covalent bond which is much stronger than the electrostatic interaction and the van der Waals force. The research work pioneered a new way for the functionalization and assembly of the nanoparticles.

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