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Alternate assemblies of thionine and Au-nanoparticles on an amino functionalized surface†

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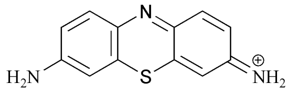
Photoactive and electroactive thionine dyes have been introduced in high-surface-area surface-confined Au-nanoparticle superstructures by layer-by-layer deposition techniques.

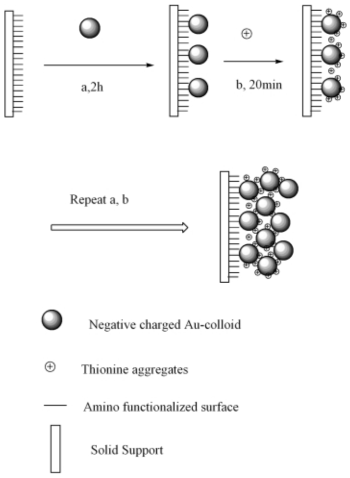
Recently, increasing interest has been focused on the miniaturization and nanoscale engineering of functional chemical assemblies.[1] The assembly of metal nanoparticles into 2-D[2] and 3-D[3] superstructures has been reported by using amio/thiolsiloxanes and dithiols/diamines/bipyridinium as cross-linkers. Furthermore, Shipway and Willner[4] incorporated electroactive and photoactive elements into such surface-confined architectures. Such functionalized superstructures have been shown to have sensoric[5] and photo-electrochemical[6] applications.

Thionine has been widely used as both a photoactive species and a charge carrier in photogalvanic cells.[7] Incorporating such functional units into high-surface-area surface-confined systems using Willner's strategy[4] might be significant for solar cell applications. It has been reported that aggregation[8] of thionine is readily observed upon addition of small amounts of negatively charged colloid to an aqueous solution of the dye. Such aggregation can also take place on surface-confined SnO_2 nanocrystalline films.[9] Here, we found similar aggregation can also take place on surface-confined gold nanoparticles. The resulting thionine aggregate layer was shown to be able to adsorb additional gold nanoparticles. As a result, the repeated treatment in gold colloid solution and thionine aqueous solution leads to the generation of alternate assemblies containing thionine and Au-nanoparticles.



Thionine, TH$^+$

The whole preparative process is outlined in Scheme 1. A clean solid support was first modified with 3-aminopropyltrimethoxysilane (APTMS) for a glass substrate (or mercaptoethylamine (MEA) for a gold electrode), and then the first layer of Au-particles (10 ± 1 nm) was assembled on the amino premodified surface using a well-defined Au colloid.[10] The resulting surface was treated with an aqueous solution of thionine (1 mM, 20 min) and subsequently with the Au colloid solution (0.1 mM, 2 h) to create the second Au-layer. By alternate treatment with 1 mM thionine aqueous solution and the Au colloid, three-dimensional nano-architectures consisting of a controllable amounts of functionalized units were generated.



Scheme 1 Fabrication of thionine bridged Au-nanoparticle superstuctures by stepwise derivatization of a colloidal Au monolayer with thionine (1 mM) and Au-nanoparticles (0.1 mM).

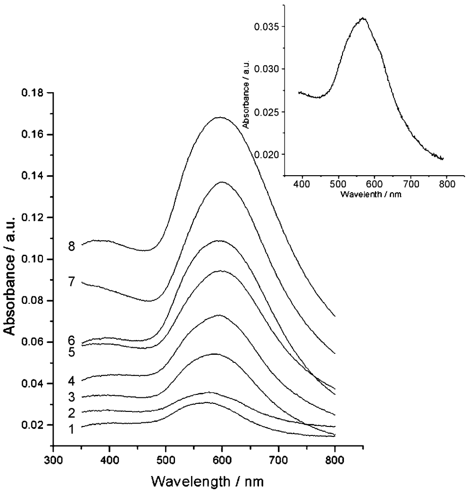


Fig. 1 UV-vis absorbance spectra of thionine bridged Au-nanoparticle superstructures on an optical glass slide. The layer numbers are labeled beside each curve and each curve was recorded including a top thionine layer. Inset: the spectrum of the first Au-nanoparticle layer that includes co-associated thionine, from which the spectrum of the first Au-nanoparticle layer assembled on aminosiloxane is subtracted.

The formation of thionine bridged Au-nanoparticle superstructures was confirmed and characterized by optical spectra and electrochemistry. Fig. 1 shows UV-vis absorbance spectra of the 3-D superstructure upon stepwise deposition of Au-nanoparticles and thionine (each curve corresponds to the respective Au-nanoparticle layer that includes a top co-associated thionine layer). The inset shows the difference spectrum obtained when the spectrum of the first Au-nanoparticle layer is subtracted from the spectrum obtained upon the association of thionine on the first Au-layer. The maximum absorbance band is blue-shifted and broadened relative to that of monomeric thionine, indicating an H-type aggregate.[9,11] Most of these adsorbed aggregates should be dimers since a characteristic absorbance at ~560 nm is the strongest.[9,11] The two shoulder peaks at ~610 and ~530 nm shows the presence of small amounts of trimer and monomer in

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† Electronic supplementary information (ESI) available: AFM images and cyclic voltammograms. See http://www.rsc.org/suppdata/cc/b2/b204004b/

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the superstructure. Thionine molecules contain aurophilic S and N atoms, both of which bind strongly to Au-nanoparticles.[4–6] Therefore, both electrostatic and covalent interactions could account for thionine anchoring on Au-nanoparticles. Such strong binding interactions were demonstrated by electrochemical measurements, where desorption of thionine did not take place even in concentrated H_2SO_4. Also, adsorbed thioine aggregates behave as oligomers with additional exposure of aurophilic groups, which could result in additional Au-nanoparticle adsorption. To prove this, we immersed the slide containing one Au-nanoparticle and thionine bilayer into the Au colloid for about 2 h, and tested optical absorbance changes. An obvious absorbance increase was noted, which can be attributed to additional Au-nanoparticle immobilization. Furthermore, repeated treatment with thionine and Au-nanoparticles resulted in 3-D superstructure generation, evidenced by the increase of the total absorbance as shown in Fig. 1. Electrostatic and covalent interactions could be the driving forces for the formation of such a superstructure. Additionally, from atomic force microscopy (AFM), we found that this superstructure was not layered, but rather an alternating pile-up of Au-nanoparticles and thionine (Au-nanoparticles and thionine fill in the voids present on the previous superstructure, ESI†). Compared with Willner's report,[4] the total broad absorbance band extending from ~500 to ~700 nm seems to be more complex, which might include the characteristic absorbance of monomer and H-type aggregates (dimer and trimer) of thionine,[8,9,11] gold surface plasmon absorbance,[12] interparticle plasmon coupling,[13] and damping effects upon thionine adsorption.[14]

The 3-D superstructure can also be self-assembled on an MEA derivatized gold electrode. The derivatizing procedure is similar to that on glass except that MEA was used instead of APTMS as the molecular linker between the substrate and superstructure. Fig. 2 shows the cyclic voltammograms of the as-prepared gold electrode surface confined superstructure. The redox wave at E^0 *ca.* 290 mV is characteristic of oxidation/reduction of dimeric thionine.[15] Electrochemical results are consistent with the optical experiment, confirming that thionine incorporated in the superstructure exists predominantly in dimeric form. Coulometric analysis of the redox wave reveals that the charge associated with thionine increases almost linearly with increasing bilayer number. This provides additional proof for the formation of a thionine bridged 3-D Au-nanoparticle superstructure. Assuming the surface density of Au-nanoparticles per layer is 0.8×10^{11} particles cm^{-2},[16] we estimate the number of associated thionine moleclues per Au-nanoparticle in the superstructure is *ca.* 120 according to the above coulometric analysis.

The superstructure modified gold electrode exhibited extremely stable electrochemical behavior in 0.5 M H_2SO_4. 1 h repetitive scans of the electrode in the potential range of –0.4 to + 0.6 V in 0.5 M H_2SO_4 aqueous solution lead to little appreciable changes in both peak current and peak-to-peak separation. Fig. S3 (ESI†) shows cyclic voltammograms of the gold electrode with 13 bilayers at various scan rates obtained in 0.5 M H_2SO_4 aqueous solution. The redox peak currents are linearly proportional to the scan rate at least up to 900 mV s^{-1} (ESI†), suggesting facile surface-confined charge transfer kinetics.

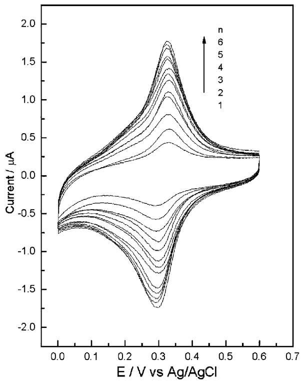

Fig. 2 Cyclic voltammograms of thionine immobilized into the as-prepared superstructure for different bilayer numbers *n* from 1 to 13 in 0.5 M H_2SO_4. Scan rate: 50 mV s^{-1}. Each curve was recorded when the adsorbing step of thionine was completed.

It should be noted that the oxidation/reduction of thionine involves protons.[17] The well-behaved electrochemical response of thionine indicates the thionine immobilized into the superstructure is accessible to protons. The increasing electrochemical response of thionine upon the build-up of the superstructure also implies that the superstructure exhibits three-dimensional electrical conductivity. This electrical conductivity of the as-prepared nanostructured Au colloid electrode is also demonstrated by its obvious electrochemical catalysis towards NADH (ESI†). The facile electron and proton accessibility of the as-prepared 3-D superstructure could find sensoric applications.[5]

In summary, functional thionine molecules have been introduced successfully into Au-nanoparticle superstructures as evidenced by optical and electrochemical experiments. Dye molecules which are electrostatically or covalently bound to colloid particles have been shown to extend their photoresponse.[18] Therefore, incorporating thionine into high-surface-area surface-confined systems might be significant for solar cell applications (such as light energy conversion devices[19]).

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