Au-colloid–'molecular square' superstructures: novel electrochemical sensing interfaces

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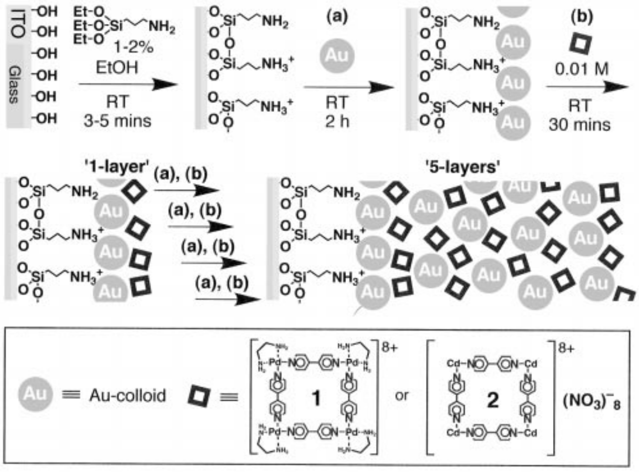
New sensing interfaces have been constructed by the non-covalent crosslinking of 12 nm Au colloids with 'molecular square' transition-metal complexes.

The development of methodologies that take advantage of supramolecular, microenvironmental or quantum effects in order to assemble highly ordered structures displaying sensoric, electronic or photoelectrochemical activites is being extensively studied.[1] Colloidal nanoparticles have been used for the organization of complex assemblies such as patterned surfaces,[2] 'strings'[3] and, in particular, multilayer architectures.[4] These nanoparticles may be passive structural elements, or may contribute to the functionality of the assembly with electronic, optical or catalytic properties.[5] We have recently reported[6] on layered superstructures of citrate-coated Au nanoparticles (12 ± 1 nm) that are crosslinked by oligocationic bipyridinium-containing receptor molecules. These assemblies are stabilized by electrostatic interactions between the negatively charged nanoparticles and the positively charged crosslinkers,[7] and exhibit three-dimensional conductivity, allowing the electrochemical sensing of a series of π-donor substrates.

Recently, a new class of water-soluble transition-metal complexes with cyclophane-like structures was developed[8] by Fujita and Stang. This series of 'molecular square' compounds, consisting of bipyridine units linked by metal ions (*e.g.* Pd^{2+} or Pt^{2+}) was examined as a general methodology for the preparation of new molecular cavities for host–guest interactions.[9] A series of square Re(I) complexes was employed for the sensing of anions by following the enhanced luminescence of the complex upon the encapsulation of an analyte.[10] Complexation results in a change of the intramolecular electron transfer quenching energetics. These molecular square complexes bear positive charges and so were anticipated to crosslink Au nanoparticles to yield novel superstructure architectures. Here, we wish to report on the organization, characterization and sensing properties of Au nanoparticle layered superstructures crosslinked by 'square-type' metal complexes.

Superstructures of Au nanoparticles were constructed on indium-doped tin oxide (ITO) conductive glass, as outlined in Scheme 1. The cleaned surface was first functionalized with 3-aminopropyltriethoxysilane to give a positively charged amine surface, which was treated with a citrate-stabilized Au colloid (12 ± 1 nm).[11] The resulting Au-colloid layer was then treated with the 'Pd-square' $[(en)Pd(4,4'\text{-bipy})]_4(NO_3)_8$ (**1**)[8a] or the 'Cd-square' $[Cd(4,4'\text{-bipy})]_4(NO_3)_8$ (**2**) to give a first receptor layer. By stepwise treatments of the superstructure with the Au-nanoparticle solution and the crosslinking component, interfaces of a controllable number of layers were generated. The resulting crosslinked Au–nanoparticle superstructures are very stable as a consequence of multi-site ion pairing, and the particles can only be removed from the ITO surface by physical scratching. The structures of the Au arrays were probed by three methods: Fig. 1(a) shows the absorbance spectrum of the array upon the stepwise assembly of layers. While the typical plasmon absorbance associated with gold nanoparticles (λ = 518 nm) is present, the growth of layers results in the appearance of an additional absorbance band at λ *ca.* 650 nm, similar to the absorbance changes experienced by an Au-colloid solution upon the formation of large (of the order of 1 μm) aggregates, and is attributed to interparticle plasmon coupling.[12] Fig. 1(b) shows cyclic voltammograms of the Au-nanoparticle surfaces in assemblies containing 1–5 layers of **1**-crosslinked Au nanoparticles. The Au surface area of the assembly increases almost linearly with the growth of the number of layers. From the diameter of the particles (12 ± 1 nm) the surface area of a single particle can be obtained, and by coulometric analysis of the Au reduction wave, the Au particle density is estimated to be 0.2×10^{11} particles $\times$ cm^{-2} per layer. The formation of the assembly of **1** and **2** and the nanoparticles is supported by XPS measurements. For a five-layer assembly, the Au : Pd ratio is *ca.* 30 : 1. This ratio is very similar to that observed for a three-layer assembly. Since the formation of the array is evident from the increase of the plasmon absorbance and cyclic voltammogram of the array, these results indicate



Scheme 1 The stepwise assembly of the three-dimensional array of the Palladium–bipyridine 'square' and Au nanoparticles on a conductive ITO support.

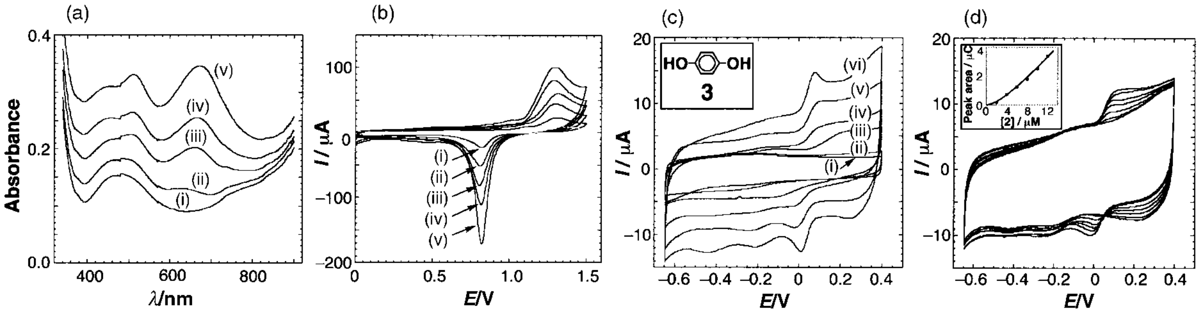


Fig. 1 (a) Absorbance spectra of the **1**–Au-colloid superstructure: (i) one Au layer, (ii) two Au layers, (iii) three Au layers, (iv) four Au layers and (v) five Au layers. (b) Cyclic voltammograms of the layered **1**-crosslinked Au-colloid assemblies corresponding to the electrochemical oxidation and reduction of the particle surface. (i)–(v) Correspond to 1–5 layers of Au particles. Experiments were carried out in 1.0 M H_2SO_4, scan rate 50 mV s^{-1}. (c) Cyclic voltammograms of the **1**-crosslinked Au-colloid arrays in the presence of hydroquinone **3** (1×10 M^{-5}). (i) ITO electrode modified only with a layer of Au colloid (ii)–(vi) 1–5 Au nanoparticle layers. All data were recorded under argon in 0.1 M phosphate buffer solution, pH = 7.2, scan rate 100 mV s^{-1}. (d) Cyclic voltammograms of a layered **1**–Au-nanoparticle array (five layers) in 0.1 M phosphate buffer (pH = 7.2) containing *p*-hydroquinone at concentrations of 0.2×10^{-6}, 0.4×10^{-6}, 0.6×10^{-6}, 0.8×10^{-6}, 1.0×10^{-6} and 1.2×10^{-6} M. Inset: Calibration curve corresponding to the electrochemical sensing of **3**. Data for (c) and (d) were recorded under argon, scan rate 100 mV s^{-1}.

that the analysis reflects the composition of the top layer of the assembly. As XPS measurements reveal a small Si signal, corresponding to the substrate surface, we estimate that *ca.* 15% of the surface is made up of unmodified domains. For the Cd^{2+}-square **2**–Au nanoparticle superstructure, the Au : Cd ratio was found to be *ca.* 100 : 1.

The crosslinker $[(en)Pd(4,4'\text{-bipy})]_4^{8+}$ **1** acts as a π-acceptor receptor for the complexation of π-donor substrates such as dialkoxybenzene derivatives.[13] Fig. 1(*c*) shows cyclic voltammograms of ITO electrodes modified with various numbers of Au-particle and **1** layers in the presence of *p*-hydroquinone **3** at a bulk concentration of 1×10^{-5} M. At this concentration no electrochemical response for **3** is observed at the electrode modified by a single Au-nanoparticle layer. Similarly, interaction of **3** (1×10^{-5} M) with an *N*,*N*′-diaminoethyl-4,4′-bipyridinium crosslinked Au-particle array (five layers)[4*b*] does not yield any noticeable electrochemical response. These observations indicate that neither the increased surface area of the electrode nor non-specific interactions of **3** with the polycationic–Au-nanoparticle assembly are the origin for the electrical response of **3**. Fig. 1(c) shows that the electrical response of **3** is enhanced as the number of layers is increased. Binding of **3** to the receptor units increases its local concentration at the electrode surface, and allows its electrochemical sensing by the three-dimensional conductive Au array. A further aspect to note is the decrease in the peak-to-peak separation of the redox wave of **3** as the number of layers is increased. This suggests improved interfacial electron transfer kinetics as the particle density of the assembly increases, presumably owing to enhanced conductivity.

Fig. 1(d) shows the electrical response of a five-layer Au-nanoparticle superstructure in the presence of different concentrations of **3**. Fig. 1(d) (inset) shows the derived calibration curve, corresponding to the coulometric assay of the electrochemical responses of **3** at different bulk concentrations. After electrochemical sensing of **3**, the analyte can be washed off by immersion of the electrode in a buffer solution, regenerating the sensing interface.

In conclusion, we have applied polycationic metal complexes as crosslinking 'molecular squares' for assembling three-dimensional conductive arrays of Au nanoparticles. The resulting superstructures act as functional interfaces for the concentration of π-donor analytes enabling their electrochemical sensing.

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