Bis-Bipyridinium Cyclophane Receptor−Au Nanoparticle Superstructures for Electrochemical Sensing Applications

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The chemical modification of surfaces with functionalized monolayers or thin films attracts significant research effort directed toward the miniaturization of devices to nanoscale dimensions.[1−4] Functionalization of electrodes with ordered arrays of redox-active molecular components[5] has yielded assemblies revealing vectorial electron transfer[6,7] and sensoric activities.[8] The functionalization of surfaces with receptor monolayers[9,10] is known to generate active and selective sensing interfaces. The assembly of ordered metal nanoparticles on solid supports has attracted substantial research efforts as a consequence of their unique electronic and optical properties.[11−14] The assembly of Au−colloid monolayers on glass or conductive glass supports has been accomplished by the self-organization of the colloid on amino- or thiolate-functionalized siloxane layers,[15−18] and colloid arrays have been deposited by the use of dithiolate cross-linkers.[19] Recently, it was demonstrated that nanometer-scale organization of metal colloids is important in order to tailor microelectronic nanodevices. Au_{55} clusters were reported to act as a tunnel resonance resistor,[20] and a Au cluster was reported to function as a single electron tunneling transistor.[21]

Here we report on a novel method for the assembly of a three-dimensional array consisting of Au nanoparticles and the receptor cyclobis(paraquat-*p*-phenylene), **1**, as a particle cross-linking reagent. We demonstrate that the receptor−colloid superlattice acts as a rough interface for the preconcentration and electrochemical sensing of π-donor substrates, e.g. hydroquinones. Our approach bridges the elements of molecular recognition and the unique features of nanoparticles to yield composite architectures with novel sensoric functions.

The superlattice of Au nanoparticles was constructed on ITO conductive glass, as outlined in Scheme 1. The cleaned surface was first functionalized with (3-aminopropyl)triethoxysilane, and then the first layer of citrate-stabilized Au colloid (13 ± 1 nm) was assembled on the ammonium-functionalized surface. The resulting Au colloid layer was then treated with cyclobis(paraquat-*p*-phenylene) (**1**) and subsequently with the Au nanoparticle solution to generate the second Au layer. By a stepwise treatment of the assembly with the cross-linking component (**1**) and the Au nanoparticle colloid solution, three-dimensional arrays consisting of a controllable number of layered cross-linked Au particles were generated. The layered structure of the Au array was supported by several analyses. Figure 1A shows the absorbance spectra of the array upon the stepwise assembly of layers. While the base layer shows the typical plasmon absorbance associated with gold nanoparticles ($\lambda = 518$ nm), the growth of further layers results in the appearance of an additional absorbance band at ca. $\lambda = 650$ nm, which moves toward longer wavelengths with increased growth. This phenomenon is similar to the absorbance changes within a Au colloid as it precipitates and has been attributed to nanoparticle aggregates.[22] Figure 1B shows the stripping voltammograms of the assembled layers of Au particles that show the surface oxidation of the Au particles and the concomitant reduction of the surface oxide layer. The roughness of the assembly or the surface area of the Au particles increases almost linearly upon the growth of the number of layers. From the diameter of the particles, 13 ± 1 nm (determined by TEM), and assuming that the entire particle surface is exposed to the solution, we estimate the lower limit of the Au particle density to be 0.8×10^{11} particles·cm^{-2} per layer. A monolayer of 13 nm of Au colloids is known to have a density of ca. 1.0×10^{11} particles·cm^{-2}.[17] Figure 1C shows the cyclic voltammograms of the cyclobis(paraquat-*p*-phenylene) (**1**) "molecular glue" component upon the growth of the superstructure. The electrochemical response of **1** increases with the number of layers, and by coulometric analysis of its redox wave, we estimate an average surface coverage of 1.6×10^{-11}

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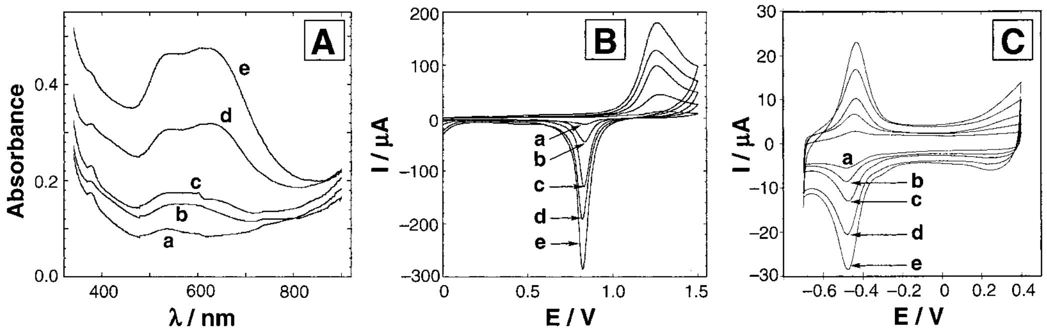
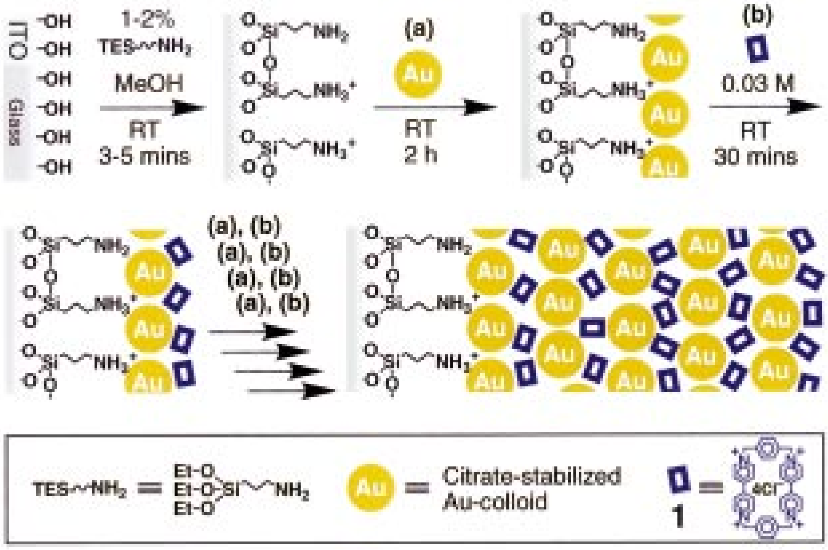


Figure 1. (A) Absorbance spectra of the layered receptor–Au colloid superlattice: (a) one Au layer, (b) two Au layers, (c) three Au layers, (d) four Au layers, and (e) five Au layers. (B) Cyclic voltammograms of the layered Au colloid assemblies corresponding to the electrochemical oxidation and reduction of particle surface: (a–e) from one up to five layers of Au particles. (C) Cyclic voltammograms corresponding to the redox activity of the cross-linker (**1**) in different layer arrays: (a–e) from one up to five layers of Au particles; electrode area = 1 cm^2. Experiments described in part B were carried out in 1.0 M H_2SO_4, scan rate 50 mV·s^{-1}, and those in part C were recorded under argon in 0.1 M phosphate buffer solution, pH = 7.2, scan rate 100 mV·s^{-1}.

Scheme 1. Stepwise Assembly of the Three Dimensional Array of the Bis-Bipyridinium Cyclophane and Au Nanoparticles on a Conductive ITO Support



mole·cm^{-2} of **1** per layer. This implies that the tetracationic cyclophane cross-links the Au particles at a density of approximately 100 molecules per particle and that the array exhibits three-dimensional conductivity. Lacking covalent or specific noncovalent interactions between the colloid and **1**, we assume that the resulting superstructure is stabilized principally by electrostatic interactions.[23]

The bipyridinium cyclophane (**1**) acts as a host for π-donor compounds such as dialkoxybenzenes or hydroquinones.[24,25] Accordingly, the **1**-cross-linked Au array was used as a sensing matrix for *p*-hydroquinone (**2**). Figure 2 shows the cyclic voltammograms of a series of ITO electrodes consisting of 0–5 Au particle layers, in the presence of **2** (1 × 10^{-5} M). At a bare ITO electrode (curve a), no electrical response for **2** is observed, due to the low concentration of **2**. Upon increasing the number of Au particle layers, as reflected by the enhanced electrical response of the molecular glue component, $E° = -0.450$ V, the amperometric responses of **2** are higher. This indicates that **2** is concentrated at the receptor cyclophane–Au colloid functionalized electrode and that an increase in the number of layers enhances the amount of **2** associated with the receptor–nanoparticle electrode assembly. The bis-bipyridinium

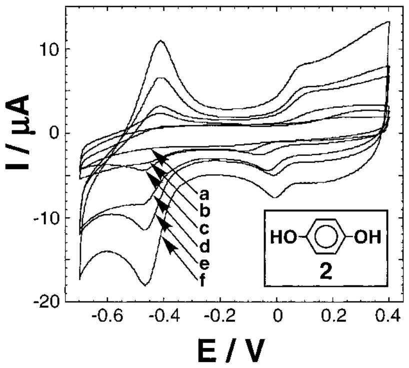


Figure 2. Cyclic voltammograms of the layered **1**–Au colloid arrays in the presence of hydroquinone (**2**) 1 × 10^{-5} M: (a) unmodified ITO electrode, (b–f) from one to five Au nanoparticle layers. All data were recorded under argon in 0.1 M phosphate buffer solution, pH = 7.2, scan rate 100 mV·s^{-1}, electrode area = 1 cm^2.

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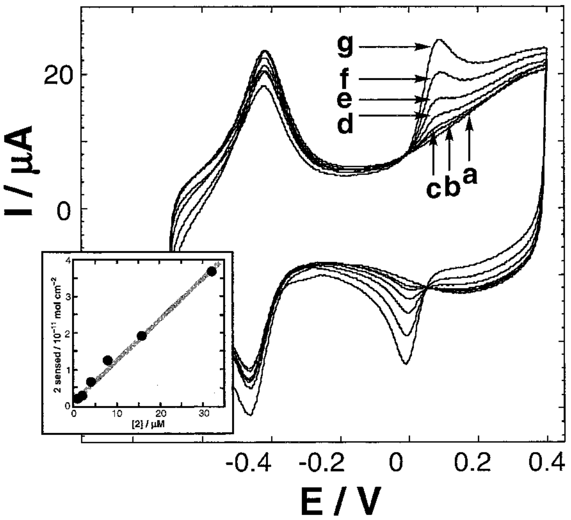

Figure 3. Cyclic voltammograms of a layered bis-bipyridinium—Au nanoparticle array (five layers) in the absence of *p*-hydroquinone (curve a) and in various concentrations of *p*-hydroquinone (**2**): (b) 1×10^{-6} M, (c) 2×10^{-6} M, (d) 4×10^{-6} M, (e) 8×10^{-6} M, (f) 1.6×10^{-5} M, (g) 3.2×10^{-5} M. (inset) Calibration curve corresponding to the electrochemical sensing of **2**. Data were calculated by coulometric assay of the reduction peak of **2**. All data were recorded under argon in 0.1 M phosphate buffer, pH = 7.2, scan rate 100 mV·s^{-1}.

cyclophane—Au system reveals high stability upon storage in water. While the hydroquinone component can be washed off from the functionalized electrode by rinsing with water, the cyclophane component remains static and in a stable structure even at a high concentration of **2** (1×10^{-4} M). The association of **2** at the functionalized electrode is attributed to the formation of π-donor—acceptor complexes between the receptor (**1**) and hydroquinone. The preconcentration of **2** at the electrode surface is improved as the number of receptor sites associated with the electrode rises. Analogous architectures constructed using a bis(aminoethyl)viologen cross-linker[23] do not exhibit hydroquinone sensing, validating our assertion that sensing is a consequence of a specific interaction, rather than the result of surface area increase, electrostatic interactions, or other nonspecific interactions.

The five-layer bipyridinium cyclophane-functionalized electrode was used as a sensing electrode for **2**. Figure 3 shows the cyclic voltammograms of the functionalized electrode at different concentrations of **2**. Upon increase of the concentration of **2**, the amperometric response of the electrode rises. This allows us to extract a calibration curve (Figure 3, inset). The functionalized electrode permits the electrochemical analysis of **2** to a level corresponding to $(2-3) \times 10^{-6}$ M. It should be noted that within this concentration range of **2**, no electrical response is observed at the bare ITO electrode. The sensing functionalized electrode reveals high stability, and the electrode performance is stable for a period of at least 1 month. The sensing interface can be regenerated by rinsing off the noncovalently linked hydroquinone. The functionalized electrode provides a sensing interface for other π-donor compounds. Effective electrochemical analyses of 3,4-dihydroxyphenylacetic acid and dopamine were accomplished with the receptor—Au particle functionalized electrode. These results will be described later in a comprehensive report. The sensing interface, however, exhibits impressive selectivity, and other π-donor substrates such as 1,1′-ferrocene dimethyl alcohol are not associated with the π-acceptor (**1**) and cannot be sensed electrochemically by the functionalized electrode.[26]

In conclusion, we have demonstrated a novel means for the construction of molecular architectures of Au nanoparticles in the form of three-dimensional arrays for sensing applications. The array acts as a powerful sensing matrix for π-donor aromatic compounds. The combination of Au colloid particles and cross-linking receptor units yields novel physicochemical features for the assembly. The receptor π-acceptor cross-linking units bind the π-donor analyte and concentrate it at the electrode surface. The Au nanoparticles provide a rough conductive array for the electrochemical sensing of the π-donor substrate. Different and broad applications are envisaged for related receptor—nanoparticle arrays. For example, the organization of mixed composites, consisting of Au and semiconductor nanoparticles cross-linked by an acceptor unit, could yield new materials for photonic applications or novel configurations for photoelectrochemical cells.

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(26) Application of cyclobis(paraquat-*p*-biphenylene) as the cross-linker of the Au nanoparticle superstructure yields a receptor of larger dimensions. The latter receptor does not associate hydroquinone, but selectively binds 1,1′-ferrocene dimethyl alcohol (Lahav, M.; Shipway, A. N.; Willner, I.; Nielsen, M.; Stoddart, J. F., unpublished results). This implies that the dimensions of the cross-linker enable tuning of the selective binding of the substrate to functionalized electrode.