Three-dimensional redox-active layered composites of Au–Au, Ag–Ag and Au–Ag colloids

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Ordered layered three-dimensional networks of Au, Ag and Au/Ag colloids are assembled in a stepwise synthesis using *N,N′*-bis(2-aminoethyl)-4,4′-bipyridinium as a redox-active crosslinker.

The ordered assembly of metal particles on solid supports, *i.e.* glass or conductive ITO-glass attracts substantial research effort due to the unique electronic and optical properties of nanoscale metal colloid particles.[1,2] Surface-enhanced Raman spectroscopy (SERS) of adsorbate monolayers on Au-colloids,[3,4] electrochemistry of redox-active monolayers associated with rough Au-colloid monolayers,[5] conductivity of three-dimensional Au-colloid assemblies,[6] and second-harmonic generation at layered Au-colloids,[7] were examined. Nanometer-size organization of the metal colloids is of importance to tailor microelectronic nano-devices. Indeed, it was shown that two Au$_{55}$ clusters could act as a tunnel resonance resistor.[8] The assembly of metal colloid monolayers was accomplished by the functionalization of glass or conductive glass supports with surface thiolate or surface amino groups, acting as a ligation monolayer for the association of the colloids.[3,4] Alternatively, functionalized capped-metal colloids were reacted with modified surfaces to yield the respective monolayers. Colloid arrays were deposited on solid supports using dithiolate crosslinkers[10] or thiol-tagged oligonucleotides.[11] The bridging units separating the dithiol or the double-stranded oligonucleotide units control the inter-particle distances and the resulting conductivity features of the colloid arrays. The optical and electronic properties of metal colloids can be tuned by the preparation of bimetallic particles. Specifically, gold/silver composites or alloys have received interest with respect to their optical and electronic features.[4–6] Layered and ordered colloidal Au/Ag composites have been studied to date only to the extent that Ag-clad Au layers are generated by the electrochemical deposition of Ag on Au nanoparticles.[12]

In the present study, we describe the novel assembly of ordered three-dimensional metal colloids composed of Au colloids, Ag colloids and composite Au and Ag colloids. The colloids are crosslinked by a redox-active molecular bridging unit. We find that the molecular redox-active unit is electroactive in the three-dimensional colloid array, implying that electron transport through the colloid particles is feasible. To our knowledge, we present for the first time a synthetic method to assemble mixed composites of Au and Ag in an ordered way.

Au colloids were prepared by citrate reduction of an HAuCl$_4$ solution to yield Au particles of 12 ± 2 nm size.[13] Ag colloids were similarly prepared by citrate reduction of AgNO$_3$ solution [in the presence of iron(II) sulfate] to generate particles exhibiting a diameter corresponding to 31 ± 2 nm.[14] Glass slides or indium tin oxide (ITO) conductive glass were functionalized with triethoxy aminopropylsilane to yield an amino-functionalized surface. Interaction of the functionalized surface with the Au or the Ag colloid for 1.5 h yields the primary metal colloid monolayer, Scheme 1. These monolayers were subsequently reacted with *N,N′*-bis(2-aminoethyl)-4,4′-bipyridinium **1**, as the crosslinking reagent of the colloid monolayers. Further interaction of the surfaces with the Au colloid or the Ag colloid yield the respective two-layer Au/Au, Ag/Ag or Au/Ag assemblies, Scheme 1. By the additional interaction of the layered colloid assemblies with the crosslinking unit **1** and the respective metal colloid, a controlled number of metal particles with the respective ordering of the metal colloid layers, could be deposited onto the glass supports. Fig. 1(A) shows the absorption spectra changes upon assembly of a four-layer assembly of Au colloids. The absorption band, $\lambda_{max} = 522$ nm, increases almost linearly upon increasing the number of colloid layers associated with the surface. At high surface coverages, an additional absorbance at *ca.* 640 nm is observed. This band was attributed to a collective interparticle clustered plasmon.[3] Similarly, Fig. 1(B) shows the absorbance changes upon the assembly of a four-layer structure of Ag colloids. The absorbance of the Ag colloid, $\lambda_{max} = 430$ nm, increases as the number of layers is increased. Fig. 1(C) shows the absorbance spectra of a composite monolayer composed of one Au and one Ag layer. The composite assembly consists of two absorbance
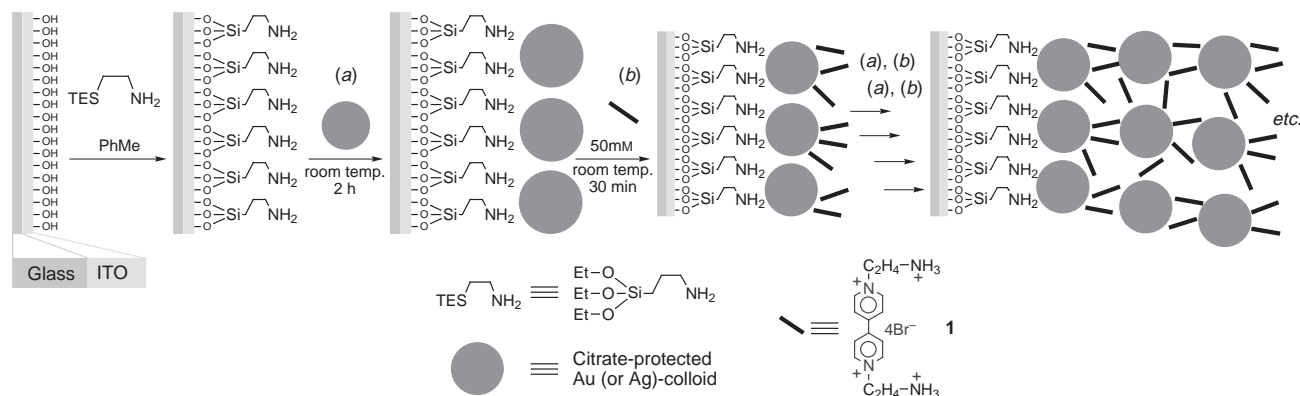
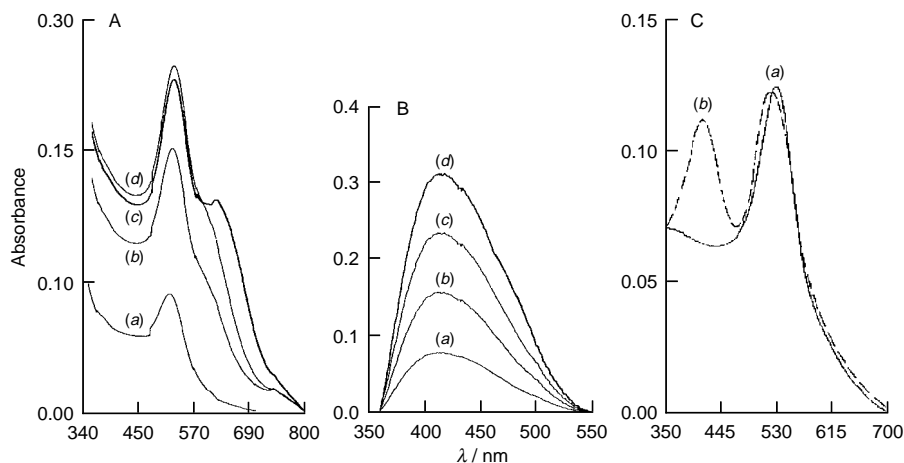**Scheme 1** Stepwise assembly of metal particle multilayer arrays

Fig. 1 (A) Absorbance spectra of an ITO glass upon the stepwise assembly of Au colloid (12 ± 2 nm, diameter layers); (*a*) 1, (*b*) 2, (*c*) 3, (*d*) 4 layers. (B) Absorbance spectra of an ITO glass upon the stepwise assembly of Ag colloid (31 ± 2 nm, diameter); (*a*) 1, (*b*) 2, (*c*) 3, (*d*) 4 layers. (C) Absorbance spectra of a composite Au/Ag metal colloid array; (*a*) one Au colloid layer assembled on an aminopropyl siloxane functionalized monolayer, (*b*) Ag colloid deposited onto the Au monolayer using **1** as crosslinker. All multilayers were assembled by functionalization of the respective colloid layer with the crosslinker **1** by the interaction of the colloid with a 50 mM solution of **1** for 0.5 h.

maxima at 520 and 430 nm, characteristic of the Au and Ag colloids, respectively.

Fig. 2 shows the cyclic voltammograms of the *N,N*′-bis(2-aminoethyl)-4,4′-bipyridinium redox-active crosslinking units upon the assembly of the four-layered Au colloid. The electrochemical response of the bipyridinium units is enhanced as the number of layers is increased. Coulometric analysis of the bipyridinium relay units associated with the first Au colloid layer, reveals a surface coverage of 7.3×10^{-11} mol cm^{-2} (geometrical area). As the surface coverage of Au colloids on glass was estimated by electromicroscopy measurements[4,5] to be *ca.* 1×10^{11} particles cm^{-2}, it suggests that *ca.* 450 bipyridinium bridging units are associated with each Au particle. Coulometric analysis indicates that the surface coverage of the bipyridinium units associated with the four-layer Au colloid assembly increases almost linearly upon the formation of the three-dimensional network (Fig. 2, inset).

In conclusion, we have demonstrated a novel method to assemble three-dimensional metal colloid networks consisting of Au, Ag or composite Au/Ag colloids and an amino-bifunctional redox-active briding unit as crosslinker. Electrostatic attraction between the crosslinker and the citrate-protected metal particles presumably leads to the assembly of

the systems. The results demonstrate the formation of ordered composite layered assemblies of Au and Ag particles and reveal a means for the pre-planned structuring of composite multilayer assemblies. The electrochemical characterization of the bridged colloid assembly reveals that the redox-active molecular components are electrically contacted in the colloid lattice. This supports the suggestion that the Au particles act as nanoparticle conductive layers for electron transport through the network.

Notes and References

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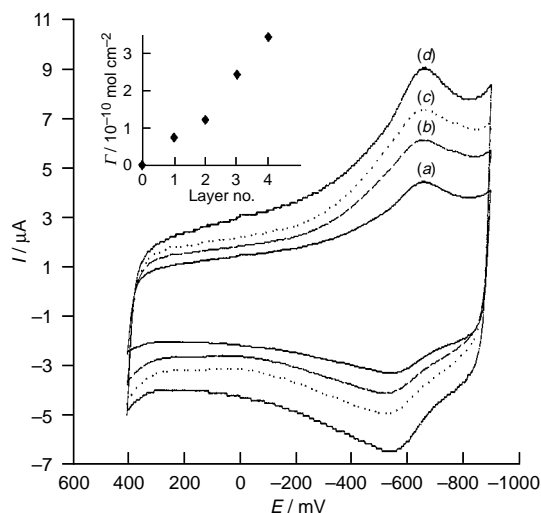
Fig. 2 Cyclic voltammograms of the Au-colloid layers functionalized by *N,N*′-bis(2-aminoethyl)-4,4′-bipyridinium **1**; (*a*) 1, (*b*) 2, (*c*) 3, (*d*) 4 layers. All measurements were recorded in phosphate buffer, pH = 7.0, scan rate 100 mV s^{-1}. Inset: Surface coverage of **1** *vs.* number of Au colloid layers.