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Gold-Nanoparticle-Enhanced Current Transport through Nanometer-Scale Insulating Layers**

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We report herein how adding a monolayer of small ($\approx$2.5 nm diameter) Au nanoparticles (NPs) on top of an approximately 5-nm-thick insulating layer significantly enhances electronic current transport through the insulator. The insulating film is sandwiched between Au and Al or Si (degenerate) electrodes to give the following sandwich configuration: Au//Au NP monolayer/5-nm-thick insulating layer//Al or Si. Enhancement is found both with hard inorganic (SiO_2) and with soft organic insulators (lipid bilayers stabilized with bacteriorhodopsin (bR)).

Citrate-stabilized Au NPs ($\approx$2.5 nm diameter, unless stated otherwise) were synthesized as described elsewhere.[1] As a model insulating layer, we prepared SiO_2 layers on the surface of conducting, degenerate (100) *n*-Si substrates ($\approx 10^{-3}\,\Omega$ cm). The Si wafers with native oxide layer ($\approx$1.8 nm) were first cleaned with organic solvents, then an oxide layer of controlled thickness was grown on top of them by plasma-assisted oxidation. The oxide-layer thickness was determined by ellipsometry. Unless otherwise stated, we used oxide layers with a thickness of (5.4 $\pm$ 0.5) nm. These samples were then used in both test and control junctions. The oxide layer was modified with (3-aminopropyl)trimethoxysilane (APTMS)[1a] to assemble the Au NPs (from a suspension with pH 5) on the oxide by binding them to the exposed APTMS amino groups.[2] After formation of a saturated Au NP monolayer (incubation time $>$6 h), the NP-covered surface was treated with 20 mM aqueous cysteamine for 30 min to passivate the surface of the colloids. The junctions were prepared by depositing Au on top of the NP-covered surface. This deposition was done by floating preformed Au pads (60 nm thick, 0.5 mm diameter, 2×10^{-3} cm^2 area) onto the Au NP-covered surface in a nondestructive manner, using the "lift-off, float-on" technique (LOFO).[3] For control experiments we also evaporated Au onto the NP-covered surface. We constructed control junctions of the type Au pad// APTMS-SiO_2 ($\approx$5 nm)//Si in a similar manner.

Current–voltage (*I–V*) measurements were performed in a class 10000 clean room at 293 K and 40% relative humidity (RH). *I–V* characteristics were measured using a W needle connected to a micromanipulator to contact the Au pad—an InGa drop on the Au pad minimizes mechanical (pressure) damage to the film—and an HP 4155 semiconductor parameter analyzer. All *I–V* measurements were performed in the dark, unless noted otherwise. As shown in curve 1 of Figure 1, in the absence of the NP layer, the current that we measured through the approximately 5-nm-thick inorganic insulating layers is within the noise level ($\approx$100 pA). Adding the NP film changes this situation; typical currents through the Au pad//cysteamine/Au NP monolayer/APTMS-SiO_2 ($\approx$5 nm)// Si junctions were 0.3–2 nA at 1 V applied bias, as shown in curve 2 of Figure 1.

This result immediately suggested that the Au NPs are in direct contact with the Si substrate via pinholes or cracks in the oxide film. It therefore became important to investigate the topography of the oxide surface. Figure 2 (top) shows a typical tapping-mode AFM map of the Si/SiO_2 layer, which gives an average root-mean-square (rms) roughness of 0.10 nm, nearly identical to the roughness that we measured for the native oxide surface of Si. This result indicates that the as-grown SiO_2 layers form in a homogeneous fashion on the Si substrate. Figure 2 (middle) shows an AFM image of a densely packed monolayer of Au NPs on the APTMS-modified Si/SiO_2 surface. This AFM image is a tip–sample

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Supporting Information for this article is available on the WWW under http://www.angewandte.org or from the author.

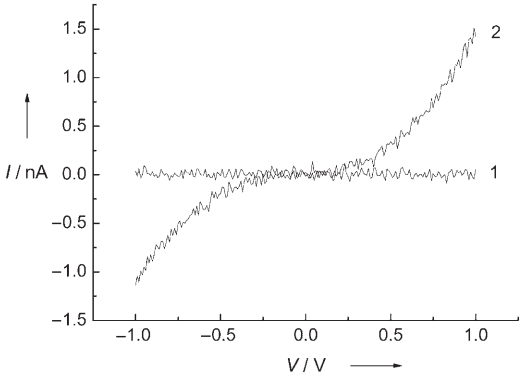

Figure 1. *I–V* curves of the Au pad (formed by LOFO or vacuum deposition)//APTMS-SiO_2 (≈5 nm)//Si junctions (curve 1) and the Au pad (formed by LOFO)//cysteamine/Au NP monolayer/APTMS-SiO_2 (≈5 nm)//Si junctions (curve 2), measured under ambient conditions and in the dark. The *I–V* curves of the Au pad (formed by vacuum deposition)//(nominal) Au NP monolayer/APTMS-SiO_2 (≈5 nm)//Si junctions are similar to curve 1. Degenerate (100) *n*-Si was used (≈10^{-3} Ω cm).

convolution. As a result of the tip size (>10 nm) and the dense packing of the NPs on the smooth substrate, the individual NPs cannot be resolved. However, section analysis of some defect sites in the NP layer shows that the average height of the features (≈2.6 nm) is consistent with the known size of the Au NPs.

As a further check we prepared top contacts by electron-beam evaporation of Au onto both control samples and samples with NPs, and compared the properties of the samples with those prepared by LOFO. Firstly, evaporated Au is known to be able to penetrate through even small defects, therefore this technique will tell us to what depth the oxide layer is defect-free. Secondly, if the current enhancement is due to the Au NPs, then evaporating Au onto them will make them merge into an Au top contact film and should destroy any enhancement. Indeed, comparing samples with evaporated and LOFO-deposited Au reveals that both the control samples (without NPs) and the NP-containing samples with evaporated Au show only noise (similar to curve 1 in Figure 1), in contrast to the NP-containing sample with LOFO-deposited Au. The possibility that the changes in junction currents arise from the exposure of the insulating film to the solution used to prepare the Au NP monolayer was ruled out by comparing the *I–V* results of the NP-containing samples with LOFO-deposited and evaporated Au. Indeed, no significant change in insulator thickness was found by ellipsometry as a result of Au NP assembly or LOFO preparation using either an NP-free aqueous subphase with the same pH value or the LOFO aqueous subphase used for actual sample preparation.

At present we can only speculate on the underlying physical origins of the observed current enhancement, but it is tempting to invoke the strong, localized electromagnetic fields associated with Au NPs, that is, some form of electric-field-enhanced current. Possible reasons for such enhancement are field emission ("lightning-rod effect", Fowler–Nordheim tunneling), Poole–Frenkel hopping, or even the

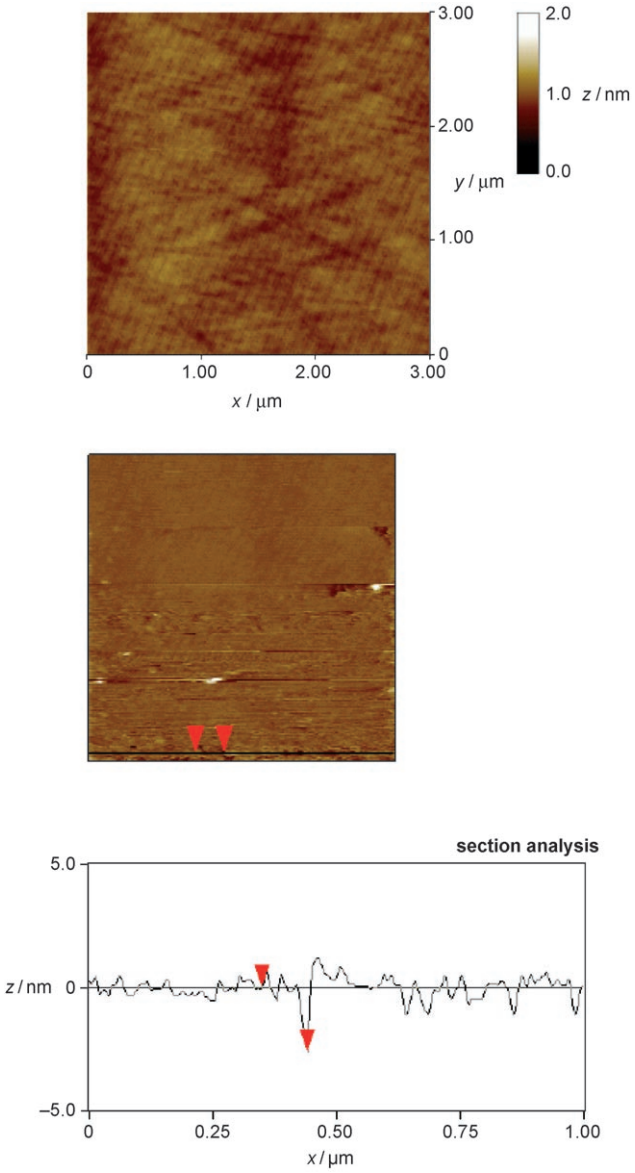

Figure 2. Representative AFM images of the oxide surface of the Si/SiO_2 (≈5 nm) substrate (top; height scale given) and a saturated Au NP monolayer self-assembled on an APTMS-modified Si/SiO_2 (≈5 nm) substrate (middle). A section analysis (bottom) shows that the average height of the Au NPs is approximately 2.6 nm (between the two red markers).

involvement of surface plasmon (SP) modes (see Supporting Information).

We note here that field enhancement increases with the inverse particle radius, so we can expect, up to a point, larger particles to show smaller effects. At the same time, in terms of optical efficiency, the propagation length of surface plasmon polaritons (SPPs) varies with the NP diameter and decays slowly (at least compared to tunneling) within the efficient propagation length (gap).[4,5]

As a preliminary check on the mechanism we used the same degenerate (100) *n*-Si as electrode (≈10^{-3} Ω cm), but now with a native oxide layer of approximately 1.8 nm to construct Au pad//octadecanethiolate (C18SH)/Au NP mon-

olayer//APTMS-SiO_x-Si junctions, with Au pad//cysteamine/Au NP monolayer//APTMS-SiO_x-Si junctions as control. The C18SH monolayers serve as spacer between the Au NPs and the Au pad (see Supporting Information for details on junction preparation and AFM images of the as-prepared monolayers). As seen from Figure 3a, microamp currents flow through this structure. These currents are only a few times smaller than those obtained for the control Au pad//cysteamine/Au NP monolayer//APTMS-SiO_x-Si junctions (Figure 3b). If the mechanism of current transport were normal tunneling through a rectangular barrier, the current should decay by some eight orders of magnitude because of the additional approximately 2-nm-thick C18SH layers.[6]

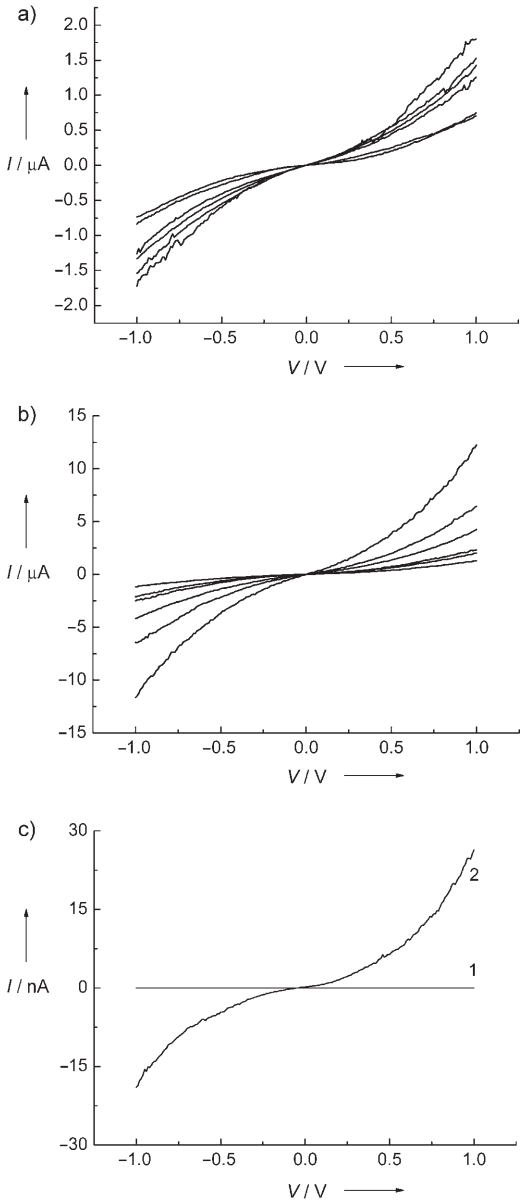

Figure 3. *I–V* curves of six independent junctions from three samples of a) Au pad//C18SH/Au NP monolayer//APTMS-SiO_x-Si junctions (currents: 0.73–1.7 μA) and b) Au pad//cysteamine/Au NP monolayer//APTMS-SiO_x-Si junctions (currents: 1.1–11.7 μA). All curves were measured under ambient conditions, and (100) *n*-Si ($\approx 10^{-3}$ Ω cm) was used. c) *I–V* curves of Au pad (formed by LOFO)//cysteamine/Au NP ($\approx$2.5 or 10 nm) monolayer/APTMS-SiO_2 (6.2 ± 0.2 nm)//Si junctions, measured under ambient conditions and in the dark. Curve 1: 2.5-nm Au NPs; curve 2: 10-nm Au NPs.

To see if the insulator thickness and NP size are independent parameters for the current enhancement, we varied both the SiO_2-layer thickness and the Au NP size. As shown in curve 1 of Figure 3c, if the SiO_2-layer thickness is increased to (6.2 ± 0.2) nm, the current flow drops to the picoamp range, even with an Au NP ($\approx$2.5 nm) monolayer. However, if we use larger Au NPs ($\approx$10 nm diameter, Sigma–Aldrich) a strong increase in current is seen, with typical currents through the (6.2 ± 0.2)-nm-thick oxide layers of 3–50 nA at 1 V applied bias, as shown in curve 2 of Figure 3c. These results can be construed as support for the involvement of SPs since the efficient propagation length of the SP field will depend on the NP size[4,5] and this length should limit the insulator thickness.

To what extent is current enhancement a general phenomenon? To explore this we looked for a soft material insulator. Because of the difficulty of preparing monolayers from pure lipid bilayers reproducibly,[7] we decided to use approximately 5-nm-thick bR-containing phospholipid bilayers as the insulator. We have previously reported the preparation of stable monolayers from these compounds, which we used to study their current transport behavior.[7] In this way we constructed Au pad//bR-lipid bilayer/Au NP ($\approx$2.5 nm) monolayer//APTMS-AlO_x-Al junctions, with Au pad//bR-lipid bilayer/APTMS-AlO_x-Al ones as control. The basic junction structure is shown in Figure 4. The description of the junction preparations and the AFM characterization of the as-prepared films can be found in the Supporting Information.

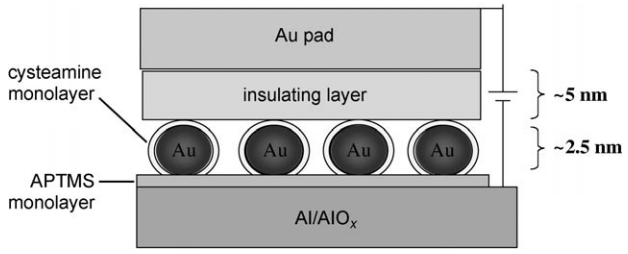

Figure 4. Schematic diagram of the Au pad//insulating layer/Au NP monolayer//APTMS-AlO_x-Al complex planar junction. An organic insulating layer is suspended over the surface of a colloidal Au monolayer by spreading negatively charged bR-containing proteoliposomes onto the positively charged colloidal Au monolayer.

The *I–V* characteristics of Au pad//bR-lipid bilayer/Au NP monolayer//APTMS-AlO_x-Al planar junctions are shown in curve 1 of Figure 5. The current is approximately (2 ± 1) μA at 1 V applied bias. For comparison, currents through control Au pad/bR-lipid bilayers/APTMS-AlO_x-Al junctions were typically (1 ± 0.5) nA at 1 V applied bias,[7] as shown in curve 2 and the inset of Figure 5. Although the currents vary slightly from junction to junction, owing to variation in effective contact area, the *I–V* measurements are reproducible with

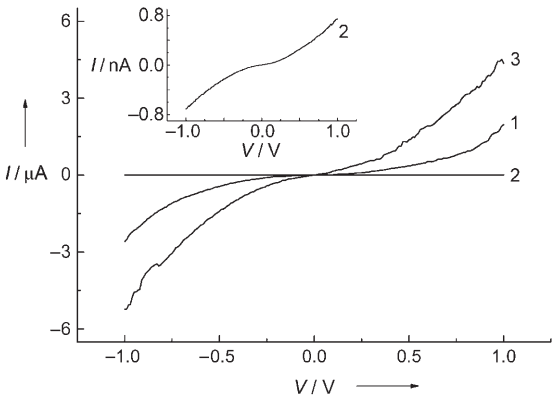

Figure 5. *I–V* curves of the Au pad//bR-lipid bilayer/Au NP monolayer//APTMS-AlO_x-Al complex planar junction (curve 1) and of the same junction without the NPs, that is, Au pad///bR-lipid bilayer/APTMS-AlO_x-Al (curve 2 and inset). Curve 3 shows a typical *I–V* curve of the control Au pad/Au NP monolayer/APTMS-AlO_x-Al junctions. All measurements were performed under ambient conditions and in the dark.

respect to the order of magnitude of the current. We can therefore state that current transport through the 5-nm-thick bR-lipid bilayers is also significantly enhanced by the introduction of an Au NP monolayer into the planar junction.

The current through control Au pad/Au NPs monolayer/APTMS-Alox-Al junctions is typically (4 ± 1) μA at 1 V applied bias,[8] as shown in curve 3 of Figure 5. Assuming that SPs on the Au NPs are involved, we note that plasmon-induced currents decay by a factor of approximately two over the 5-nm gap between the STM tip and the sample surface.[9] In such a scenario, the 4-μA current that flows through the control Au pad/Au NPs monolayer/APTMS-Alo_x-Al junction will decrease to 2 μA upon separating the Au NPs from the top electrode by a 5-nm-thick insulator, in close agreement with our experimental observations (curves 1 and 3 in Figure 5).

In view of the idea that SPs might be involved in the process, we checked the effect of illumination on current transport through the as-prepared junctions. We have previously found that the current of the Au pad/Au NP monolayer/APTMS-AlO_x-Al junctions can be significantly enhanced (the increment is approximately 3 μA at 1 V) by resonant excitation of the surface plasmon resonance (SPR) with green light ($\lambda > 550$ nm, which is close to the NP SPR wavelength).[8,10] While the current increment of the Au pad//bR-lipid bilayer/Au NP monolayer//APTMS-AlO_x-Al junctions upon irradiation with green light is typically 0.5 μA at 1 V applied bias (not shown), no pronounced light effect was observed for the Au//Au NP monolayer/$\approx$5 nm SiO_2 layer//Si junctions, and further experiments are underway to elucidate the mechanism that underlies the observed current enhancements.

In conclusion, we have found that even though adding Au NPs to a planar tunnel junction enlarges the distance between the two electrodes, it also enhances current transport significantly. Although the underlying physical origins of the observed current enhancement are not yet clear, our results suggest that strong, localized electromagnetic fields, associated with the Au NPs, play a role. If borne out by further experiments and by theory, such field effects on electronic current flow through ultra-thin insulators may also need to be considered when interpreting results for transport through insulating molecules in particular. They may well lead to interesting new avenues in nanoelectronics as, irrespective of the underlying physical picture, this enhancement may improve the sensitivity of devices like sensors.

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