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Photovoltaic action in a self-assembled monolayer of hemicyanine dyes on gold from dissociation of surface plasmons

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Hemicyanine dye molecules, containing a thiol functionality, form a self-assembled monolayer (SAM) on thin films of gold. The combined SAM-gold layer system supports surface plasmons and can be converted into a diode using a liquid electrolyte top contact. Diodes fabricated on a quartz prism allow for incoupling of incident light to surface plasmons and show a spontaneous photocurrent under short-circuit conditions. Measurement of the short-circuit photocurrent as function of incident angle of the light shows that the photocurrent arises from dissociation of surface plasmons into pairs of charge carriers. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.

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Surface plasmons (SPs) are excitations of electrons at a metal-dielectric interface.¹,² Surface plasmons can be guided on chip via plasmonic nanostructures and offer interesting possibilities for high bandwidth data transport and manipulation.³ To realize this potential, electro-optical transducers need to be developed.⁴

Conversion of surface plasmons into electrical signals has been realized making use of, e.g., photocurrent generation involving bulk semiconductors⁵⁻⁹ or nanowires,¹⁰ light induced changes in the tunneling in gold quantum point contacts,¹¹ the thermoelectric effect in metallic structures¹² or superconductors,¹³ and hot carrier extraction in metal-insulator-metal structures.¹⁴⁻¹⁷

Here, we show electrical detection of surface plasmons using self-assembled monolayers (SAMs) of hemicyanine dye molecules on gold. Short-circuit photocurrent generation using molecular monolayers has been demonstrated previously.¹⁸⁻²¹ We find that surface plasmon-polaritons on a thin gold film functionalized with a monolayer of hemicyanine dye can generate a photocurrent under short-circuit conditions, i.e., can be detected electrically without consumption of electrical power. Additional advantages of this type of detection are the intrinsic nanoscopic dimension of the self-assembled monolayers and the possibility to use easy, solution based deposition methods (e.g., printing).

The chemical structure of the hemicyanine dyes (1-(10-acetylthiohexadecyl)-4-[2-(4-dimethylaminophenyl)vinyl] quinolinium hexafluorophosphate (1) and 1-(10-acetyl sulfanilidecyl)-4-[2-(4-dimethyl-aminophenyl)vinyl] pyridinium hexafluorophosphate (2)) is illustrated in Figure 1. After hydrolysis of the thioester group, these molecules form dense self-assembled monolayers on gold.²⁰,²²,²³ SAMs of these hemicyanines were completed to a photovoltaically active diode by complementing them with a second liquid electrolyte contact involving hydroquinone as redox mediator (0.1 mM in water) and KCl (1.0 mM) as supporting electrolyte. Indium tin oxide (ITO) coated glass was used as transparent top electrode.

To excite SPs in a thin gold film, we apply the Kretschmann configuration using a quartz prism (see Figure 1) and illuminate with p-polarized light from a HeNe laser at 1.96 eV photon energy into a prism (n(1.96 eV) = 1.46), on which a thin gold is deposited. Thin gold films were deposited by vacuum sublimation on the rase face of right angle quartz prisms. To obtain robust metal films, a thin (<5 nm) Cr adhesion layer is deposited on the quartz before subliming the Au layer. SAMs were grown by immersing the prisms in a solution of the dye.²⁰ Reflection spectra for the bare Au film and Au/SAM layers were measured in air in the Kretschmann configuration, using a variable angle scanning ellipsometer (J. A. Woollam & Co.). To measure short-circuit current generation as function of incident angle, the prisms were mounted on a rotation stage and illuminated with ~20 mW intensity of 1.96 eV photons with p-polarization. Short-circuit photocurrents and photovoltages were measured using mechanical modulation of the incident light (273 Hz modulation frequency) and direct lock-in detection of the current or voltage.

FIG. 1. (a) Chemical structures of the molecules 1 and 2 for SAMs. (b) Schematic picture of the photovoltaic cell.
Figure 2(a) shows the internal reflection spectra for \( p \)-polarized light for monolayers of 1 on the gold coated prism (100 nm Au) for different angles of incidence. The reflection spectra show a minimum, characteristic of the surface plasmon resonance (SPR) due to resonant coupling of incoming photons to SPs and subsequent non-radiative decay of the SPs. Upon modification of the gold surface with the SAM, the minimum in reflection at \( \Theta_{SPR} = 45.0^\circ \) shifts to slightly higher photon energy, indicating that the plasma oscillations of the dynamics of the free electrons at the gold surface are modified upon binding of the monolayer. From the incident angle \( \Theta_{SPR} \) (for definition, see Figure 1), the wavevector \( k_{SPR} \) for the surface plasmons can be calculated.

In Figure 2(c), we plot the photon energy associated with the minimum in reflection as function of \( k_{SPR} \) for the surface plasmons can be calculated. In Figure 2(c), we plot the photon energy associated with the minimum in reflection as function of \( k_{SPR} \), for the surface plasmons can be calculated. The resulting dispersion curve is characteristic for SPs1 and deviates from the linear dispersion behavior of photon indicated by the dashed line. The binding of the SAM hardly changes the fundamental dispersion relation for the SP. Also for SAMs of molecule 2, the dispersion curves were determined and here also the thickness of the gold film was varied (see Figure 2(d)). We conclude that gold films decorated with a SAM can support surface plasmon excitations for a variety of layer thicknesses of the gold layer.

Excitation of surface plasmons in a thin gold film functionalized with a SAM on a quartz prism with transparent liquid electrolyte top contact (see Fig. 1) results in a photovoltaic effect. In Figure 3(a), we show the short-circuit photocurrent, generated in the SAM diode upon illumination with 1.96 eV photons. The photocurrent is measured for different internal angles of incidence of the photon on the gold film. As can be seen, for incidence angle below 45\(^\circ\), the spontaneous photocurrent is essentially zero. For angles equal and exceeding 45\(^\circ\), a significant photocurrent is detected. The angle corresponding to the onset of photocurrent generation matches with the onset angle for excitation of surface plasmons in the gold film. This indicates that a surface plasmon can dissociate into an electron hole-pair of photogenerated charge carriers of which each carrier can be collected at the appropriate electrode.

Also for diodes incorporating a SAM of 2, photocurrents can be detected. These are shown in Fig. 3(b), as function of the incident angle. The use of thin Au films (20 nm) results in large photocurrents. We find that the photocurrent decreases approximately exponentially with the thickness of the gold layer. Apart from a short-circuit current, the diodes can also generate an open-circuit voltage. This is illustrated in Fig. 3(c), which shows the photovoltage as a function of internal angle of incidence. Also here we find that the angle corresponding to the onset of photovoltage generation matches with the angle at which excitation of surface plasmons sets in.

The photophysical processes involved in generation of the photocurrent and photovoltage are illustrated in Fig. 4(a). The incoming photon of 1.96 eV energy can excite a surface plasmon. At the metal surface, plasmons of different energies exist and depending on the angle of incidence, a particular plasmon is created with energy of <1.96 eV. The surface...
plasmon can decay via electron capture from the monolayer, resulting in the formation of a charge transfer (CT) state, indicated by Au\textsuperscript{\textsuperscript{+}}/SAM\textsuperscript{\textsuperscript{+}}. The quinone (Q) redox mediator in the electrolyte solution can neutralize the monolayer by donating an electron. The oxidized mediator (Q\textsuperscript{\textsuperscript{+}}), in turn, can be reduced at the transparent ITO top electrode after diffusion though the liquid electrolyte. In order to assess the importance of the lowest excited singlet (S\textsubscript{1}) state of hemicyanine molecules in the monolayer, we have first tried to determine the energy of the singlet state. Measurement of the optical absorption of \textit{1} and \textit{2} in solution and as monolayer on a very thin gold film (5 nm) is shown in Figs. 4(b) and 4(c). The transition from the ground state to the S\textsubscript{1} excited state is optically allowed and can be used to estimate the energy of the S\textsubscript{1} state. Measurement of the optical absorption of \textit{1} and \textit{2} in solution and as monolayer on a very thin gold film (5 nm) is shown in Figs. 4(b) and 4(c). The transition from the ground state to the S\textsubscript{1} excited state is optically allowed and can be used to estimate the energy of the S\textsubscript{1} state.

FIG. 3. (a) (Left axis) Photocurrent versus the internal incidence angle \(\Theta_{\text{SPR}}\) for a SAM of \textit{1} on a 100 nm thick gold film on a prism with liquid electrolyte top contact. (Right axis) \(p\)-polarized reflectance versus photon energy for the same SAM/Au layers. (b) Photocurrent versus \(\Theta_{\text{SPR}}\) for a SAM of \textit{2} on a 20 nm thick gold film and reflectance. (c) Photovoltage for a SAM of \textit{2} on a 20 nm thick gold film and reflectance.

plasmon can decay via electron capture from the monolayer, resulting in the formation of a charge transfer (CT) state, indicated by Au\textsuperscript{\textsuperscript{+}}/SAM\textsuperscript{\textsuperscript{+}}. The quinone (Q) redox mediator in the electrolyte solution can neutralize the monolayer by donating an electron. The oxidized mediator (Q\textsuperscript{\textsuperscript{+}}), in turn, can be reduced at the transparent ITO top electrode after diffusion though the liquid electrolyte. In order to assess the importance of the lowest excited singlet (S\textsubscript{1}) state of hemicyanine molecules in the monolayer, we have first tried to determine the energy of the singlet state. Measurement of the optical absorption of \textit{1} and \textit{2} in solution and as monolayer on a very thin gold film (5 nm) is shown in Figs. 4(b) and 4(c). The transition from the ground state to the S\textsubscript{1} excited state is optically allowed and can be used to estimate the energy of the S\textsubscript{1} state. Note that due to excited state interactions between the dye molecules in the tightly packed monolayer, the absorption spectrum of the SAM changes in comparison with the spectrum for isolated molecules in solution.\textsuperscript{20} For \textit{1}, we find that the onset of absorption, both in solution and in film, is below 1.96 eV and so in the experiment the S\textsubscript{1} state of the dye is, in principle, energetically accessible via illumination. For \textit{2}, however, the energy of the S\textsubscript{1} state is estimated to be above 1.96 eV and so the S\textsubscript{1} state is energetically inaccessible and cannot play a major role in the photocurrent generation process. Hence, in the photocurrent generation process, surface plasmons can decay directly into charge transfer states consisting of a spatially separated electron (on the Au metal electrode) and a hole (in the monolayer).

The mechanism proposed here seems similar to the photovoltaic effect from plasmon derived, hot carriers in junctions of wide bandgap metal oxides and gold.\textsuperscript{15–17,24} The approach followed here using a junction comprised a self-assembled monolayer of organic molecules has the advantage that the junctions require only a minimal amount of space. The monolayers can be fabricated easily on complex metal electrode shapes supporting localized surface plasmons, allowing for direct incoupling of light into surface plasmons.\textsuperscript{24} Finally, the hemicyanine endgroups of the groups organic molecules in the monolayer support charge transport via the quinone/hydroquinone redox electrolyte and thus facilitate electrochemical conversion of the photogenerated charges. An additional advantage of the organic self-assembled monolayers is that the endgroup may be varied so that also other electrochemical reactions can be catalyzed that convert photogenerated carriers into other useful fuels.

In conclusion, we find that thin gold films modified with a self-assembled monolayer of \(\pi\)-conjugated molecules with semiconducting properties show photovoltaic activity resulting from dissociation of surface plasmon excitations into...
charge carriers. The charge generation does not require participation of the singlet excited state on the hemicyanine moiety, indicating a hot carrier mechanism. The monolayer facilitates charge transport via a redox electrolyte, indicating a potential for direct electrochemical conversion of (localized) surface plasmons by molecular monolayers on gold structures.

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