RAPID COMMUNICATION

On-substrate, self-standing Au-nanorod arrays showing morphology controlled properties

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Summary We use supported alumina templates and electrodeposition to fabricate self-standing Au-nanorods (Au-NR) arrays. Depending on electrolyte and deposition conditions two different NR morphologies with either corrugated or smooth topologies are fabricated. We show that the properties of the NR arrays, including amphiphilic and optical, very much depend on their morphology. Smooth NR arrays are hydrophobic while the corrugated ones are hydrophilic. Also the optical reflectance, though it shows plasmon resonances at very similar wave lengths, is much lower for the corrugated NR arrays. The activity of the NR arrays as substrates for molecular detection using Raman scattering, and Rhodamine 6G (R6G) as model dye, also strongly depends on their morphology. R6G concentrations down to 1 pM are detected on the corrugated arrays yielding an effective enhancement factor (EF) of approximately 1 × 109. In contrast an over-estimated (because of their hydrophobic character) EF of 6 × 106 is obtained for the smooth NR arrays.

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Introduction

Porous-template based processing of nanostructures allows various critical parameters to be controlled to a high degree as the template moulds the nanostructure via its pore order-
On-substrate Au-Nanorod arrays was used; the pH was adjusted to 2 by adding glacial acetic acid, yielding an end volume of 80 ml. Deposition was performed in an electrochemical cell under constant voltage of \(-1.4\,V\) (vs. Ag/AgCl). The Au-nanorods obtained from this process are designated NRs-P1 in the following. In the second process the nanorods (NRs-P2) were fabricated using a commercial electrolyte (Metakem, Germany) applying repetitive pulsed voltages of \(-0.55\,V\) (vs. Ag/AgCl)/10 ms followed by \(-0.35\,V/90\,ms.

**Characterization**

Microstructure was investigated by means of high resolution scanning electron microscopy (Zeiss Ultra Plus, Germany) and X-ray diffraction (X’Pert Pro, PanAnalytical, Holland). UV–vis–NIR diffuse reflectance spectra were obtained on a Lambda 950 (Perkin-Elmer) equipped with an InGaS integration sphere. Spectralon was used as reference. Specular reflectance was performed at different incidence angles using a Lambda 35 photospectrometer (also from Perkin Elmer). Water contact angles (WCA) were measured with a commercial set-up (Dataphysics Instruments, Germany).

For surface enhanced Raman spectroscopy (SERS) measurements, \(10^{-3}\,M\) aqueous solution of Rhodamine 6G (Sigma–Aldrich, Germany) was prepared and diluted successively to the required concentration. 2 μl of the solution was dropped on the surface of the sample. After drying Raman measurements were performed on a Raman microscope (Senterra, Bruker) using a 532 nm laser radiation and laser power of 0.2 mW. The integration time was 10 s. The Raman signal was recorded using a CCD camera. As reference for the calculation of Raman enhancement factors, a 50 nm Au was sputtered on SiO2/Si substrate and the Raman measurements were performed on \(10^{-3}\,M\) dye solution using similar conditions.

**Results and discussion**

**Microstructure**

The Au-NR array that ensues from the first process (NRs-P1) shows specific features displayed in Fig. 1(a and b). While the corrugated character of the NR-tips constitutes at first their most salient feature, the morphology of their inner-parts, as a further salient feature, could only be revealed after mechanical damage to the array. Fig. 1(c) clearly shows that the inner-parts of the NRs are composed of nanoparticle agglomerates. The NR-surfaces seem to be quite smooth so that it may be surmised that first an Au-film instantaneously nucleates on AAO pore walls, and that subsequently diffusion controlled growth of Au-nanoparticles (NPs) on the Au-film takes place. The current–time curve recorded during deposition supports this assumption (see supporting information, Fig. 1s). When the concentration of \((\text{AuCl}_4)^{-}\) ions in the electrolyte was reduced by tenfold, keeping otherwise the voltage constant, only Au-NTs are formed, as demonstrated in Fig. 1(d). This growth behavior, i.e. NRs made of nanoparticles welded together, has been also observed for the electrodeposition of Cu2O into AAO templates from concentrated CuCl2 solutions [22], and should be amenable to chloride ions adsorption on film walls and subsequent reduction, cluster formation and growth giving rise
to a rough interface between the solid front and the electrolyte. The corrugated character of the NRs-P1 shown in Fig. 1(a) thus arises from this particular growth mechanism.

The NRs obtained from the second process (NRs-P2) are shown in Fig. 2. A smooth NR morphology ensues from this process, and there is no evidence of particles in the inner parts of the NRs. Au-deposition under these conditions is film-like.

The XRD patterns displayed in Fig. 3 show very much similar (1 1 1)-texture for both arrays, though the NRs-P1 exhibited a higher crystallinity (as may be inferred from the higher peak intensity of their patterns) and degree of (1 1 1)-texture (in contrast to the NRs-P2, where the polycrystalline nature of the NRs is inferred from the presence of higher order reflections [23] only the 1 1 1 and a weak 2 0 0 reflections were seen for the NRs-P1).

**Morphological effects on amphiphilic properties**

Morphological features may influence materials properties decisively. For instance the amphiphilic properties were reported to strongly depend on surface morphology, e.g. see the review article by Ma and Hill [24]. Water contact angle (WCA) measurements performed on NRs-P1 and NRs-P2 show large differences, Fig. 4. While the NRs-P1 array is hydrophilic, NRs-P2 is strongly hydrophobic with a WCA of approximately 134°. In fact clean Au-surfaces are
On-substrate Au-Nanorod arrays

Figure 3  XRD patterns of NRs-P1 (upper patterns) and NRs-P2 (lower patterns). Notice the presence of higher order reflections in NRs-P2 that indicates a more pronounced polycrystalline microstructure.

hydrophilic but become hydrophobic when impurities are adsorbed on them or when they are intentionally treated with specific molecules [20, 25—27]. In the present case no surface treatment was performed and the amphiphilic properties of both nanostructures seem to be governed by morphological effects.

Confirmation that morphology controls the hydrophobicity of NRs-P2 was sought in two ways. First, an Au-film that was deposited on a stainless steel substrate using the same electrolyte and deposition conditions had resulted in a superhydrophilic film with WCA of nearly nil, despite the somewhat rough structure obtained (see supporting information, Fig. 2s). Second, a heat treatment of NRs-P2 was performed at 300 \degree C for 30 min in order to pyrolize eventual organic contaminants, but no substantial change in WCA was observed. Unfortunately higher heat treatment temperatures did only lead to collapse of the NRs array. Nevertheless these results strongly suggest that no impurity adsorption from the commercial electrolyte could have changed the wetting behavior of NRs-P2.

Although electrochemically deposited fractal and dendritic copper microstructures were reported to be hydrophobic with WCA of up to 160\degree (without surface treatment), Au-surfaces of different morphologies, fabricated using various techniques, were hydrophilic in the absence of surface treatment [20, 25—27]. Bok et al. [20] report on the electrochemical synthesis and properties of vertical Au-NRs with two different morphologies using commercial AAO templates (poor pore ordering and pore size of 250—300 nm; deposition was probably stopped after reaching some Au-NRs length in order to get perpendicular Au-NRs). Also in this case the NRs arrays were hydrophilic and became hydrophobic only after surface treatment. While NRs-P1 are hydrophilic, and in this respect show similar properties to those of Bok et al., the hydrophobic character of NRs-P2 is unambiguous. Mainly two different models, i.e. Wenzel [28] and Cassie—Baxter [29] were extensively used in literature to explain wetting of heterogeneous surfaces, both hydrophobic and hydrophilic, by water (these models were controversially discussed by Gao and McCarthy [30]). The apparent contact angle \( \theta_A \) is given by Eq. (1) for the case of Wenzel and Eq. (2) for Cassie—Baxter model:

\[
\cos \theta_A = \phi \cos \theta, \quad (1)
\]

\[
\cos \theta_A = -1 + f_s(\cos \theta + 1) \quad (2)
\]

where \( \phi \) is the roughness factor (defined as the ratio of the total surface to the projected area in the horizontal plane), \( f_s \) is the area fraction of the liquid—solid interface and \( \theta \) is the contact angle from the Young’s equilibrium equation.

If we follow these models we should use Wenzel for NRs-P1 and Cassie—Baxter for NRs-P2, similarly to Martínez et al. [31] (hydrophilic nanostructures, e.g. nanopits, were hydrophobized without shape change). However, this will not help us explaining the specific behaviors observed here: Wenzel states that a hydrophobic (hydrophilic) surface would become more hydrophobic (hydrophilic) when it is roughened, while Cassie—Baxter is more appropriate for hydrophobic surfaces [32]. In our present case there is a hydrophobic—hydrophilic ”transition” when the Au-NRs become corrugated, i.e. rough, which is contrary to what is predicted by Wenzel’s model. As we have shown above that Au-films fabricated using the same electrolyte and deposition conditions as for NRs-P2 are, even when they are rough, superhydrophilic (see Fig. 2s), we may suggest that morphology change to a more regular and smooth NRs induces hydrophobicity, without changing rod spacing, i.e. the fraction of solid under the drop remains constant. Abdelsalam et al. [33] did also observe this unusual wetting behavior on gold films that were deposited through polystyrene templates, and had shown that the wetting angle increased from 70\degree (hydrophilic) for an unmodified film to approximately 130\degree for a film with ordered porosity. We believe

Figure 4  Water contact angles (WCA) (a) on NRs-P1, and (b) on NRs-P2.
that this unusual wetting behavior observed in the present work is dictated by the particular array topology; it cannot be explained in terms of known wetting models, and should be the subject of intensive investigations in the future.

Morphological effects on optical properties

Effect of morphology on the optical properties of nanomaterials is well known. In the case of Au-NRs a number of factors such as aspect ratio, dielectric medium and shell layer all have strong effects on the extinction properties of Au-NRs, e.g. see the review article by Pérez-Juste et al. [34]. In the case of self-standing and embedded Au-NRs two modes were discussed and the accompanying peaks in extinction and reflection spectra reported [16,35—37]. These spectra could be theoretically well reproduced by a local treatment of the geometry with finite-element calculations [35] as well as by a global approach, using effective dielectric constants for the layers [16,36,37]. The two peaks were designated transverse and longitudinal modes in account of their dependence on the polarization of the electric fields [16,36,37]. The diffuse reflectance spectra displayed in Fig. 5 in principle show an absorption minimum and a shoulder at approximately 450 and 650 nm that can be related to these transverse and longitudinal modes, respectively. Indeed specular reflectance spectra unambiguously show that the mode at 600—650 nm is largely attenuated when the specular angle increases, Fig. 5(b): the increasing projection of the electric field along the long axis of the rods allows for stronger coupling and thus increasing absorption. This behavior was also observed and discussed by Wurtz et al. [16]. However, a salient difference between NRs-P1 and NRs-P2 is the substantially lower reflectance of NRs-P1. Following the theoretical discussion based on effective dielectric constants for entire layers, a similar intensity reduction has been reported by Bartlett et al. on macroporous Au and Pt films [38] where the reflectance properties were drastically diminished in comparison to plain films. In our case the lower reflectance of NRs-P1 could arise from their corrugated and somewhat porous character that should lead to a higher scatter of incident light. So although the loci of the extinction peaks of both arrays are typical for Au nanorods and are not changed by their morphologies, as the aspect ratios are similar, the reflectance properties can be tuned by changing the microstructure of individual rods. Also the absorption minima and shoulders observed here are broader than reported elsewhere [16,35], which should be attributed to the somewhat poorer ordering.

Figure 5 (a) Diffuse reflectance spectra of NRs-P1 (lower curve) and NRs-P2 (upper curve). Notice the similar Loci of the absorption minima and shoulders in both spectra and the substantial difference in reflectance. (b) Specular reflectance of NRs-P2 at different angles. The structure at approximately 920 nm is an artifact of the apparatus.

Figure 6 SERS spectra of two concentrations of R6G on NRs-P2. (a) For 100 pM and (b) 1 nM. In both cases measurement was done at the approximate location of the cross.
Application to molecular detection

The application of noble metal nanostructures to molecular sensing is quite well known. The mechanism relies on the interaction between localized surface plasmons and molecules. One of the well investigated applications is undoubtedly surface enhanced Raman spectroscopy (SERS) [e.g. see 39,40]. The most widely studied SERS substrates are self-assembled SERS active metal NPs (Ag, Au, Cu) that, depending on particle size and gap between particles, may lead to so huge a signal enhancements (hot-spots) that single molecules may be detected [41]. For instance, a colloidal suspension of noble metal particles or self-assembled monolayers of them, was reported with a distribution of SERS enhancement factors (EF) within $3 \times 10^4$ to $4 \times 10^{10}$ (the latter is required for few to single molecules detection) [42]. Substrates with reproducibly and constantly high SERS EF thus appear to be highly desirable and are a prerequisite for a wider application of SERS beyond fundamental studies. In previous work we have shown that dye molecules can be detected down to 1 fm on suitable Ag-nanostructures that were processed using electrodeposition in conventional AAO templates [43]. Effective SERS enhancement factors of up to $10^{11}$ were obtained, making single molecules detection possible. Nevertheless, on-substrate, self-standing NR arrays should have a substantial advantage over huge aspect ratio NWS obtained in conventional AAO templates as they are robust, easy to handle and should lead to reproducibly high SERS EF.

The SERS investigations were carried out using an aqueous solution of R6G. Once more the NR arrays behaved differently. While NRs-P1 was wetted easily with the solutions, thus allowing after drying a homogeneous distribution of the dye molecules on the NRs to be achieved, the lower wetting of NRs-P2 (see above) had resulted in the formation of a droplet on top of the surface that, after drying, gave rise to a higher concentration of the dye molecules at its periphery. Fig. 6 shows the Raman scattering spectra of R6G on Au-NRs-P2, measured on the periphery of the drop (dark regions with higher concentration), and indicated on the inset micrographs, Fig. 6(a and b). Of the two different concentrations of 100 pM and 1 nM a substantially enhanced signal was obtained for the latter with the characteristic vibrations of R6G being very well resolved and superposed on a fluorescent signal. In both cases no signal was obtained in areas away from the dark region.

In comparison to NRs-P2 an overall enhanced signal of R6G was obtained all over NRs-P1 for a concentration of 1 pM, Fig. 7. It should, however, be pointed out that a strong resonance contribution to enhancement is expected as R6G has its extinction peak at the laser wave length of 532 nm used in the present work.

The magnitude of SERS effect may be described by Eq. (3), which allows an empirical approach to SERS EF to be obtained:

$$\text{EF} = \left( \frac{I_{\text{sers}}}{I_{\text{rs}}} \right)$$

where $I_{\text{sers}}$ is the Raman-band intensity corresponding to the concentration $C_{\text{sers}}$ of the substance analyzed on the SERS Substrate, and $I_{\text{rs}}$ and $C_{\text{rs}}$ the intensity and concentration on non-SERS substrate, respectively.

The results above impressively show that rod morphology determines the magnitude of SERS enhancement, and should point to means for improving the activity of SERS substrates by promoting suitable morphologies. Under the same conditions, the detection limit of the corrugated NRs (NRs-P1) is with 1 pm of R6G at least 3 orders of magnitude better than that of smooth NRs (NRs-P2), and is most probably due to higher electromagnetic field enhancement associated with the irregular NR tip morphology shown in Fig. 1(b). Few reports were published on the application of supported Au-NRs for SERS, and, to our knowledge, none among them was used with R6G. Gold nanoneedle arrays with different needle lengths were fabricated by Yang et al. [44], who reported

<table>
<thead>
<tr>
<th>Band position (cm$^{-1}$)</th>
<th>$A_{\text{EF}}$ (NRs-P1) $\times 10^3$</th>
<th>$A_{\text{EF}}$ (NRs-P2) $\times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1649</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td>1574</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>1532</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>1509</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>1363</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>1179</td>
<td>1.4</td>
<td>0.5</td>
</tr>
<tr>
<td>772</td>
<td>2.1</td>
<td>0.5</td>
</tr>
<tr>
<td>612</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td>$A_{\text{EF}}$</td>
<td>1.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>
a detection limit of 1 μM for arylmethane dye malachite green with a laser excitation wave length of 632.8 nm. The only results that could be compared to those reported here were obtained on gold decorated ZnO-NRs using R6G and a 532 nm excitation wave length [45]. The SERS enhancement factor obtained in their work was 10^6 (based on Eq. (3)) and the detection limit was 100 nM. For Au-NPs and dendritic structures SERS EF reported were in the range from 10^6 to 10^7 depending on particle size and particle gap, though it should be pointed out that other substances than R6G were tested [46,47]. However, it is not our aim to highlight the results obtained in this work in contrast to those obtained elsewhere, but to emphasise once more the crucial role of rod’s morphology in determining the magnitude of SERS activity.

Conclusions

Self-standing Au-NR arrays of approximately 500 nm length, 80 nm diameter and 100 nm gap were processed using electrodeposition into supported AAO template films. Two different morphologies were obtained depending on electrolyte and deposition conditions. A chloride containing electrolyte and high deposition voltages resulted in corrugated NRs that appeared to be made of Au-nanotubes filled with Au-nanoparticles. In contrast, a commercial plating electrolyte and pulsed voltage did lead to smooth NR arrays. These morphologies imparted specific properties to the arrays in question. The corrugated arrays revealed a hydrophilic surface while the smooth ones contrasted with their hydrophobicity. These different behaviors are not easily described by existing wetting models. Characteristic transverse and longitudinal extinction peaks were obtained at fairly the same wave lengths for both arrays from diffuse reflection spectra, but the corrugated arrays did show a substantially lower reflectance, exactly because of their hydrophilic character. These morphologies imparted specific properties to the arrays. These morphologies imparted specific properties to the arrays in question. The corrugated arrays revealed a hydrophilic surface while the smooth ones contrasted with their hydrophobicity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.nantod.2010.11.001.

References

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Claus-Henning Solterbeck received his Diploma in Physics from the Christian-Albrechts-University, Kiel, where he continued his research in the field of theoretical surface physics on numerical photoemission. He joined IMST in 2001 where he is since senior scientist and mainly involved in establishing characterization methods of multifunctional materials and thin films. He has authored or co-authored 55 papers in international peer reviewed journals.