- Supporting Information -

Tailored gold nanostructure arrays as catalysts for oxygen reduction in alkaline media and single molecule SERS platform

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S1. Electrodissolution of disk-shape microelectrode

Electrodissolution of the gold microelectrode causes progressive recession of the metal surface. However, the flux of $AuCl_4^-$ ions remains unchanged. We did not observe any significant tip current change during 20 minutes experiment producing the recessed microelectrode. This is probably caused by self-compensation of two effects. The first one is extending diffusion length for electrogenerated $AuCl_4^-$ ions between recessing metallic surface and the negatively polarized ITO substrate, where these ions are eliminated by electrodeposition at diffusion limiting rate (surface concentration is zero). The second effect is increasing surface concentration of $AuCl_4^-$ at the source electrode. This helps keeping its concentration gradient unchanged despite growing diffusion length. Due to kinetic limitation of Au electrodissolution (see Figure 1A in the main article text), increasing surface concentration product results in decreasing current density when the electrode is polarized at constant potential. A constant current can be maintained by growing surface area of dissolving electrode. In fact, we observed faster dissolution of Au near the circumference of the disk microelectrode resulting in formation of a gap between the metal and the glass sheath (Figure S1).



Fig. S1. SEM images of Au microelectrode before (left) and after (right) electrochemical etching at 0.95 V for 5 minutes. Electrolyte: 3 mol dm⁻³ NaCl, reference electrode: Ag|AgCl. Samples are tilted by 45 °.

This behavior cannot be caused by facilitated Cl⁻ ions transport to the electrode edge, because these ligands are regenerated on the substrate surface just 20 μ m beneath the tip (see equation 2 in the main article text). It can be caused by a positive charge (electron deficiency) accumulated at the Au surface when a quite high potential (+0.95 V) is applied to the electrode. Apparent positive charge is then self-repelled to the circumference of a cylindrical wire. This phenomenon is under investigation by our group.

In order to maintain stable geometric conditions during electrorefining of larger quantities of raw metal, which causes substantial tip recession, periodic renewal of the recessed tip is required, e.g. by removing the excess of the glass sheath by polishing. This is more important in the case of smaller electrodes, because of the faster relative recession of raw metal at the same current density. Then the distance between dissolving metal source and the target support becomes longer, which causes a substantial change of the electrorefining conditions. For example, a nanoelectrode would suffer huge relative recession after preparation of a few nanostructures. This is not the case, when a larger source electrode is used. Then, its electrodissolution results in only a minor relative recession. We successfully used 0.5 mm diameter gold electrode for preparation of 1 cm² samples covered with AuNS. At the same source potential, the resulting current density is similar to that obtained with a smaller microelectrode, and the metal ions flux is proportional to the source electrode area. When one intends to obtain a sample with a similar surface concentration of deposited metal, the source translation rate must be increased proportionally to its linear size. There is no theoretical limitation on the source size for electrorefining except electrochemical cell and SECM positioner range restrictions.

S2. Collection efficiency at dynamic conditions

Collection efficiencies (θ) calculated for moderate overpotentials and dynamic conditions, when the source translated parallel to the ITO surface, are lower than in the case of stationary source (see the main article text), especially for higher translation velocities (Figure S2).



Fig. S2. Absolute charge ratios of the substrate-to-tip currents recorded at various potentials applied to the substrate (ITO) during localized Au electrorefining. The tip translated 2 mm parallel to the sample at a vertical distance of 20 μ m. Velocities: 50 μ m s⁻¹ (**■**) and 200 μ m s⁻¹ (**●**). Tip potential: +0.95 V. Tip diameter: 100 μ m. Electrolyte: aqueous 3 M NaCl.

A larger amount of gold transferred to the bulk electrolyte as $AuCl_4^-$ instead of being deposited on the ITO likely results from convection caused by the tip moving through the solution. For substrate potentials more negative than -0.2 V cathodic currents on the support are higher than anodic currents corresponding to Au tip electrodissolution. Collection

efficiencies calculated as the charge ratio are larger than 100%. No current flows through the unmodified ITO substrate polarized at these potentials, when the tip is not polarized anodically to dissolve Au (no Au electrodeposition on ITO). This means that parallel cathodic faradaic processes occur on freshly formed Au deposit at more negative potentials. The only possible process under these conditions (substrate potential and solution composition) is the oxygen reduction reaction (ORR), which certainly influences the electrodeposition process due to alteration of solution near the substrate (e.g., increased pH). Quantification of the amount of deposited Au on the basis of cathodic charge passed at high overpotentials would be then highly overestimated. Taking into account similar collection efficiencies as obtained for potentials applied to the ITO substrate within a range -0.2 V to +0.2 V, we assumed that the amount of Au deposited at more negative potentials is the same as in deposits obtained when no ORR occurs. Au electrodeposition rate within a whole potential range applied to the ITO substrate (-0.6 V to +0.2 V) at such a high cathodic overpotentials (compare electrodissolution above +0.85 V in Figure 1A in the main article text) is diffusion-limited, so the amount of deposited Au depends only on the amount of AuCl₄ generated and the collection efficiency determined by geometric (distance) and dynamic (translation velocity) conditions. Regardless of the potential applied to the substrate, the surface concentration of deposited Au is the same for fixed tip current density (70 mA cm⁻²), tip-to-substrate distance (20 µm), translation velocity and collection efficiency. The last parameter is a function of the previously mentioned geometric and dynamic parameters and the insulating sheet thickness of the tip. For longer distances more metal ions generated at the tip may diffuse to the bulk without being deposited on the support. Application of bigger source electrodes at the same distance would result in higher collection efficiency due to shorter normalized distance.^{S1} For faster tip lateral translation more AuCl₄⁻ diffuses out from the tip/substrate gap and the amount of metal deposited within the same time is lower (see Figure S2). A thinner insulating sheath of the moving microelectrode would also deteriorate θ . The amount of deposited Au per unit area (surface concentration) is independent of the potential applied to the substrate, since the rate of this process (equation 2) is diffusion-limited.

S3. Sharpness and width of the micro-bands obtained by electrorefining with translating microelectrode

The micro-bands of metallic nanostructures obtained by localized electrorefining using a 100 μ m diameter source electrode moving 20 μ m above the support have about the same width as

the source diameter. Their edges are slightly blurred due to diffusion of the precursor ions generated at the microelectrode (see an example in Figure S3.1). Morphologies of the deposited NS within the centers of stripes are uniform.



Figure S3.1. SEM image (left) of a micro-band of Au nanostructures obtained by localized electrorefining using a 100 um diameter disk-shape Au microelectrode moving 20 μ m above the ITO support. Translation rate: 50 μ m s⁻¹, Substrate potential: -0.6 V. Other parameters as in Figure S2 caption. The chart (right) represents the averaged signal intensity of vertical lines of SEM image.

For longer tip-to sample distances the microbands are wider and more blurred. Supporting Information contains a Windows Media Video file representing electrorefining process that uses 100 μ m dia. Au microelectrode moving 50 μ m above the ITO electrode polarized at -0.2 V vs. the Ag|AgCl reference electrode. The source microelectrode was polarized at +0.95 V. Translation rate: 10 μ m s⁻¹, Translated distance: 5.6 mm, Electrolyte: 3 mol dm⁻³ KCl. The movie is accelerated 40 times versus real time experiment. One can notice that the obtained stripe of electrorefined Au is wider than the diameter of the source microelectrode (100 μ m). A frame extracted from the movie is inserted below.



Figure S3.2. A frame extracted from the movie available online.

An important issue regarding localized electrorefining is a precise tilt adjustment, i.e., alignment of the sample parallel to the XY plane of SECM. For example, assuming an

acceptable maximal vertical distance difference of 10 μ m, the angular misalignment when the tip moves horizontally by 2 mm corresponds to 0.28°.

S4. High magnification SEM images of samples prepared at different translation rates



Figure S4. Higher magnification SEM images of the same samples as presented in the bottom row of Figure 2 in the main article text. Substrate potential: -0.6 V. Translation velocities: 50 μ m s⁻¹ (left), 100 μ m s⁻¹ (center), 200 μ m s⁻¹ (right).

S5. Estimation of surface concentration of the deposited metal by microscopic analysis

Gray-scale SEM images were converted to 1-bit monochrome ones with a threshold adjusted to get black projections of Au nanostructures on a white background. The separated nanostructures were counted and the projected area of each spot was calculated by pixel area integration (Figure S5.1).



Figure S5.1. An example of particle size estimation by microscopic analysis. Raw SEM image (left) calibrated to real distance was converted to particles mask (center). Particle size distribution (right) estimated as hypothetical spheres with the same projected area.

Figure S5.1 represents an example of difficult particles size estimation by analysis of SEM images. Peak-shaped (non-spherical) particles are connected together into bigger aggregates. In order to minimize the particles size estimation errors, their projected areas (black regions in the mask image) were separated by intuitive manual cutting in the graphics software. The projected areas of each particle were evaluated using the ImageJ free software. The results of the example presented here are listed in Table S5. Their 'diameters' ($d = (4A/\pi)^{1/2}$) and volumes (Equation S5) were estimated under the rough assumption of spherical shape:

$$V = \frac{4A^{3/2}}{3\pi^{1/2}}$$
(S5)

where A is the projected area of the nanostructure.

In most of samples presented in this paper the particles are well separated and the analysis of their SEM images did not require such manual separation. Apart from projected area of the particles, ImageJ software calculates a shape parameter of their projections – circularity (the ratio between the diameters of the inscribed and the circumscribed circles). The sum of volumes of all the particles visible in the SEM image divided by the image area ((5×4.307) μ m² in the presented example) and multiplied by the Au density (19.28 g/cm³) provides the surface concentration of electrorefined metal. This estimation is accurate exclusively for ideal spheres. For example, the volume of hemisphere is half of the value calculated by Equation S5. SEM images of tilted samples (Figure S5.2) reveal Au nanostructures whose shapes are non-spherical, but are grown rather perpendicularly to the ITO surface. This is in accordance with precursor concentration gradient normal to the substrate surface. Application of Equation S5 to assess the volume of such perpendicularly grown particles on the basis of their projected area should therefore result in rather underestimated values.

Patricle #	Projected	Estimated	Estimated	Circularity
	area [nm²]	diameter [nm]	volume [nm [°]]	
1	17786	150	1784358	0.287
2	18167	152	1842071	0.512
3	172162	468	53736572	0.362
4	156307	446	46487089	0.471
5	39696	224	5949703	0.507
6	122308	394	32177328	0.465
7	227522	538	81639686	0.385
8	356769	673	160304418	0.282
9	107836	370	26638748	0.795
10	160479	452	48360783	0.46
11	126934	402	34019742	0.503
12	303626	621	125855548	0.335
13	53548	261	9321559	0.83
14	185847	486	60269573	0.594
15	326561	644	140382226	0.263
16	164031	457	49975436	0.776
17	180602	479	57736160	0.779
18	156927	446	46763904	0.742
19	10323	114	789052	0.293
20	267696	583	104190362	0.427
21	211071	518	72947370	0.398
22	112032	377	28208637	0.802
23	121688	393	31933016	0.602
24	149202	435	43353811	0.785
25	183272	483	59021367	0.472
26	134420	413	37073326	0.762
27	301814	619	124730608	0.447
28	303292	621	125648069	0.439
29	195980	499	65265199	0.519
30	235438	547	85936883	0.391
31	98061	353	23100001	0.329
32	96035	349	22387630	0.603
33	289607	607	117240453	0.397
34	162577	454	49312268	0.391
35	177526	475	56267612	0.359
36	66328	290	12850192	0.698
37	88381	335	19765500	0.624
38	132799	411	36404639	0.674
39	40316	226	6089608	0.742
40	69594	297	13810998	0.45
41	77009	313	16075989	0.716
42	160574	452	48403898	0.496
43	72097	302	14562858	0.348
44	35095	211	4945789	0.522

 Table S5.2. Geometric parameters of Au particles from the example presented on Fig. S5.1

 Patricle #
 Projected
 Estimated
 Circularity



Figure S5.2. SEM images of tilted (45 °) samples of Au nanostructures obtained by localized electrorefining using 100 μ m diameter disk Au microelectrode translated 20 μ m above the ITO substrate at velocity 50 μ m s⁻¹. Substrate potential: 0 V (left image), -0.6V (right image).

S6. Comparison of Au nanostructures deposited at most negative potentials



Figure S6. SEM images of electrorefined Au nanostructures obtained at the sample potential -0.5 V (left) and -0.6 V (right). Other parameters as in Figure 2 in the main article text.

Although the sample obtained at -0.6 V contains a larger number of smaller nanoparticles than the sample obtained at -0.5V, they are more aggregated and therefore this sample exhibits lower catalytic activity towards ORR in alkaline media. This can be caused by restricted access of the substrate onto NPs covered by other ones. A lower number of corners and edges is also seen in the SEM image of the sample deposited at -0.6V.

S7. Automated micro-patterning

A variety of two-dimensional micropatterns composed of metallic nanostructures, or continuous layers (in the presence of appropriate electroplating additives), can be 'printed' using SECM. Anodically polarized source microelectrode can translate over the support surface in a programmed way like vector graphic printing by a computer plotter. Another possibility is scanning with an unbiased (or polarized at potential at which no electrodissolution occurs) tip over the support with switching potential to get source electrodissolution when it translates over the area programmed to be modified. An example of the latter approach is presented in the Windows Media Video file available online. The movie is sped up 100 times. A frame extracted from the movie is inserted as Figure S7.



Figure S7. A frame extracted from the movie available online (left), and SERS map of 343 cm⁻¹ band intensity (a.u.) of porphycene preadsorbed on the same sample (right). Fabricated pattern "IChF" is the Polish abbreviation of the authors' institution.

A 25 μ m diameter Au microelectrode was translated 20 μ m above the ITO surface in 25 μ m steps during 20 ms and remained stationary for 1.2 s. The substrate was polarized at -0.2 V, whereas the tip was polarized at 0.5 V (no reaction) and +0.95 V (Au electrodissolution) when staying in programmed image grid points accordingly. The electrolyte was aqueous 3 mol dm⁻³ KCl.

S8. SERS measurements

2D maps ($60 \times 60 \ \mu m^2$) of Raman spectra were recorded with 1 μm resolution revealing inhomogeneous intensity distribution of bands (Figure S8). The sample prepared at the substrate potential $E_s = -0.6$ V, and translation velocity $v = 100 \ \mu m \ s^{-1}$ exhibits the highest surface concentration of highly enhancing "hot spots". This procedure has been chosen for preparation of SERS support to attempt a single molecule study. At each point of the 2D map raster, Raman spectra were recorded continuously for 4.5 min, every ca. 0.54 s.



Figure S8. Left side – 2D maps ($60 \times 60 \ \mu m^2$, 1 μm resolution) of distribution of SERS signal of preadsorbed porphycene from a 10⁻⁸ mol dm⁻³ solution on pristine Au nanostructures obtained by localized electrorefining at different sample potentials and source translation rates. White spots correspond to 343 cm⁻¹ band intensity above 100 a.u. (the lowest detectable Raman signal). Right side, signal intensity distribution (number of spots) in the corresponding maps; left bars, high intensity (>10000 a.u.), middle bars, moderate intensity (1000-10000 a.u.), right bars – low intensity (100-1000 a.u.).

References

S1. J. L. Fernandez, A. J. Bard, Anal. Chem., 2004, 76, 2281.