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Patterning Cu nanostructures tailored for CO₂ reduction to electrooxidizable fuels and oxygen reduction in alkaline media†

Magdalena Michalak, Agata Roguska, Wojciech Nogala * and Marcin Opallo *

Due to limited availability of noble metal catalysts, such as platinum, palladium, or gold, their substitution by more abundant elements is highly advisable. Considerably challenging is controlled and reproducible synthesis of stable non-noble metallic nanostructures with accessible active sites. Here, we report a method of preparation of bare (ligand-free) Cu nanostructures from polycrystalline metal in a controlled manner. This procedure relies on heterogeneous localized electrorefining of polycrystalline Cu on indium tin oxide (ITO) and glassy carbon as model supports using scanning electrochemical microscopy (SECM). The morphology of nanostructures and thus their catalytic properties are tunable by adjusting the electrorefining parameters, i.e., the electrodeposition voltage, translation rate of the metal source and the composition of supporting electrolyte. Activity of obtained materials towards carbon dioxide reduction (CO₂ RR), oxygen reduction reaction (ORR) in alkaline media and hydrogen evolution reaction (HER), is studied by feedback mode SECM. Spiky Cu nanostructures obtained in high concentration of chloride ions exhibit enhanced electrocatalytic activity.

Nanostructures deposited under high cathodic overpotentials possess high surface-to-volume ratio with large number of catalytic sites active towards reversible CO₂ RR and ORR. CO₂ RR yields easily electrooxidizable compounds – formic acid and carbon monoxide. HER seems to occurs efficiently at crystallographic facets of Cu nanostructures electrodeposited under mild polarization.

Introduction

The unique properties of nanostructured materials attributed to increased surface area, altered electronic states, or lattice structure are utilized in many applications. One of the most important technologies, which use nanomaterials and affects the society and the environment is energy conversion and storage. Carbon dioxide reduction reaction (CO₂ RR) and oxygen reduction reaction (ORR) are key chemical processes employed in these technologies. The crucial issue in further development of these technologies is tunable preparation of the nanostructured electrode materials for better efficiency of electrode reactions. Deposition of nanoobjects on the conductive surface is one of the possibilities of tailoring the electrode structure. Apart from nanoobjects of various shape, researchers focus at formation of larger objects with unique surface structure at nanoscale and their catalytic properties. Such materials are commonly called nanostructures. Although nanostructured surfaces possess features, which dimensions are larger than individual nanoobjects (e.g. nanoparticles, nanotubes, nanorods), they preserve such features as large exposed surface to volume ratio and large number of low coordination surface atoms (at edges, corners and vacancies). These features are usually beneficial for (electro)catalysis providing numerous catalytic centers to enhance the kinetics of heterogeneous processes.

Copper is the most abundant group 11 metallic element and one of the most abundant transition metals. Besides its use as coinage metal, in many applications it is a cost efficient material competitive with noble metals (e.g. Au, Pt, Pd). Plenty of potential applications of copper nanostructures (CuNS) were already proposed. Roughened copper is well known as effective material for applications utilizing localized surface plasmon resonance (LSPR), such as surface enhanced Raman spectroscopy (SERS) and surface enhanced fluorescence. Due to high thermal conductivity and volumetric heat capacity of copper, its nanostructures are used as dopants for thermal energy storage materials and thermal interface materials. Uniquely high absorptance of nanostructured Cu surfaces in a broad spectrum covering ultraviolet, visible and infrared radiation allows their use in photothermal conversion. They were also applied as quantum dots in solar cells. Cu exhibit catalytic, photocatalytic, antibacterial, superhydrophobic and self-cleaning properties. Due to their high electric conductivity and electrocatalytic properties CuNS are useful electrode materials, e.g. for electroreduction of NO₃⁻ and H₂O₂. Although CuNS are unstable in acidic environment under anodic polarization or unbiased, their anodic treatment in alkaline solutions causes formation of CuOx nanostructures exhibiting catalytic activity towards...
Electrooxidation of various organic substances, such as L-tyrosine,20 glucose,21,22 hydrazine,22 and water.23,24

Even though there is a number of successful applications of noble metal (Pt, Pd) based nanocatalysts to electrochemical conversion of CO$_2$,25–27 copper is the most promising catalyst for CO$_2$RR yielding valuable, high energy density products as hydrocarbons,28–31 alcohols,28,29,32 formic acid and other carbonyls,28,29,32–35 It was demonstrated that the morphology and therefore electrocatalytic properties of Cu nanostructures towards CO$_2$RR can be tuned by the addition of phosphate and electrodeposition potential36 or appropriate selection of Cu complex precursor.34 Copper-based materials also exhibit electrocatalytic properties towards ORR36 and are considered as replacement of platinum.37,38 Low overpotential of ORR in alkaline media with Cu nanoparticles39 and nanoflowers40 was reported.

There is a plenty of surfactant-free8,9,13,16–18,41,42 and surfactant-assisted11,14,39,40,43–46 methods to obtain CuNS, such as sonoelectrochemical process43 precipitation of Cu(II) complex nanocrystals and their further calcination,16 plasma-induced decomposition of Cu complex,47 homogenous hydrothermal synthesis by reduction of Cu(II) salts with hydrazine,14,44 reduction in solution by NaBH$_4$,45 microwave assisted synthesis,8 disproportionation of CuCl$_2$,11,46 biogenic synthesis by bacteria, fungi, and plant extracts,48 simple redox replacement by immersing of iron plate in Cu(II) salt solution,42 electroless deposition,49 and thermal annealing of Cu$_2$O-dopped glasses in hydrogen atmosphere.9 Surfactant-assisted methods of synthesis yield nanostructures with a protecting layer on their surfaces, preventing their further growth and aggregation. Although properly coordinated surface ligands promote catalysis on metal nanoparticles via steric interactions and electronic modifications,50,51 their presence may hinder access of the reactants to the metal surface and decrease catalytic activity.52 Therefore bare (non-capped) nanostructures are desirable for catalysis.

For electrocatalysis the most useful are CuNS deposited on conductive surfaces. This can be achieved by laser ablation of copper surface,13,41 plasma etching,19 dealloying,53 electrochemical polishing,53 thermal annealing,54 or electrodeposition.10,18,20,22,43,55,56 Gowthaman and John demonstrated that the applied substrate potential during Cu electrodeposition affects geometry of the obtained deposit. They obtained cubic, spherical, dendritic and prickly CuNS from the same solution.22

Local electroless deposition of copper has been done by Schmuki group on AFM-produced nanosized scratches on Si(111) surfaces covered with an organic monolayer.49 The same group electrodeposited micropatterns of CuNS on a similar surface modified with an electron beam.57 In a method based on scanning ion-conductance microscopy (SICM)58–60 a micropipette with Cu salt solution and Cu anode inside was used as a source of copper. Two-dimensional Cu microcircuits were fabricated by lateral scanning over indium-tin oxide (ITO) cathode in a Cu-free electrolyte.54 Mueller et al. applied a similar approach with bipotentiostatic control of both electrodes.60 Unwin group developed SICM-based method for fabrication of three-dimensional Cu structures with dual-channel nanopipette, with one channel for metal precursor delivery and the second for maintaining constant distance between the nanopipette and electrodeposited metal.59 Another micropipette-based method for local electrodeposition has been proposed by Staemmler et al.61 The capillary filled with Cu salt solution and equipped with auxiliary and reference electrode was brought close to the substrate working electrode to assure its contact with the pipette electrolyte. This technique, called scanning electrochemical cell microscopy (SECCM)62 was widely employed by Unwin group, also for local electrodeposition of other metals.63–67 The same technique was also used for visualization of increased activity towards CO$_2$RR at grain boundaries of polycrystalline Au electrode.68 A very similar approach utilizing scanning meniscus confined electrodeposition has been applied to preparation of nanoscale Cu connections,69 line arrays,70 and three-dimensional nanostructures.71

One of the most powerful method for localized deposition of microarrays of metallic nanostructures, as well as for analysis of their electrocatalytic properties is scanning electrochemical microscopy (SECM).72,73 SECM was used for localized electrodeposition of Cu microstructures using its direct mode of operation.74 In this mode a microelectrode (SECM tip) made of an inert metal (Pt) was used as positionable auxiliary electrode. The source of copper was electrolyte containing Cu$^{2+}$. Micrometer-size Cu columns were obtained by retracting the microelectrode with a feedback loop maintaining constant current of electrolysis. Microstructures of copper were also deposited from solution of its stable complexes by using the SECM chemical lens concept.75 Electrolyte beneath the SECM tip is locally acidified by electrogeneration of protons. This causes local decomposition of complexes, thus facilitates electroless or galvanic deposition of Cu at the surface below. Sarkar and Mandler employed SECM and SICM for indirect local deposition of Cu.76 First, Pd nanoparticles were locally deposited and used as the catalyst for Cu electroless deposition by immersing Pd catalyst in the deposition bath. Various methods of manufacturing of metal structures at the micrometer scale, which could be possibly applied to copper, are reviewed in refs.77,78.

Here we present a method of fabrication of bare (non-capped) copper nanostructures with tailored morphology and catalytic activity towards ORR in alkaline environment and CO$_2$RR with generation of compounds, which are electrochemically reoxidizable to CO$_2$ at moderate anodic potentials. Micropatterns of CuNS are obtained by localized electrefining of polycrystalline Cu wire from sacrificial microelectrode (Fig. 1, inset). Such approach allows simple preparation of multiple patterns of nanostructures deposited on single support sample under various conditions influencing catalytic properties of obtained nanomaterials. This enables rapid scanning electron microscopy (SEM) and microscale SECM analyses79–82 and optimization of experimental parameters of electrorefining process. Morphology, thus
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Electrocatalytic properties of CuNS are tuned by adjusting electrolyte composition, electrodeposition potential and Cu source translation rate. Although micrometer size model samples were fabricated and analyzed in microscope, one can apply the methodology presented herein to larger scale fabrication of CuNS.

Experimental methods

Chemicals

\( \text{H}_2\text{SO}_4, \text{HCl, NaNO}_3 \) (Chempur), KCl (Sigma-Aldrich), NaOH (Fluka), HCOOH (Sigma-Aldrich), NaH_2PO_4 (Sigma) and Na_3P_2O_5 (POCh) were used for aqueous electrolyte preparation with deionized water purified by Elix system (Millipore). Argon N5.0 was from Multax.

Microelectrodes preparation

Microelectrodes were fabricated according to the procedure described previously. Simply, a 25 µm or 100 µm diameter wires of Pt (Mint of Poland), Au, or Cu (Alfa Aesar) were inserted in the borosilicate glass capillary. Then their were inserted into the PC-10 micropipette puller (Narishige) to melt the glass and to seal the wire tightly inside the capillary under vacuum conditions to avoid gas bubbles. The end of the microelectrode was polished with P2000 grit silicon carbide sand paper.

Electrodeposition of Cu nanostructures

All electrochemical experiments were performed using homemade scanning electrochemical microscope controlled and operated under SECMx software. The equipment consists of ivium CompactStat bipotentiostat and mechOnics XYZ positioning system, allowing positioning of microelectrode (SECM tip) close to the sample – consists of Ivium CompactStat bipotentiostat and mechOnics XYZ positioning system, allowing positioning of microelectrode (SECM tip) close to the sample – glass capillary. Then their were inserted into the PC-10 micropipette puller (Narishige) to melt the glass and to seal the wire tightly inside the capillary under vacuum conditions to avoid gas bubbles. The end of the microelectrode was polished with P2000 grit silicon carbide sand paper.

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Results and discussion

Morphology and composition of deposited Cu nanostructures

Microsamples composed of CuNS were prepared by localized electrorefining of 100 µm diameter Cu microelectrode positioned 30 µm above the ITO support. The faradaic current recorded at the Cu source microelectrode upon its anodic polarization corresponds to electrodissolution of Cu (Fig. 1). Cathodically polarized ITO substrate (~3.14 cm²) exhibits residual background current of few tens of µA (depending on applied potential) due to sluggish reduction of oxygen. Once electrodissolution of Cu microelectrode starts, cathodic current at ITO support starts to grow accordingly yielding under the quiescent condition (without Cu-tip movement) nearly 100 % of coulombic collection efficiency (see Supplementary Information S1).

The elemental composition of CuNS on ITO coated glass support was confirmed by the EDX analysis (Fig. 2). The EDX spectrum shows the presence of copper in addition to other elements originating from ITO (Sn, In, O) coated glass substrate (Si, Al, Ca, Mg).

Sample characterizations

In order to overcome known problems caused by instability of Cu, before removal of CuNS samples from an SECM cell, an acidic electrolyte was exchanged gradually to 0.1 M phosphate buffer pH 7.2 under continuous cathodic polarization. The samples were rinsed with deionized water and dried with argon. The surface morphology and chemical composition of deposited CuNS were observed/examined with the use of a scanning electron microscope (SEM, FEI Nova NanoSEM 450 equipped with an EDAX energy dispersive X-ray spectroscopy (EDX) detector and GENESIS software). EDX analysis was performed at a primary beam energy of 20 kV.
CuNS electrodeposited on ITO using 0.5 M aqueous H$_2$SO$_4$ as electrolyte are always rounded, regardless of potential value applied to ITO substrate. Neither distinct edges nor sharp corners are seen in their SEM micrographs. The size of obtained CuNS depends on the translation rate of electrodissolving Cu microelectrode. Faster horizontal translation rates of Cu source result in smaller nanostructures (Fig. 3 a-c). This is caused by shorter time of exposure of certain area of ITO support to Cu$^{2+}$ flux evolving from translating Cu microelectrode, whereas stable electrodissolution rate is maintained (constant anodic current observed at the Cu microelectrode). When electrodeposition potential is shifted to lower (more negative) values, the rounded shape of CuNS is not affected, however, they are smaller and the number of objects per unit area increases (Figure 3d).

Another factor influencing morphology of CuNS is the composition of the electrolyte. Addition of KCl to H$_2$SO$_4$ solution, as well as complete substitution of H$_2$SO$_4$ for solution containing only Cl$^{-}$ anions – 1 M KCl acidified with 10 mM HCl (in order to prevent hydrolysis of Cu$^{2+}$ and to facilitate electrodissolution of Cu) – alters the shape of the CuNS substantially (Fig. 3 d-f). Cl$^{-}$ at 1M concentration causes formation of stable CuCl$^+$ and CuCl$_2$ complexes.$^{84,85}$ Moreover, Cu(I) complexes (CuCl$_2$$^+$, CuCl$_2$) are also stable under these experimental conditions, thus electrorefining of Cu can occur with one electron per Cu atom stoichiometry. Amount of deposited copper estimated by analysis of SEM images is in good accordance with faradaic charge passed for 2 electron reaction in H$_2$SO$_4$ solution and 1 electron process in the presence of chlorides (see Supplementary Information S2).

Application of chloride electrolyte decreases electricity consumption required for electrorefining of Cu. This is especially important for large scale industrial processes. CuNS obtained with acidified KCl electrolyte are larger, less crowded on ITO support and exhibit number of sharp edges and corners (Fig. 3 f). This is caused by slower kinetics of nucleation and growth of Cu deposits from chloride-complexed copper ions. Negatively charged complexes are also repelled from the electrical double layer at the substrate upon its cathodic polarization (negatively charged substrate). Inhibited nucleation on ITO surface causes larger separation of formed nuclei. Further growth of nanostructures causes depletion of copper ions around them preventing nucleation around. Kinetics of outer sphere electroreduction of stable complexes depends on the type of crystallographic facet, therefore electrodeposition on certain surface facets occurs faster than on others. This causes symmetry breaking and growth of prickly shape CuNS. Preferential adsorption of Cl$^{-}$ on certain crystallographic facets can also play a role in formation of peaky nanostructures. The influence of facet-dependent conductivity on chemical kinetics cannot be excluded.$^{86}$

The increase of roughness of Cu deposits in the presence of Cl$^{-}$ in alkaline media (right).

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Scheme 1. Schemes (not to scale) of processes occurring during feedback mode SECM analysis of carbon dioxide reduction reaction (left) and oxygen reduction reaction in alkaline media (right).
anions was recently reported by Suzuki et al.\textsuperscript{87} The electrodeposition of Cu on glassy carbon (GC) from solution containing Cu-Cl complexes also produces CuNS with numerous edges and corners (Fig. 3 g). More negative electrodeposition potential applied to GC produces aggregates of smaller CuNS. Although similar amount of Cu is deposited, its larger surface is exposed with possibly large number of low coordination Cu atoms at edges, corners and defects (Fig. 3 h,i). Such morphology is expected to be beneficial for electrocatalysis.

**CO\textsubscript{2}** reduction at Cu nanostructures

Catalytic properties of electrodeposited nanostructures towards CO\textsubscript{2}RR and ORR were studied using feedback mode SECM (Scheme 1). Feedback mode CO\textsubscript{2}RR was realized utilizing CO\textsubscript{2} electrogeneration by oxidation of formic acid on Pt electrode.\textsuperscript{82} CO\textsubscript{2} from Pt microelectrode (SECM tip) positioned above CuNS diffuses to the studied catalyst. At neutral pH it is reduced mainly to HCOOH,\textsuperscript{33–35,82} generating additional flux of tip reaction substrate. There are also other possible paths of CO\textsubscript{2}RR yielding carbon monoxide, formaldehyde, methanol, ethanol, methane and ethylene.\textsuperscript{79} Contrary to other products, CO can be also reoxidized at the SECM tip to CO\textsubscript{2} at moderate applied potentials. Continuous cycling of charge carriers (CO\textsubscript{2} – dominating oxidized form, HCOOH – dominating reduced form) between Pt-tip and CuNS sample assures feedback mode and allows testing of catalytic properties of CuNS by feedback current measurement at the tip. In neutral (pH 7) buffered solution hydrolyzed CO\textsubscript{2} (pK\textsubscript{a}(H\textsubscript{2}CO\textsubscript{3}) = 6.35)\textsuperscript{88} and HCOOH (pK\textsubscript{a} = 3.75)\textsuperscript{88} occurs as bicarbonate (HCO\textsubscript{3}\textsuperscript{−}) and formate (HCOO\textsuperscript{−}), respectively. CuNS deposited at ITO are not suitable for CO\textsubscript{2}RR due to instability of ITO under strong cathodic polarization,\textsuperscript{89} required to drive CO\textsubscript{2}RR. Therefore, we employed glassy carbon as a support for electrodeposition of CuNS for their further study as CO\textsubscript{2}RR catalyst.

For comparative studies of catalytic properties of CuNS towards CO\textsubscript{2}RR we prepared parallel microstripes of nanostructures deposited at various potentials applied to glassy carbon support. All the microstripes were prepared under the same source translation rate (50 μm s\textsuperscript{−1}) to assure equal amount of deposited metal in each stripe. This sample was analyzed by SECM in buffered solution of HCOOH with Pt microelectrode tip. Fig. 4 shows horizontal line scans perpendicular to axes of CuNS microstripes. Anodic feedback current recorded at the SECM tip is enhanced when scanning above cathodically polarized CuNS than when the tip scans above non-modified glassy carbon surface. Positive feedback current is due to catalytic regeneration of HCOOH on electrodeposited CuNS. CuNS protrudes only up to ~1 μm above the flat support (see Supplementary Information S3). Therefore an influence of sample topography on feedback current can be neglected (tip-to-sample distance: 30 μm). Since the CuNS were prepared at different electrodeposition potentials a plot of tip current vs. horizontal tip position is used to compare catalytic activities of these nanostructures. Clearly, there is a strong influence of electrodeposition potential on electrocatalytic activity of CuNS. For CO\textsubscript{2}RR carried out at moderate potentials, down to -1.1 V vs. Ag/AgCl, the optimal value of electrodeposition potential is c.a. -0.7 V. When CO\textsubscript{2}RR is driven at more extreme cathodic polarizations, CuNS obtained at -0.4 V acquire maximum activity, instead. At potentials below -1.1 V applied to the CuNS sample, hydrogen evolution reaction (HER, by electroreduction of water) may occur simultaneously with CO\textsubscript{2}RR and contribute to the SECM feedback current. This result shows that HER occurs faster at other types of active sites at CuNS than CO\textsubscript{2}RR. Because CuNS deposited at more negative potentials possess more developed surface and less exposed flat crystallographic facets (see Fig. 3 g-i), one could conclude that chemically reversible CO\textsubscript{2}RR, contrary to HER, occurs preferentially at low coordination sites (edges and corners) rather than at crystallographic facets of CuNS. This is in accordance with Ledezma-Yanez et al.\textsuperscript{90} observation that acetaldehyde reduction occurs at lower overpotentials at more open facets of Cu.

Another reason for this behavior can be larger increase of
solution pH upon CO$_2$RR close to the CuNS with more developed structure due to a steric hindrance of mass transport of reactants near concave structures. Such effect shifts HER (1e/1H$^+$ stoichiometry) onset potential towards more negative values by 59 mV/pH, contrary to ~30 mV/pH in case of CO$_2$RR (2e/1H$^+$ stoichiometry). Another reason of larger SECM feedback current at CuNS with more developed structure can be related to CO$_2$RR pathways.$^{29}$ For HCOOH evolution and CO evolution, these products can be easily reoxidized to CO$_2$ at Pt microelectrode polarized at moderate anodic potentials. Other possible products of CO$_2$RR – HCHO, CH$_2$OH, CH$_4$, C$_2$H$_5$OH and C$_2$H$_4$, despite their value as combustible fuels, are not as easily electrooxidizable as HCOOH and CO under applied experimental conditions (0.7 V vs. Ag|AgCl). Suppressed selectivity for multi-carbon compounds formation upon CO$_2$RR on roughened Cu nanocubes was reported.$^{91}$

SECM feedback mode screening of CO$_2$RR catalyst provides valuable information not only about sample activity. Chemical reversibility related reaction pathways also affects the feedback. This is especially important when application of CO$_2$RR is considered in electrochemical energy storage (reversibility required). It is worth to remind at this point that all the stripes of CuNS contains approximately the same amount of Cu per unit area of the support. This is due to the fact that at deposition potentials less than -0.2 V CuNS growth rate is limited by diffusion. The same amount of Cu ions is delivered per unit area of the substrate (constant parameters: electrodissolution current, tip translation rate, tip-to-sample distance).

In order to analyze an influence of the electrolyte composition applied for electrorefining of copper on the catalytic properties of obtained CuNS, a SECM mapping of CuNS prepared at the GC electrode with three different solution compositions was performed. Localized electrorefining under quiescent conditions, i.e. without translating of Cu microelectrode was performed in the following electrolytes: (1) 0.5 M H$_2$SO$_4$, (2) 0.5 M H$_2$SO$_4$ + 0.1 M KCl, (3) 1M KCl + 10 mM HCl, at three different potentials applied to the GC (-0.3 V, -0.4 V, -0.5 V). A map of SECM feedback current recorded in a similar way as described above is presented in Fig. 5.

CuNS obtained in electrolyte containing only Cl$^-$ anions (without SO$_4^{2-}$) exhibit the highest catalytic activity towards CO$_2$RR. CuNS obtained with 0.5 M H$_2$SO$_4$ and H$_2$SO$_4$ with an addition of 0.1 M KCl exhibit similar activities substantially lower than these obtained with acidified electrolyte containing only chloride anions. Thus, optimization of electrolyte composition should be focused towards providing high concentration of chloride and avoidance of sulphates. When stable Cu-Cl negatively charged complexes are formed, which require higher cathodic polarization for nucleation and growth of CuNS, then CuNS with exposed crystallographic facets are deposited (see Fig. 3). Such a structures are preferred as catalyst for CO$_2$RR at high overpotentials, when HER is also possible. In order to prevent hydroslysis of Cu$^{2+}$/Cu$^{2+}$ ions and precipitation of Cu(OH)$_2$ pH has to be kept around 2 (10 mM HCl). Further pH decrease shifts hydrogen evolution potential to higher values affecting electrodeposition of CuNS. The largest activity towards CO$_2$RR was obtained for CuNS deposited at -0.5 V. This electrodeposition potential is lower than in the case of electrorefining of Cu with the microelectrode translating horizontally at 50 μm s$^{-1}$ (Fig. 4). It shows that the mechanism of electrodeposition of CuNS is significantly affected by hydrodynamic conditions caused by electrode motion. Indeed the morphology of CuNS obtained under quiescent conditions differs from that obtained with translating microelectrode (see Supplementary Information S4). The most active CuNS, obtained at -0.5 V applied to the GC support, are the smallest among those obtained under quiescent conditions. Their exposed surface area is the largest per amount of Cu deposited. Contrary to the spherical CuNS obtained without chloride ions in electrolyte, crystallographic planes are visible at their surfaces. This result confirms that CO$_2$RR with generation of electrooxidizable compounds and possible contribution of HER under strong cathodic polarization, besides spots with low coordination surface atoms, occurs also at flat crystallographic planes.

**Oxygen reduction at Cu nanostructures**

We also employed feedback mode SECM to study catalytic activity of CuNS towards ORR in alkaline solution.$^{52}$ O$_2$ is generated at the SECM tip (Au microelectrode) by OH$^-$ oxidation$^{53}$ (Scheme 1) and diffuses to CuNS where is reduced to OH$^-$, generating additional flux of OH$^-$ anions enabling SECM feedback at Au tip. Since H$_2$O$_2$ does not undergo oxidation at Au microelectrode, the SECM positive feedback reveals only 4-electron ORR at examined CuNS. Due to less negative onset potential of ORR as compared to CO$_2$RR, we were able to apply ITO as the support for electrodeposition of catalytic CuNS and to compare the effect of support (GC vs. ITO). Fig. 6 shows results of SECM line scan analysis of catalytic activity of microstripes of CuNS towards ORR. Microstripes were deposited on GC or ITO and analyzed under the same...
Fig. 6. Feedback mode SECM line scan analysis result of ORR occurring on the microspots of CuNS obtained by localized electrorefining at various substrate potentials and materials (marked in the figure). Other electrorefining parameters as in Fig. 5. In analytical experiment a 100 μm diameter Au microelectrode (tip) was translated 30 μm above the sample perpendicular to micro-bands (see the inset in Fig. 5) of CuNS at 10 μm s⁻¹. Tip potential: +1.6 V; sample potential: -0.7 V; reference electrode: Ag/AgCl; electrolyte: 0.1 M NaNO₃ + 10 mM NaOH.

One can see a bit higher feedback currents for CuNS deposited on GC and maximal activity for CuNS deposited at different potentials, however, the influence of support material on resulting activity of CuNS is not significant. Feedback currents are at a similar level, but the contrast is higher for the sample deposited on GC support. Lower current contrast for ITO supported sample is due to higher residual activity of ITO towards ORR than residual activity of GC. The most active CuNS towards ORR were prepared on glassy carbon for -0.7 V applied to the sample during electrorefining. This corresponds to the same conditions as in case of CO₂RR under moderate polarization, when HER is not involved. Therefore, a similar methodology can be applied for preparation of CuNS for both CO₂RR and ORR. The same strategies of catalyst preparations does not apply to HER. With ITO substrate the highest activity towards ORR exhibit CuNS deposited at -0.75 V. One can suspect that electrodeposition at more negative potentials could yield CuNS even more active. However, ITO electrodes are not suitable for polarization at lower potentials. Similarly to CO₂RR, ORR occurs more efficiently at CuNS obtained with the use of electrolyte containing high concentration of chloride ions (Fig. 7). This approach facilitates symmetry breaking and formation of spiky-shaped crystalline CuNS, which both for CO₂RR and ORR are more active than amorphous structures obtained without chloride ligands.

Conclusions

We have presented a simple methodology of preparation of bare (non-capped) copper nanostructures from polycrystalline metallic source. This procedure relies on localized electrorefining of copper microwire constituting a tip of scanning electrochemical microscope. The size and morphology of the obtained nanostructures and thus their catalytic properties can be tuned by adjusting the electrorefining parameters, i.e., the applied voltage, the source translation rate and the composition of supporting electrolyte. Scanning electrochemical microscopy analysis of microarrays of nanostructures allows their quick characterization and optimization as catalyst for CO₂RR to electrooxidizable fuels useful for storage of renewable energy. Electrorefining of copper with use of chloride ions at high concentration results in peaky shape nanostructures exhibiting highest catalytic activity. Structures deposited under high cathodic overpotentials possess high surface-to-volume ratio with large number of catalytic sites active towards carbon dioxide reduction process yielding easily electrooxidizable compounds. Oxygen reduction reaction in alkaline media occurs effectively at the same sites, whereas hydrogen evolution reaction occurring simultaneously with CO₂RR at high cathodic overpotentials is probably catalyzed rather at crystallographic facets of larger copper nanostructures electrodeposited under moderate overpotentials. Despite catalytic properties of bare Cu nanostructures, their non-capped surface is prone to corrosion and adsorptive contamination resulting in activity deterioration. In case of electrocatalysis long-term activity can be provided by periodic depassivation and electrodeodesorption enforced by polarization of electrode within available potential window.

Conflicts of interest

There are no conflicts to declare.

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