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Electrochemically-grown Chloride-free Cu₂O Nanocubes Favorably Electroreduce CO₂ to Methane: The Interplay of Appropriate Electrochemical Protocol --Manuscript Draft--

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Abstract:	<p>Nowadays, electrochemical CO₂ reduction reaction (CO₂RR) to value-added products represents one of the major challenges in electrocatalysis. Copper-based nanocubes (Cu NCs) have been proposed as the front-runner's catalyst for the production of C₂+ products at the industrial level. However, their selectivity (C₁ vs. C₂ product distribution) is rather complex depending on the dynamic structural transformations, the presence of mixed Cu⁺/Cu⁰ states, the microenvironment, and nanocatalyst-support interactions. Commonly, electrochemically-grown Cu NCs are prepared in the presence of chlorides that acts as a shaping agent. In this study, an optimized electrodeposition method for the synthesis of Cl⁻-free Cu₂O nanocubes on a glassy carbon substrate with uniform size, shape, and loading is established. The successful preparation of chloride-free cuprous oxide nanocubes (Cu₂O NCs) was confirmed with X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) analyses. We report how the electrochemical double-layer capacitance (EDLC) method for electrochemical surface area (ECSA) determination with(out) subsequent return to the open-circuit potential (OCP) conditions before electrolysis influences the CO₂RR activity/selectivity. When Cu₂O NCs are subjected to the EDLC method (often considered a non-invasive method) and exposed to the OCP before electrolysis, they become active for methane (CH₄) formation. Moreover, the influence of the potential window width (i.e. 200 and 400 mV) in which the EDLC-ECSA is employed and its correlations with the selectivity is presented. We underline the importance of the ECSA determination method and OCP on/off state as a triggering factor for reactivity/selectivity of particular Cu₂O NCs for CO₂RR and further emphasize the reconstructive nature of Cu₂O NCs under CO₂RR relevant conditions.</p>

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Electrochemically-grown Chloride-free Cu₂O Nanocubes Favorably Electroreduce CO₂ to Methane: The Interplay of Appropriate Electrochemical Protocol

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Abstract: Nowadays, electrochemical CO₂ reduction reaction (CO₂RR) to value-added products represents one of the major challenges in electrocatalysis. Copper-based nanocubes (Cu NCs) have been proposed as the front-runner's catalyst for the production of C₂₊ products at the industrial level. However, their selectivity (C₁ vs. C₂ product distribution) is rather complex depending on the dynamic structural transformations, the presence of mixed Cu⁺/Cu⁰ states, the microenvironment, and nanocatalyst-support interactions. Commonly, electrochemically-grown Cu NCs are prepared in the presence of chlorides that acts as a shaping agent. In this study, an optimized electrodeposition method for the synthesis of Cl⁻-free Cu₂O nanocubes on a glassy carbon substrate with uniform size, shape, and loading is established. The successful preparation of chloride-free cuprous oxide nanocubes (Cu₂O NCs) was confirmed with X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) analyses. We report how the electrochemical double-layer capacitance (EDLC) method for electrochemical surface area (ECSA) determination with(out) subsequent return to the open-circuit potential (OCP) conditions before electrolysis influences the CO₂RR activity/selectivity. When Cu₂O NCs are subjected to the EDLC method (often considered a non-invasive method) and exposed to the OCP before electrolysis, they become active for methane (CH₄) formation. Moreover, the influence of the potential window width (i.e. 200 and 400 mV) in which the EDLC-ECSA is employed and its correlations with the selectivity is presented. We underline the importance of the ECSA determination method and OCP on/off state as a triggering factor for reactivity/selectivity of particular Cu₂O NCs for CO₂RR and further emphasize the reconstructive nature of Cu₂O NCs under CO₂RR relevant conditions.

KEYWORDS: *Copper nanocubes, CO₂ reduction, selectivity, methane, support effect*

1. Introduction

Unfolding the energy, together with the climate crisis, once again warned that investment in the cutting-edge science of electrochemical technologies for energy storage and conversion will be of paramount importance to sustain energy demands. In the last two decades, tremendous efforts have been undertaken to develop these technologies to become independent of current energy derivatives (coal, gas, oil). Until now the majority did not reach a cost-effective commercial level.[1] Despite the overoptimistic assertion that electrocatalytic carbon dioxide reduction reaction (CO₂RR) could potentially contribute to CO₂ removal from the atmosphere, the technology has sparked interest in sustainable means of converting CO₂ into value-added products, ideally powered by renewable energy.[2,3] The main hurdle in the process remains the “under-performance” of the electrocatalysts. Copper and copper-based materials are the only ones that can convert CO₂ to multicarbon products at a decent yield.[4] Among the complex interplay of various Cu-based catalyst parameters (morphology,

1 composition, oxidation state, shape, size, interparticle distance, loading, etc.) to improve the CO₂RR
2 reactivity, the shape effect has attracted significant interest due to the tunable approach toward
3 selectivity of certain facets.[5] In several well-studied single-crystal copper surfaces, certain facets
4 provided favorable product selectivity. As a result of a significantly lower CO dimerization energy
5 barrier, surfaces with abundant Cu(100) have been shown to selectively reduce CO₂ to C₂H₄. Likewise,
6 it has been shown that Cu(111) is more selective toward CH₄. [6,7] Subsequently, the researchers have
7 been trying to transfer this knowledge of single-crystal studies to the nanoparticles and synthesize
8 shaped-like nanocatalysts with abundant particular facets.
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10 Inline, cube-shaped copper (Cu NCs) nanoparticles with Cu(100)-rich surfaces have been
11 recognized in the CO₂RR community as the propitious catalyst for the production of ethylene (C₂H₄)
12 for future industrial applications.[8–12] Among various preparation methods for the synthesis of shaped
13 nanoparticles[5], electrodeposition emerged as a prominent method because it is inexpensive, quick,
14 requires simple equipment, and permits the precise tuning of electrochemical parameters for the
15 generation of versatile self-supported nanostructures.[13] A group led by prof. Roldan Cuenya studied
16 in detail the growth dynamics and morphological evolution of Cu₂O NCs using pulse-electrodeposition
17 wherein nanocubes are grown in chloride-containing electrolytes. Moreover, the authors also reported
18 the reactivity of electrochemically-grown Cu₂O NCs and their complex dynamic degradations behavior
19 under CO₂RR-relevant conditions.[9,12,14] Grosse *et al.*[9] emphasized the support effect as one of the
20 crucial factors for the determination of the product selectivity for the Cu NCs. Copper cubes on copper
21 foil predominantly produce C₂₊ products, while copper cubes on carbon support tend to be more
22 selective for C₁ products. Early works on Cu NCs towards enhancing activity/selectivity have neglected
23 copper's reconstructive nature, focusing only on the as-prepared morphologies.[8,15,16] This has
24 overshadowed the dynamics of the reconstruction as one of the most important steps to gain more
25 insight into the structure-performance relationship. The Cu NCs have been proposed to undergo
26 reconstruction due to the different reaction factors such as applied bias[17], CO₂RR intermediate-related
27 adsorbates[18], local pH[19], etc. Lately, numerous in situ/operando studies have been devoted to the
28 in-depth understanding of its influence on catalytic active sites, which is one of the most unclear and
29 debatable topics for CO₂RR.[20,21] Most recently it has been shown that Cu surfaces are surprisingly
30 stable under highly reducing conditions, thus, the reasonable explanation for the structural evolution
31 can be described as sometimes unintentional surface oxidation and subsequent anisotropic reduction
32 accompanied by the processes such as dissolution/redeposition.[22–24]
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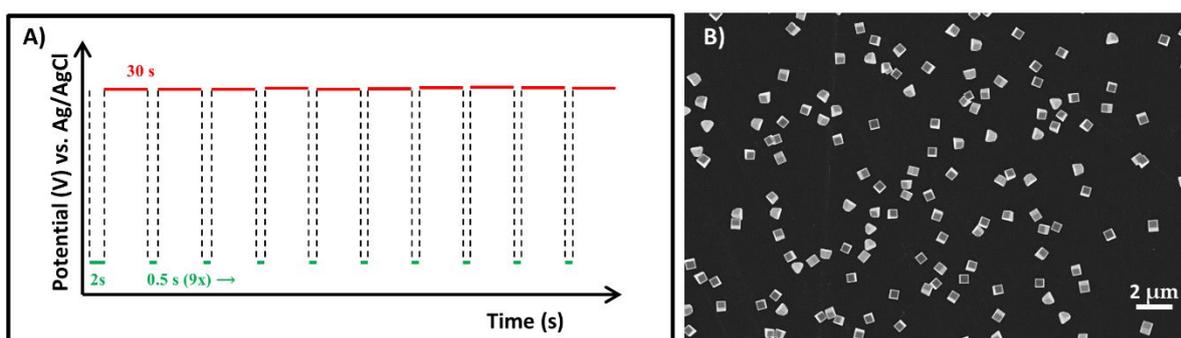
39 Further development of in-situ/operando techniques will be pivotal to gaining a clearer picture of
40 the dynamic reconstruction and identifying catalytic active sites during CO₂RR.[25,26] As a result of
41 all of the above, Cu(100) surface cannot be considered as the only determining factor for C₂₊ product
42 formation, but rather there exists a synergism between dynamic structural transformations[27], and the
43 presence of mixed Cu⁺/Cu⁰ oxidation states[28], microenvironment[25], and nanocatalyst-support
44 interactions[9]. The reconstructive nature of Cu-based catalysts imposes one more obstacle to
45 accurately and properly validating the catalyst's intrinsic activity, which is, the electrochemical surface
46 area determination (ECSA). As the crucial figure of merit for accurate assessment of CO₂RR-current
47 density, ECSA has often failed to be determined in a non-invasive and non-destructive manner. Few
48 studies stress the importance of measuring ECSA in a minimally invasive, time-resolved, and
49 destructive manner for a valid comparison of the catalyst's intrinsic activity, however, this remains
50 elusive.[12,29,30] While employing statistical methods such as ex-situ SEM imaging[9] and AFM
51 measurements[31] for the active surface area determination, always rises a question of reliability. The
52 underpotential deposition (UPD) of Pb on copper acts destructively (most likely quasi-irreversible) by
53 impurity presence.[32,33] Currently, one of the most popular, supposedly non-destructive, and
54 widespread methods for ECSA determination in the CO₂RR community is the electrochemical double-
55 layer capacitance (EDLC) method, often considered reliable for metal oxide that has high electrical
56 conductivity.[34] However, in this study, we show that the EDLC-ECSA determination method such
57 as method indeed affects catalysts' properties. It behaves as an electrochemical "activation protocol"
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1 that boost the activity/selectivity of Cu NCs. Meticulously, we present an optimized pulse-alternating
2 electrochemical protocol to produce Cu₂O- nanocubes (Cu NCs) with uniform size, shape, and loading.
3 We for the first time demonstrate that, by tuning the stirring rate of the solution, reproducible Cu NCs
4 can be synthesized in a 10 mM CuSO₄ electrodeposition bath in the absence of Cl⁻ ions, which were
5 emphasized in the literature to be a critical additive for shaping Cu nanostructures and were shown to
6 affect their selectivity.[14] We show that the addition of Cl⁻ is unnecessary to obtain Cu-based cubic-
7 shaped nanoparticles and prove that the synthesized Cu-based NCs are indeed made out of cuprous
8 oxide (Cu₂O). The electrocatalytic performance of as-prepared Cu₂O NCs on glassy carbon substrate
9 showed no CO₂RR activity. Furthermore, the samples that underwent the EDLC-ECSA determination
10 without subsequent return to OCP predominantly produced H₂. Interestingly, when the Cu-based NCs
11 underwent the protocol in the form of a double-layer capacitive cycling method for the determination
12 of ECSA, often considered a non-invasive method, before CO₂RR in combination with exposure to the
13 OCP, they become active for methane formation. We also present the influence of different ECSA
14 potential windows on the activity/selectivity and reveal the catalyst's morphological evolution before
15 and after CO₂RR to gain newer insights into the structure-activity and structure-stability relationships
16 of Cu-based systems.
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19 2. Experimental Section

20 2.1. Chloride-free Electrodeposition of Cu₂O NCs

21 Among the various technologies for the synthesis of copper-based nanocatalysts[35],
22 electrodeposition stands out as a powerful synthesis method with some major advantages such as 1)
23 good adhesion of the deposits; 2) the absence of organic surfactants usage; 3) the usage of inorganic
24 »shaping-agents« to tune catalysts shape.[14,36] Standing with the latter one, it is commonly accepted
25 that chloride ions (Cl⁻) in the precursor solution encourage nanocube formation, both with nucleation
26 of the Cu₂O cubes and the stabilization of the Cu {100} facets. The extensive studies on
27 electrodeposition of Cu NCs have emphasized that the concentration of Cl⁻ "had the most drastic effect
28 on the catalyst size distribution and coverage". Moreover, the benchtop method for the electrodeposition
29 of Cu NCs on glassy carbon substrates has been established through the so-called pulse-alternating
30 method.[36] In this study, we posit the pulse-alternating electrochemical protocol in 10 mM CuSO₄
31 electrodeposition solution without the addition of chlorides to produce a uniform shape, size, and
32 loading of Cu₂O NCs. Figure 1, Supplementary note 1, and Figures S1-S7 provide an in-depth
33 description of the experimental procedure and optimization of the synthesis.
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51 Figure 1. A) Pulse-alternating electrochemical protocol for electrodeposition of Cu₂O NCs. 10 mM CuSO₄
52 electrodeposition solution and stirring rate of 500 rpm are used for optimized synthesis. In total, 10 reductive
53 pulses consisted of a first pulse of 2 s and 9 consecutive pulses of 0.5 s whereas the 30s-long oxidative pulses
54 were selected; B) SEM micrograph of as-prepared Cu NCs.
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60 3. Results and discussion

3.1. Characterization of as-prepared Cu NCs

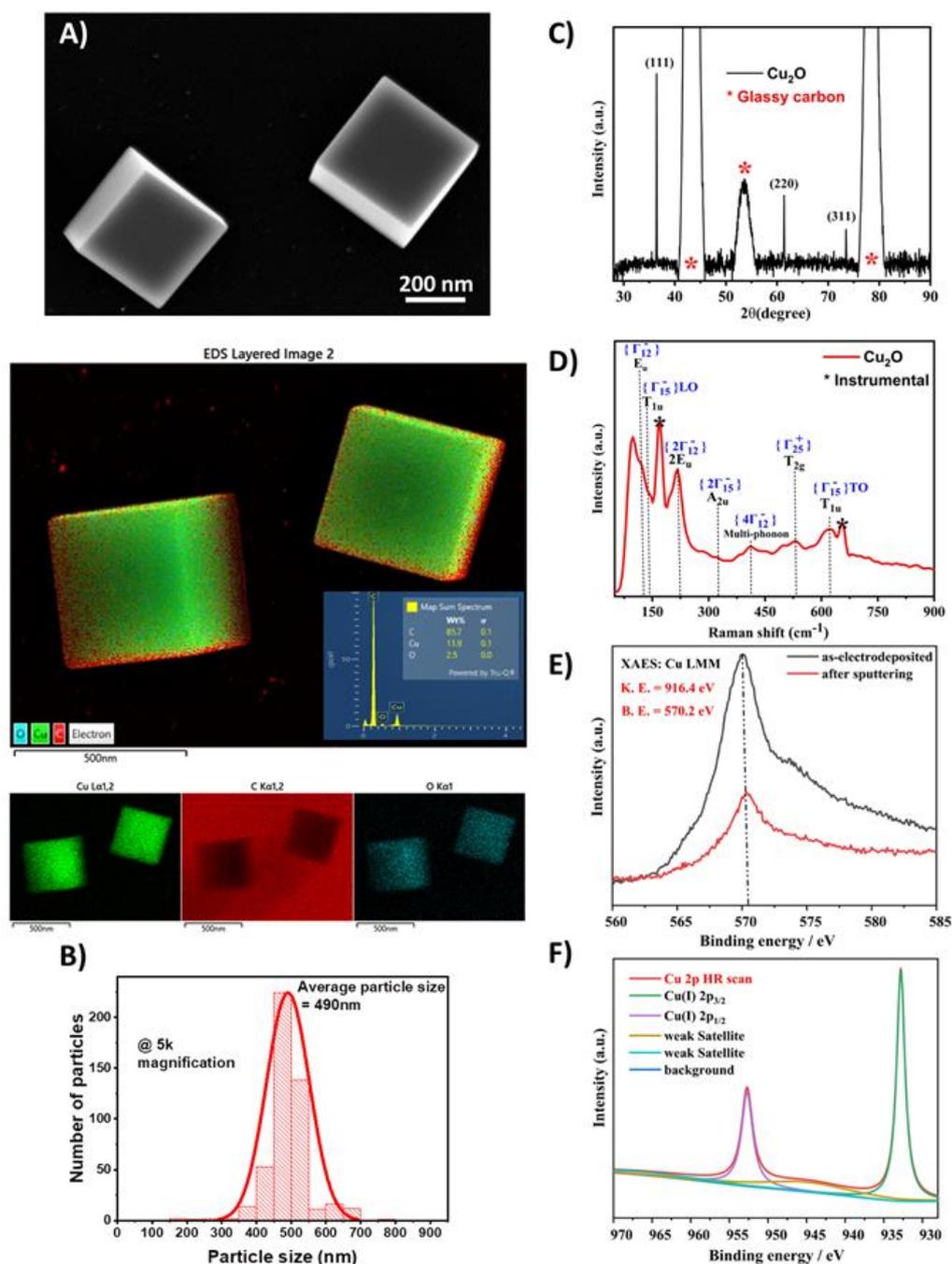


Figure 2. A) Scanning electron microscopy (SEM) images of as-prepared Cu-based NCs with corresponding mapping EDX image and inset of quantitative map spectrum; B) Particle size distribution of as-prepared Cu NCs extracted from the 5k magnification SEM image with peak for average particle size at 490nm (Image J software); C) X-ray diffraction (XRD) pattern with assigned Cu₂O diffraction peaks excluded from glassy carbon signal as support (marked *); D) Ex-situ Raman spectroscopy data of as-prepared Cu NCs with assigned vibrational modes (*-instrumental band); E) Cu LMM XAES spectra with the peak at 570.2 eV of argon sputtered as-prepared Cu NCs F) XPS spectra of an argon-sputtered as-prepared sample of Cu 2p region.

The morphology of self-supported, chloride-free as-prepared Cu₂O nanocubes on a glassy carbon substrate is characterized by high-resolution scanning electron microscopy (HR-SEM), and the corresponding well-defined cubic shapes are shown in Figure 2. A with the additional mapping images

1 of energy dispersive X-ray analysis (EDX) to confirm the elemental composition. The complete particle
2 size distribution analysis for the optimized electrochemical protocol (Figure 1) is shown in Figure S5
3 with tabulated average particle size and loading for three independent samples. Hereby, the
4 representative particle size distribution analysis is presented in Figure 2. B with the average particle
5 size at the value of (490 ± 80) nm. To have a comparable number of 400-500 particles each time (in a
6 given/certain area), the magnification of SEM images for the particle size distribution analysis was
7 5000. In further text, the particle size of Cu NCs will be denoted as “500nm”. X-ray diffraction (XRD)
8 was obtained to further confirm the composition of as-prepared Cu-based NCs. Figure 2. C shows the
9 XRD pattern of Cu NCs which corroborates that electrochemically-grown Cu nanocubes are composed
10 of pure Cu_2O without any metallic phase. The corresponding diffraction peaks for Cu_2O are assigned
11 as (111), (220), and (311) at diffraction angles of 36.6° , 61.3° , and 73.5° , respectively. Looking at the
12 reference of Cu and Cu_2O , the diffraction peak at 73.5° might be assigned either as Cu(220) or
13 $\text{Cu}_2\text{O}(311)$. Further, the absence of diffraction peaks for Cu(200) and Cu(311) at 50.4° and 89.9° ,
14 respectively infers that as-synthesized Cu NCs belong to the Cu_2O phase. Nevertheless, the intensity of
15 the diffraction peak at 61.3° , for the above-mentioned $\text{Cu}_2\text{O}(220)$, is 1.5-fold higher than that of the
16 peak at 73.5° , which is a good correlation with Cu_2O reference patterns.[37] The expected signal of
17 higher-order $\text{Cu}_2\text{O}(100)$ -rich surface at Cu-based NCs, namely $\text{Cu}_2\text{O}(200)$, overlapped with the signal
18 of glassy carbon at 42.6° . The Raman spectrum of as-prepared Cu NCs is shown in Figure 2. D. Starting
19 from the lowest Raman shift, a peak at 110 cm^{-1} and 141 cm^{-1} (longitudinal optical), assigned to the E_u
20 and T_{1u} symmetry, correspond to the rotations of Cu tetrahedra around their centers in the Cu_2O
21 lattice.[38] A Raman mode near 217 cm^{-1} known as the second-order mode of 110 cm^{-1} is also observed.
22 A small hump near 405 cm^{-1} can be associated with a fourth-order overtone of Cu_2O .[39] Moreover,
23 the peak at 529 cm^{-1} related to the only Raman-active mode of T_{2g} symmetry, consists of the out-of-
24 phase motion of the two oxygen sublattices to each other with the copper sublattice remaining fixed. In
25 addition, the peak at 620 cm^{-1} is IR-allowed transverse optical mode is also seen. Nonetheless, we did
26 not observe any characteristic bands of the cupric oxide (CuO) phase in the Raman spectrum nor any
27 diffraction peaks corresponding to CuO.
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33 Despite ascertaining the as-electrodeposited nanocubes with Cu_2O -phase from ex-situ XRD and
34 Raman measurements, further confirmation of the Cu_2O composition is provided by x-ray Auger
35 electron spectroscopy (XAES). Figure 2. E shows Cu LMM Auger electron spectra (XAES) acquired
36 from the argon-sputtered and as-prepared sample (Supplementary Note 2). The peak at 570.2 eV
37 binding energy corresponds to the Cu_2O phase in argon-sputtered and as-prepared samples, which is in
38 agreement with the x-ray photoelectron spectroscopic (XPS) measurements of the Cu 2p region where
39 Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are positioned at 932.84 and 952.7 eV, respectively. Since XPS is the surface-
40 sensitive technique, we found that the shake-up satellites in as-prepared Cu NCs (without ion-
41 sputtering) contain Cu^{2+} species on the surface. The satellite features at 933.5 and 943 eV correspond
42 to the Cu(II) which we ascribed to partial near-surface oxidation of the already confirmed Cu_2O bulk
43 structure (Figure S8). However, the absence of such features in argon-sputtered samples additionally
44 indicates that the rest of the nanocubes (towards bulk) are pure Cu_2O -phase (Figure 2 F). Further, the
45 modified Auger parameter (MAP) for as-electrodeposited and argon-sputtered copper nanocubes is
46 found to be $1849.2 (\pm 0.1)$ eV. It is evident from this MAP value that the chemical state of copper in
47 the as-electrodeposited copper nanocubes is Cu(I) which is corresponding to the pure Cu_2O phase. To
48 sum up, even though the electrodeposition method from the Cu^{2+} -rich electrolyte intuitively should
49 produce metallic copper state Cu NCs ($\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^0$), the pulse-electrodeposition protocol consisted
50 of, time-wise, mostly oxidative generation pulses (red pulse at Figure 1) at open-circuit potential (OCP),
51 had two implications. The first one is that the final composition of bulk Cu- based NCs is Cu_2O and
52 secondly, an oxidative period also served as the regime for the dissolution of non-cubic shapes.[36]
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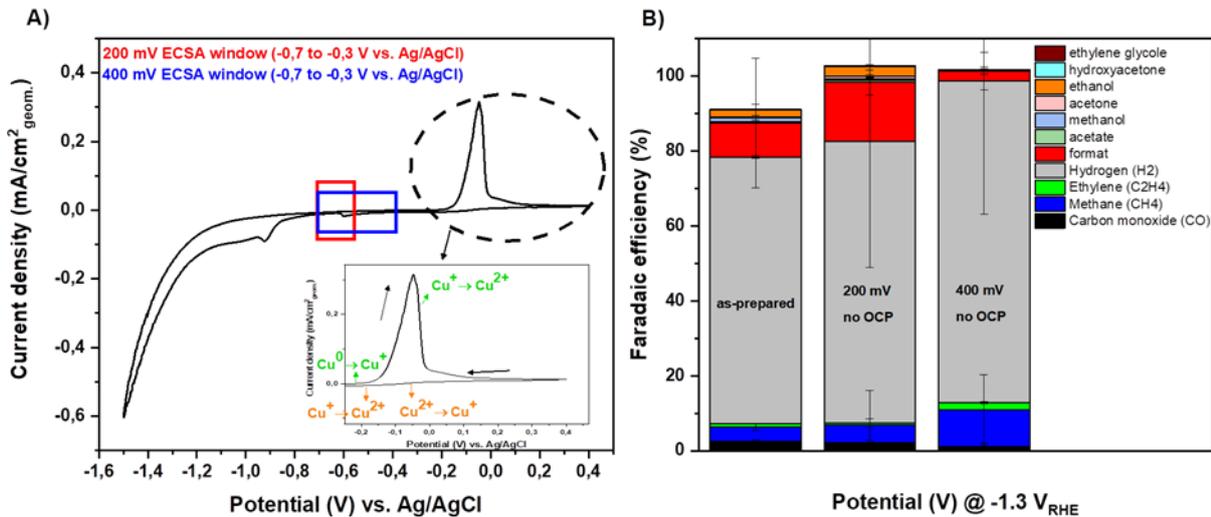


Figure 3. A) Cyclic voltammogram of the as-prepared Cu NCs with labeled potential windows used for ECSA from -1.5 to 0.4 V vs. Ag/AgCl with 5 mV/s scan rate. Change of oxidation states of copper during CV is assigned according to the in-situ analysis of Timoshenko *et al.*[40]; B) Faradaic efficiency for the inactivity of the Cu NCs is based on the “pre-treatment” viz, as-prepared, Cu NCs- NOOCP200 and Cu NCs- NOOCP400 samples at -1.3 V vs. RHE for 1h of electrolysis (no subsequent return to OCP between EDLC-ECSA determination method and CA measurements).

3.2. Electrocatalytic CO₂RR activity

The electrocatalytic measurements of electrochemically-grown Cu-based NCs were performed in a custom-made sandwich-type cell (Supplementary note 3). The as-prepared Cu-based NCs were tested in CO₂-saturated 0.1M KHCO₃ (pH=6.8) at various potentials (-1.1 to -1.4 V_{RHE}) with appropriate gaseous and liquid product detection/quantifications (Supplementary note 5). The electrocatalytic activity of Cu-based NCs under different electrochemical protocols is examined at various potentials. However, the estimation of the electrochemical surface area (ECSA) for the as-prepared Cu-based NCs remains elusive, even though ECSA assessment can be done through SEM statistical approach (Figure S5), further catalyst's intrinsic activity evaluation is practically inaccessible. We chose and stress the importance of the often assumed »non-invasive« double-layer capacitance method for ECSA determination and correlate its influence on the CO₂RR activity/selectivity with(out) subsequent return to open-circuit potential (OCP) between EDLC-ECSA and chronoamperometric (CA) measurements. Figure 3. A shows the cyclic voltammogram of as-assembled and as-prepared Cu-based NCs with corresponding oxidation and reduction peaks. Accordingly, we chose two potential windows for ECSA determination inside the double-layer capacitance region where no Faradaic processes are present. The two potential windows for ECSA determination used in the study are 200 mV (-0.7 to -0.5 V vs. Ag/AgCl) and 400 mV (-0.7 to -0.3 V vs. Ag/AgCl) as depicted in the graph Figure 3. A. It is noteworthy, that for each independent electrolysis measurement the EDLC-ECSA determination method was repeated twice before electrolysis (CA) measurement at 5 different scan rates (20, 50, 100, 200, and 300 mV/s). Therefore, in the further text, we denote the Cu-based NCs samples as »Cu NCs-NOOCP200« and »Cu NCs-NOOCP400« when there is no return to OCP in-between double-layer cycling (ECSA determination method) and chronoamperometry measurements. Figure 3. B) represents the CO₂RR Faradaic efficiency of three different »pre-treated« Cu-based NCs samples at -1.3V vs. RHE. Adequately, throughout the optimization of the electrodeposition method, we achieved a uniformity of loading to have the same ECSA each time (Figure S5) so the as-prepared Cu-based NCs were imposed directly to the reductive potential without further measuring ECSA. Surprisingly, as-prepared Cu-based NCs showed almost no activity towards CO₂RR with negligible production of CH₄, formate, and ethanol (first stacked column Figure 3. B).

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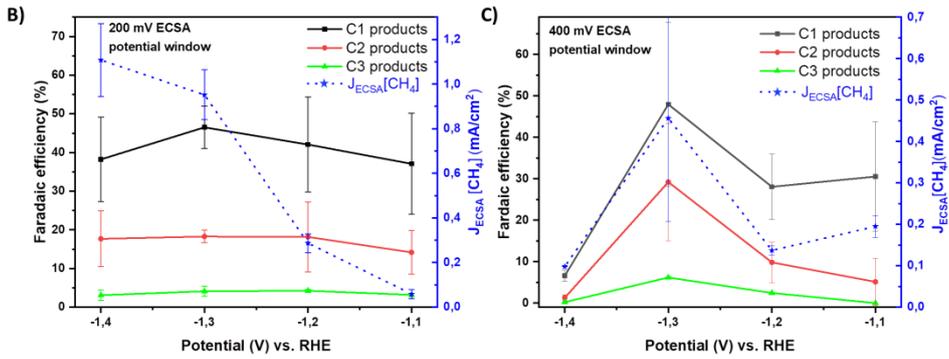
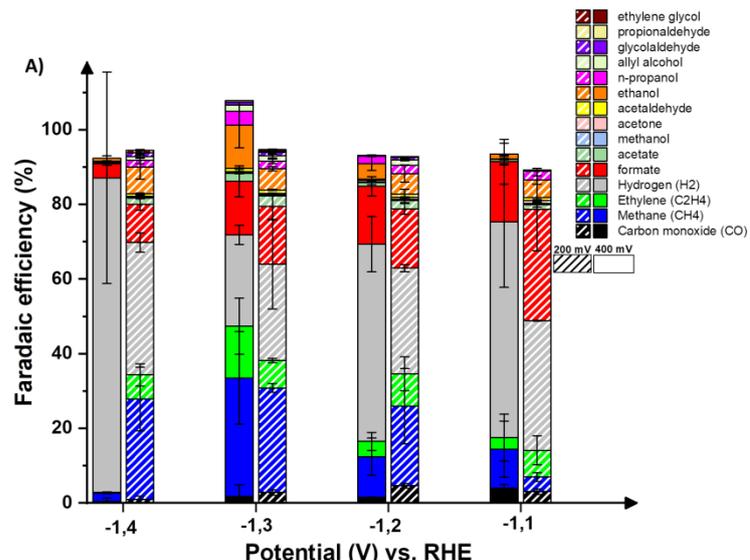


Figure 4. A) Potential-dependent Faradaic efficiency plots for Cu NCs-OCP200 (striped columns) and Cu NCs-OCP400 samples. FEs of C₁, C₂, and C₃ products at various potentials for B) Cu NCs-OCP200 and; C) Cu NCs-OCP400 samples.

Hydrogen, as an ever-present undesirable product in the CO₂RR, was the main product impacting 83% of total Faradaic efficiency. Given the high susceptibility to Cu NCs reconstruction under CO₂RR-relevant conditions[12,14,16], this was an indication that the initial (as-prepared) size, shape, and composition of the catalyst do not govern the final selectivity. The absence of significant change upon exposure only to the 0.1M KHCO₃ electrolyte, except for slight shrinking due to the reduction and dissolution, allowed us to refer to the performance of as-prepared Cu-based cubes (Figure S17 A). The facets' roughening and loss of the edge sharpness with substantial small redeposited nanoparticles ~5-10 nm after electrolysis also confirm previous findings by Reske *et al.*[41] where hydrogen evolution reaction (HER) is dominant on Cu nanoparticles with dimensions below 5nm (Figure S16. A). To further confirm the non-selectivity of as-prepared Cu NCs, we did the long-term electrolysis at -1.3 V vs. RHE for 10h. Even though, in the first 30 min of electrolysis Cu NCs showed some selectivity toward methane and ethylene at around 10% of faradaic efficiency (FE), after 1.5h of CO₂RR reaction time the FE dropped below 5% and remained throughout the whole reaction time of 10h. The HER dominates, as also shown for the 1h reaction, with a slight increase with time (Figure S16. B).

Therefore, we employed the double-layer capacitance method with two potential windows of 200 and 400 mV, with no breakup between EDLC-ECSA and CA measurements. The idea is to prevent the Cu surface from undergoing oxidation at OCP. This induces besides the addition of more oxygen in the Cu

1 NCs also its subsequent dissolution[42], where dissolved Cu ions can serve afterward for additional
2 reconstruction through redeposition at an applied negative bias. Unlike the as-prepared Cu NCs exposed
3 only to the electrolyte, we observed slight changes in the Cu nanocubes' morphology after only exposing
4 them to the ECSA determination protocol (Figure S17 B, C). In both cases, the analysis of ex-situ SEM
5 images reveals loss of facets' sharpness, roughness increment, and redeposition of small nanoparticles
6 (NPs), where the process is shifted toward more positive potential (accounting for the end scan in the
7 ECSA determination method of -0.7V vs. Ag/AgCl) than the potential reported by Grosse *et al.*[12]
8 where re-deposited Cu NPs form right below -0.3 V_{RHE}. Nevertheless, even though the Cu NCs
9 exhibited slight morphological changes due to the EDLC-ECSA treatment the selectivity remained
10 similar to as-prepared Cu NCs. The marginal increase in CH₄ formation of Cu NCs-NOOCP200 and
11 NOOCP400 samples reaching up to FE of 9% to the latter one was overshadowed by a dominant HER
12 that exceeded 80% at -1.3V vs. RHE. Furthermore, we studied the Cu NCs at various potentials with
13 200 and 400 mV ECSA window range, whereas in the electrochemical protocol between EDLC-ECSA
14 and CA measurements, Cu NCs were allowed to return to OCP. The fact that Cu NCs are further
15 exposed to OCP at around +0.5V_{RHE}, leaves room for secondary dissolution after the first one when the
16 electrolyte was introduced.[26] Figure 4. A shows the FEs of Cu-based NCs with a different employed
17 ECSA window range apriori electrolysis from -1.1 to -1.4 V vs. RHE. Accordingly, to a previous
18 notation, hereby, the samples are denoted as “Cu NCs-OCP200” and “Cu NCs-OCP400”. At -1.1 V vs.
19 RHE, both samples show activity for multiple products, where formate stands out as the predominant
20 product with a top-high for all the studied potentials. A distinctive characteristic of C₁ products is the
21 exchange in production of the formate and CH₄ by increasing overpotential, where at the lowest
22 overpotential formate is dominant. Interestingly, this is the onset potential for methane (CH₄), with a
23 considerable for Cu NCs-OCP400 of 10,5%. Even though both samples do not follow the same trend
24 in CH₄ production by increasing reductive potential, they reach the best performance at -1.3V vs. RHE
25 with FE_{CH₄} of 28.0% and 31.7% for Cu NCs-OCP200 and Cu NCs-OCP400, respectively. Expectedly,
26 the HER dominates for both samples at the highest overpotential of -1.4 V vs. RHE. Moreover, Figure
27 4. B and C represent the C₁, C₂, and C₃ products trend, and ECSA-normalized partial current densities
28 for CH₄ for Cu NCs-OCP400 and Cu NCs-OCP200, respectively. Cu NCs-OCP200 sample tracks a
29 mild volcano-shaped trend, with the highest selectivity towards CO₂RR products at -1.3V vs. RHE,
30 whereas the prevalence of C₁ products leads to FE of 46.5%. However, the partial current for CH₄ does
31 not follow the same trend, and it is increasing by increasing overpotential, reaching the highest observed
32 current density for all samples of 1.108 mA/cm² at -1.4V vs. RHE. Worthnotly, Cu NCs-OCP200 shows
33 to exchange C₁ products selectivity between peak potential at -1.3V and -1.1V, where at the latter one
34 selectivity is foremost shifted towards the formate production. Cu NCs-OCP400 follows a similar trend,
35 with a more prominent peak for all the products at -1.3 V vs. RHE. C₁ products ruled the selectivity at
36 a peak potential reaching 49.0% with predominant methane production of FE_{CH₄}=31.7%. In contrast to
37 the 200 mV window width case, the Cu NCs-OCP400 sample follows an analogous trend for a partial
38 current density of CH₄ as for C₁, C₂, and C₃ product distribution, with a twice reduced current density
39 of 0.456 mA/cm² in comparison with Cu NCs-OCP200.

47 **3.3. Morphological evolution under CO₂RR**

48 The decent selectivity toward methane for both Cu NCs-OCP200 and Cu NCs-OCP400 samples at a
49 peak potential of -1.3V vs. RHE, we further correlate with the ex-situ SEM before and after images.
50 Figure 5. reveals different morphological motifs after 1h of electrolysis at the peak-selectivity potential
51 of -1.3V vs RHE depending upon ECSA potential window with(out) exposure to the OCP in-between
52 electrolysis step. Figures 5. A and B show the morphological evolution of the Cu NCs when the surfaces
53 have not been exposed to the OCP after the ECSA determination step with 400 and
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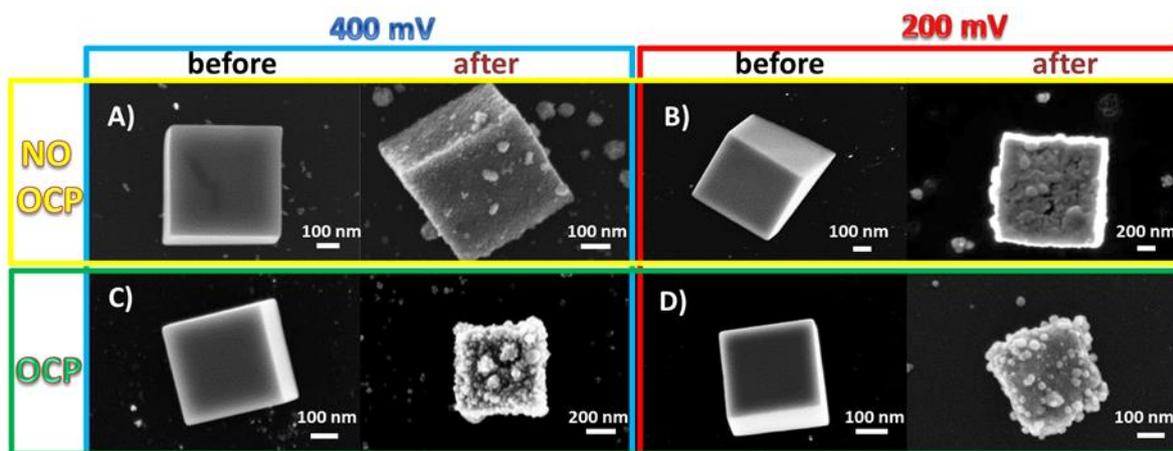


Figure 5. Different morphological evolution of Cu NCs with(out) exposure to OCP in-between ECSA and electrolysis based on ECSA potential window. All SEM after images were done after 1h electrolysis at $-1,3 V_{RHE}$. A) Cu NCs - NOOCP400 sample; B) Cu NCs – NOOCP200 sample; C) Cu NCs - OCP400 sample; D) Cu NCs – OCP200 sample.

200 mV potential windows, respectively. Pronounced roughness and moderate redeposition of NPs endorse structure-performance relationship as in the case for as-prepared Cu-based NCs. We posit that in both cases, the preservation of the abrupt morphological transformation and depletion of the near-surface oxygen leads to the Cu-rich surface formation that predominantly produces H_2 . [43,44] However when the Cu-based NCs were exposed to the OCP in-between EDLC-ECSA measurements (Supplementary note 4) and static CO_2RR electrolysis further roughening and irreversible morphological transformation is noticeable. Figure 5. C and D display the morphological evolution of Cu NCs-OCP400 and Cu NCs-OCP200 samples, respectively. Considering that additional dissolution of Cu occurred by exposing the already distressed cubes to the OCP (Figure S17 B, C), the Cu ions served for intense reconstruction through the dissolution/redeposition process similar to the Ostwald ripening after applying negative bias. [22,24] The redeposited fragments in the range of 20-40 nm form highly granular morphology and increased the surface roughness for CuNCs-OCP400 samples. The redeposition can be observed also in the vicinity of the cubic particles. Hence, the evolved surface displays a more than threefold enhancement of CH_4 formation ($FE_{CH_4}=31\%$) compared to the Cu NCs-NOOCP400 sample. Likewise, Cu NCs-OCP200 has a similar morphological transformation with slightly alleviated redeposited fragments, but it is still highly granular, exhibiting again threefold enhancement with doubled partial current density relative to the Cu NCs-OCP400 sample.

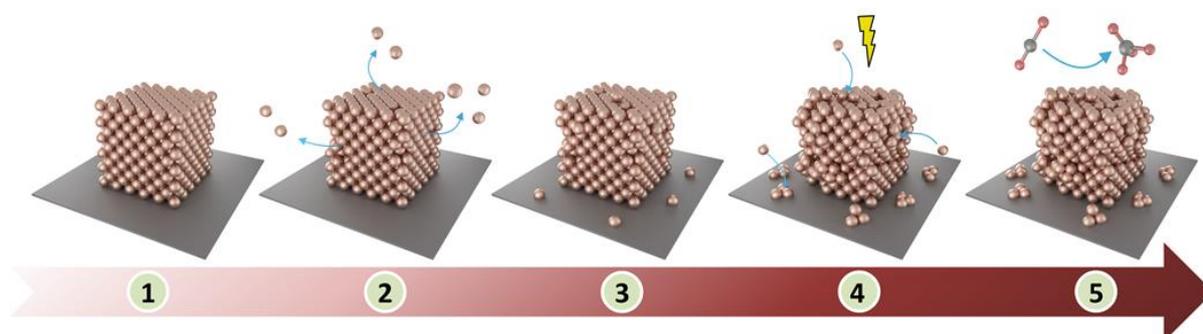


Figure 6. The schematic representation of the morphological and structural evolution of the Cu NCs during CO_2RR . Step 1. as-prepared Cu NCs; Step 2. introduction of electrolyte dissolution of Cu_{24,42}; Step 3. favorable reconstruction during double-layer cycling (ECSA determination); Step 4. negative applied bias: i) redeposition due to exposure to OCP after ECSA, ii) reduction of near-surface oxide, iii) CO_2RR ; Step 5. dynamically evolved surface – decent production of methane.

1 Our results are in alignment with the recent literature on Cu NCs, where Grosse *et al.*[9] emphasized
2 the influence of support for favorable production of CH₄ on the Cu cubes on carbon support. Most
3 recently, Timoshenko *et al.*[40] reported that enhancement in CH₄ production is attributed to the
4 irreversible increase in surface roughness and granular morphology. Since Cu⁰-dominated catalyst
5 surfaces favoring the CH₄ have been demonstrated[27,45,46], we propose that the bulk Cu₂O core
6 surrounded by a granular island/fragments of Cu⁰ in the near-surface are the main active sites, that have
7 been proposed to form in a few seconds after cathodic potential.[40] Considering all the above
8 discussion, we posit the morphological and structural evolution of the electrochemically-grown Cu-
9 based NCs on glassy carbon support for favorable CO₂ electroreduction to CH₄ through schematic
10 representation as shown in Figure 6. As-synthesized Cu₂O nanocubes endure transformation
11 immediately after the introduction of 0.1M KHCO₃ electrolyte (step 2), which is dissolution[24,42].
12 The EDLC-ECSA seems to have a positive influence on the lattice rearrangement (step 3), but favorable
13 reconstruction occurs after exposing the Cu surface once again to OCP (additional dissolution). Hence,
14 by applying a negative bias of -1.3 V vs. RHE when additional redeposition occurs, making Cu
15 nanocube's surface highly granular with increased roughness (step 4). As a result of the highly granular
16 morphology created during redeposition, combined with a higher surface roughness in Cu⁰/Cu₂O
17 composition, CH₄ is favorably produced (step 5). To sum up, the chloride-free ~500 nm Cu nanocubes
18 are synthesized by a simple pulse-alternating electrodeposition method from a 0.01M CuSO₄ bath. We
19 show that the determination method (double-layer cycling) of one of the critical parameters for reporting
20 a catalyst's intrinsic activity, namely electrochemical surface area (ECSA), plays an important role as
21 the initiator for the enhancement of catalytic reactivity of Cu-based NCs.
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27 4. Conclusions

28
29 In this study, we successfully synthesized and characterized the electrochemically grown chloride-
30 free Cu NCs on a glassy carbon substrate. Under the appropriate electrochemical protocol, which
31 consists of electrochemical double-layer cycling and subsequent exposure to the OCP before
32 electrolysis, the activity can be increased threefold for CO₂ to CH₄ conversion. The maximum Faradaic
33 efficiency of 31.7% of CH₄ is achieved due to the formation of highly granular morphology with
34 increased surface roughness with most probably Cu⁰/Cu₂O composition, which is in agreement with the
35 current in-situ studies.[40] To further elaborate on the preferential selectivity toward methane on Cl-
36 free Cu NCs, we noticed the positive effect of chloride anions on the CO chemisorption (stabilization)
37 on the copper surface according to the DFT calculations (see Supplementary note 7), which was
38 previously proposed for the formation of C₃-C₄ products in the study of Seunghwa *et al.*[47] As well as
39 in our previous studies[16,22], we stress a practical note of Cu NCs catalyst favorable reconstruction
40 under mentioned conditions, which can mimic the operation of CO₂RR electrolyzer under the start/stop
41 conditions.
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46 Credit authorship contribution statement

47
48 S.P. had a major contribution. M.A.N. had the second most contribution, with involvement in the
49 nanocubes characterization, electrocatalytic measurements, DFT calculations as well as writing
50 supervision. P.Š. established an NMR protocol for liquid product detection. L.S. contributed to the
51 design and construction of the sandwich-type electrochemical cell. K.M.K, B.L., L.P., A.K.S., and M.B.
52 contributed equally. N.H. conceived and supervised the project. All authors have approved the final
53 version of the manuscript.
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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data available on request from the interested.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at xxxxxx

Includes, the synthesis of Cu₂O nanocubes (Cu NCs) –floating method; Influence of the stirring rate of electrolyte; Chloride effect on the synthesis of Cu NCs; Tuning electrochemical protocol to control the size of Cu NCs; XPS measurements of as-prepared Cu NCs; XRD measurements of as-prepared Cu NCs; Raman measurements of as-prepared Cu NCs; The electrochemical custom-made cell configuration; Electrochemical surface area determination: Electrocatalytic measurements and products detection; Electrocatalytic performance of as-prepared Cu NCs; Morphological evolution of Cu NCs; Effect of specifically adsorbed chloride anions.

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Highlights:

- Electrodeposition of chloride-free Cu NCs
- Activation of Cu NCs by appropriate electrochemical protocol
- Support effect towards the selective formation of methane on Cu NCs
- Influence of electrochemical double layer cycling and OCP in tuning the activity and selectivity of Cu NCs

Graphical abstract:

