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Size Dependent Catalytic Activity of Reusable Subnanometer Copper(0) Clusters

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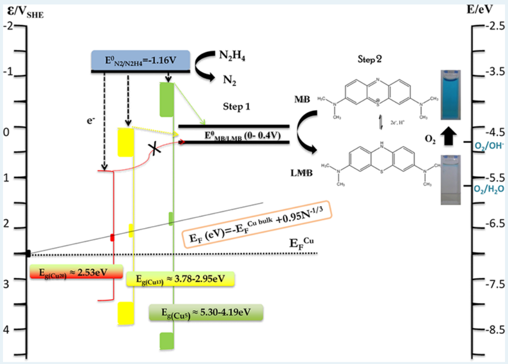
S *Supporting Information*

ABSTRACT: The catalytic reduction of methylene blue (MB) to leucomethylene blue (LMB) by hydrazine in the presence of size-selected copper clusters (CuCLs, Cu_N, N = number of atoms, $2 \leq N \leq 20$) is demonstrated here. Only copper clusters smaller than ≈10−13 atoms enhance the rate of the reduction of MB. Cluster-mediated electron transfer through the cluster's lowest unoccupied molecular orbital (LUMO) frontier orbital is proposed as the main step for the catalysis. Catalyst recycling and stability were also studied demonstrating that they can be used as effective, stable, and reusable catalysts, which could be also employed in different types of redox reactions with important technological applications.



KEYWORDS: *clusters, copper, catalyst*

The main goal in catalysis is to find highly selective catalysts for particular reactions. In this sense, catalysis by noble metal nanoparticles and clusters is now becoming very important because of the high selectivity displayed by these materials.[1] The great catalytic activity of metal clusters is considered to be due to their intrinsic electronic properties, which are characterized by the appearance of a bandgap at the Fermi level. It has been shown that the bandgap mainly depends on the number of atoms of the cluster.[2]Over the past few years, size-dependent catalytic activity of clusters has been studied for different kind of reactions. For example, recent works for selective oxidation and hydrogenation processes have been explored by Zhu et al.[3] and Liu et al.,[4] using well-defined $Au_n(SR)_m$ clusters as model catalyst; and a strong size dependence has also been reported[5] for this catalyst against the selective oxidation of stryrene. Ag clusters supported on alumina also show a size-dependent catalytic activity on the chemoselective reduction of nitrostyrene,[6] and selected supported silver clusters enhance the reduction of several nitro compounds.[7] Although it is well-known that Cu(I) or Cu(II) complexes are good catalyst for different types of reactions,[8−10] the catalytic properties of Cu(0) clusters (CuCLs) have not received much attention up to now, mainly because of the lack of synthesis procedures. Catalytic activities of supported CuCLs have been reported for the cyclotrimerization reaction[11] showing high selectivity; for the Suzuki cross-coupling reaction of various aryl halides with phenylboronic acid;[12] for the cycloaddition of azides with terminal alkynes;[13] and very recently[14] for the electroreduction of oxygen.

The catalytic properties of Cu(0) clusters (CuCLs) are very important not only because the cluster bandgap may play an important role in the catalytic properties but also because the Fermi level of Cu, which determines the position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies (valence, VB, and conduction bands, CV, respectively in normal semiconductors), is very different from Au or Ag. Therefore, different catalytic behaviors can be expected. Here, we report the size-dependent catalytic properties of unsupported Cu(0) CLs for the reduction reaction of methylene blue (MB) by hydrazine (N_2H_4). The reaction forms the colorless leucomethylene blue (LMB), which can be transformed again to blue MB just by allowing the oxygen to enter into the reaction media. This reaction has been used before to evaluate the catalytic activities of various nanocatalysts, including Ag,[15] Au,[16,17] Pd,[18] Pt,[19] and Cu-based nanoparticles.[20−22] In our case, this clock reaction has been chosen because of its reversible color change, which can be conveniently used for the study of the recycling properties of the cluster catalysts. It was found that the cluster activity depends on the cluster size and that the activity remains for, at least, 42 reaction cycles.

CuCLs of three different sizes were synthesized by some modifications of an electrochemical method reported before.[23]

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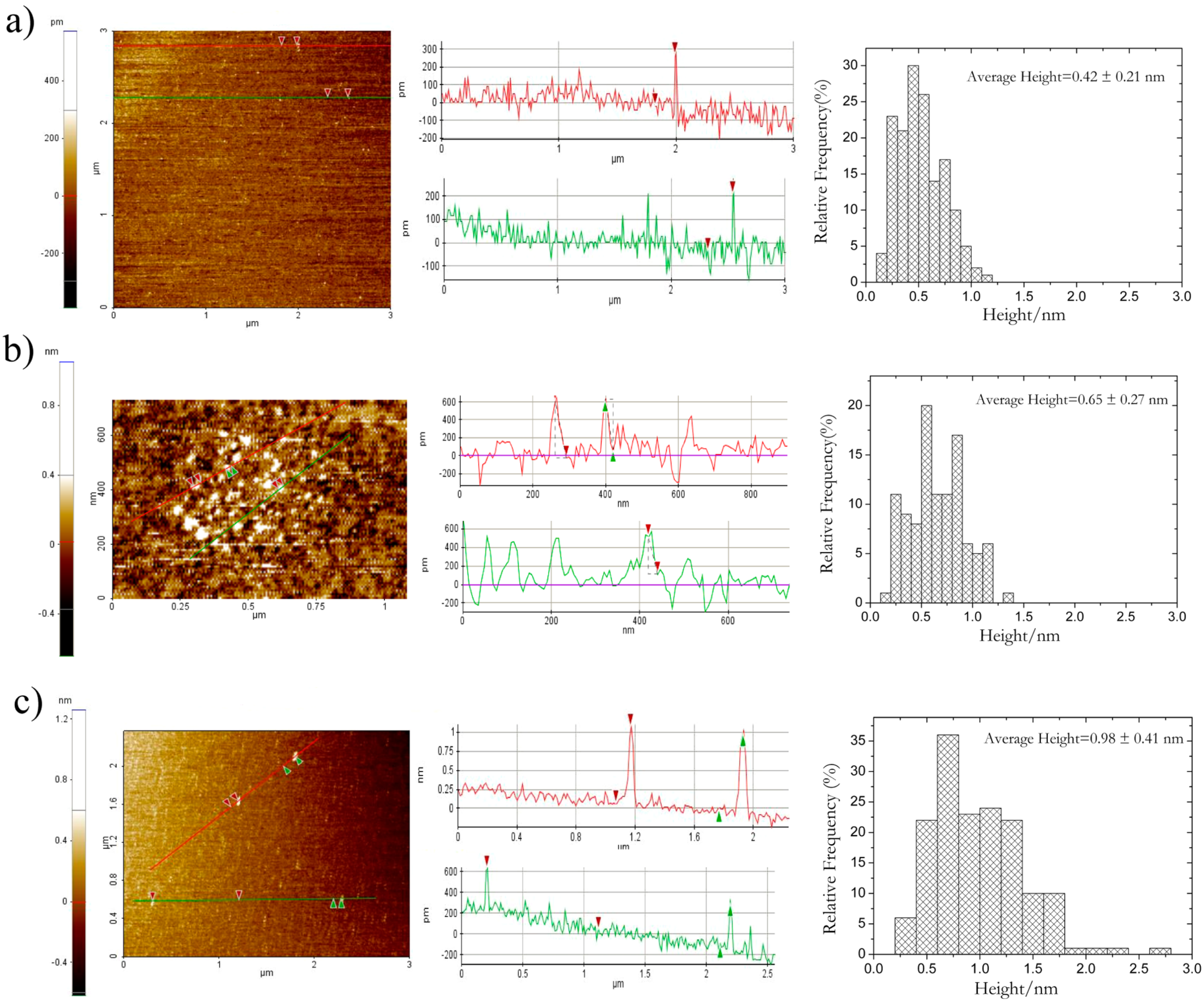


Figure 1. NC-AFM topography images of CuCLs deposited on mica substrates (rms ≈ 150 pm): (a) Cu_5, (b)Cu_{13}, and (c) Cu_{20} (left). Section analysis of the solid lines of AFM images (middle) and their corresponding histogram distributions heights (right).

Medium size clusters, named as Cu_{13} (N = number of atoms = 7−13), were previously synthesized and characterized using LDI-mass spectrometry and the Jellium model, which seems to be a good approximation for metal clusters.[24,25] Using different purification and heat treatments we were able to prepare also smaller (Cu_5) and larger clusters (Cu_{20}) (see Supporting Information, Experimental Section and Scheme S1).

Figure 1 displays noncontact atomic force microscope (NC-AFM) images of the different types of CuCLs deposited on mica substrates (with a rms ≈ 150 pm). The calculated average sizes were Cu_5 (0.42 ± 0.21 nm), Cu_{13} (0.60 ± 0.27 nm), and Cu_{20} (0.98 ± 0.41 nm). It has to be noticed that the calculated size for the Cu_{13} cluster agrees with the size estimated for a closed-shell cuboctahedral or icosahedral structure.[26]

Figure 2A shows the optical absorption spectra of the different Cu clusters. Unlike the UV−vis spectra of Cu nanoparticles, which displays a surface plasmon resonance around 560 nm, all CuCLs used here do not display the plasmon band indicating that they do not have any conduction electrons. Instead, they show different absorption bands located at 275 nm (Cu_5), 297 nm (Cu_{13}), and 430 nm and 280 nm (Cu_{20}). In contrast to nanoparticles, clusters exhibit a semiconductor or molecule-like behavior with new properties including photoluminescence, as it was previously shown for the Cu_{13} clusters.[23] The photoluminescence (PL) of the three samples can be seen in Figure 2B. Clusters display emissions at increasing wavelengths ($\lambda_{emCu5} < \lambda_{emCu13} < \lambda_{emCu20}$) showing that the cluster size increases in the order $Cu_5 < Cu_{13} < Cu_{20}$ because of the quantum confinement.[2,27]The optical band gap, E_g, can be also calculated by the Tauc's approach used for semiconductors (Supporting Information, Figure S1):[28] $(\alpha h\nu) = A(h\nu - E_g)^n$, where $h\nu$ is the photon energy (h is Plank constant and ν is the frequency of the radiation), α is the absorption coefficient, A is a constant, and n = 1/2 because clusters usually display a direct transition behavior.[23] The E_g values obtained from the Tauc's fittings are 5.30−4.19 eV for Cu_5, 3.78 eV for Cu_{13}, and 2.53 eV for Cu_{20}. From these values, and applying the Jellium approximation, $E_g = AN^{-1/3}$, where $A = E_F$ (7 eV) = Fermi energy of the bulk material[29] and N is the number of atoms per cluster, the average cluster size population of the different Cu_N samples are $N \approx 2-5$ for Cu_5, $N \approx 7-13$ for Cu_{13}, and $N \approx 20$ for Cu_{20}.

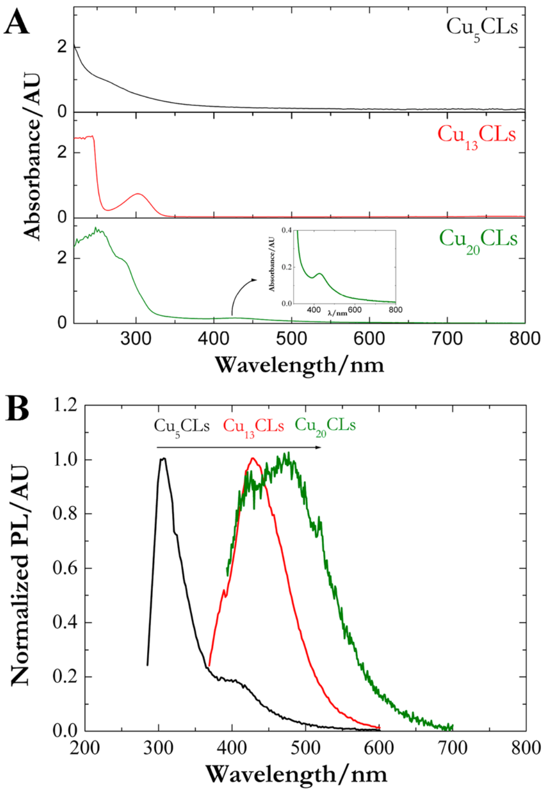


Figure 2. (A) Absorption spectra of the CuCLs: Cu_5, Cu_{13}, and Cu_{20}. (B) Emission spectra of the different CuCLs excited at 275 nm (Cu_5), 330 nm (Cu_{13}), and 380 nm (Cu_{20}) showing an increase of the emission wavelength with the cluster size.[2].

X-ray photoelectron spectroscopy (XPS) measurements (see Supporting Information, Figure S2) were carried out to investigate the oxidation state of Cu in CuCLs. The obtained $Cu2p_{3/2}$ binding energies (BE) values were 933.37, 933.51, and 932.89 eV for Cu_5, Cu_{13}, and Cu_{20}, respectively.

The lack of the characteristic shakeup satellite peaks around ≈945 eV for Cu(II) ions suggests that clusters are not oxidized. Identical bulk spin−orbit ($Cu2p_{3/2}$ and $Cu2p_{1/2}$ BE difference) has been found for the three CuCLs sizes. This result agrees with other studies[30] on mass selected CuCLs onto silicon. It has to be pointed out that the obtained BE values are slightly higher than that corresponding to Cu_{bulk} (932.2−932.5 eV), which can be explained by the BE increase in metal clusters with decreasing cluster size.[31,32]

As it was reported before for medium size clusters,[23] CuCLs (protected by tetrabutylammonium nitrate, used as supporting electrolyte for the electrochemical synthesis) are very stable showing the same emission spectra after more than one year stored at ambient temperature (see Supporting Information, Figure S3). The high stability of clusters is due to their large HOMO−LUMO bandgap, which, contrary to Cu nanoparticles or bulk Cu, makes them very stable against oxidation of reduction. This can be proved by the PL properties of CuCLs, which remain intact after each catalytic reaction cycle (see below), as it can be clearly seen in the Supporting Information, Figure S8.

The reduction of MB in water, using N_2H_4 as the reducing agent, in the presence of CuCLs was studied by UV−vis spectroscopy following the absorbance at the λ_{max} of MB (665 nm). Kinetic studies were first carried out using the Cu_{13} clusters. The experimental conditions are given in the Supporting Information, Table S1. Figure 3 shows the progress of the reaction in presence and absence of Cu_{13} clusters for the experiments R1 and R8 of Supporting Information, Table S1. In absence of Cu_{13} (Figure 3A-1) the absorbance intensity remains almost unaltered in agreement with the literature[16,17,20] but in presence of clusters (Figure 3A-2) a fast reduction of MB is observed, which indicates that the Cu_{13} clusters catalyze this reaction.The absorbance versus time (Figure 3A-3) for the catalytic reaction follows an exponential decrease: $\ln A = -k_{obs}t$, where A = Absorbance, t = time, and k_{obs}= observed reaction rate constant. Supporting Information, Figure S4 shows a good linear relationship of ln A versus t for all the performed experiments.

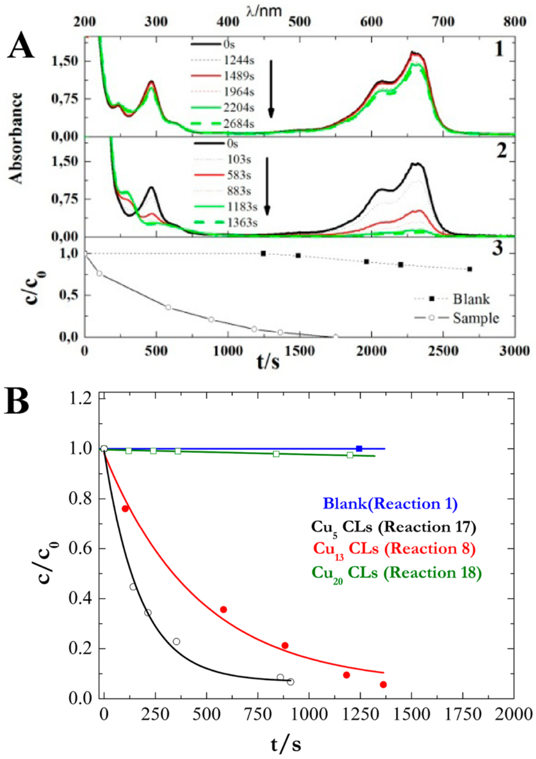


Figure 3. (A) (1) UV−vis spectra of the reduction of MB with N_2H_4 as a function of time in absence (1) (Supporting Information, Table S1-Reaction 1) and in presence (2) of Cu_{13} (Supporting Information, Table S1-Reaction 8). Comparison of the MB reduction for 1 and 2 (3). (B) Comparison of the rate of reduction of MB without and with different subnm Cu cluster catalysts.

Experiments were carried out at different concentrations of N_2H_4 and CuCLs (see Supporting Information, Table S1, Reactions 2−11). It is observed that k_{obs} increases linearly with both, catalyst and reducing agent (Supporting Information, Figures S4-A and B and Figure S5-A). Therefore, $k_{obs} = k^0 [N_2H_4] [Cu_{13}]$, with $\langle k^0 \rangle = (0.9 \pm 0.3) \times 10^3\ M^{-2}\ s^{-1}$. From these results the following mechanism for the catalytic reaction can be proposed:

$$MB + Cu_{13cluster} \leftrightarrow MB\text{-}Cu_{13ads},\ K \qquad (1)$$

$$MB\text{-}Cu_{13ads} + N_2H_4 \rightarrow LMB,\ k \qquad (2)$$

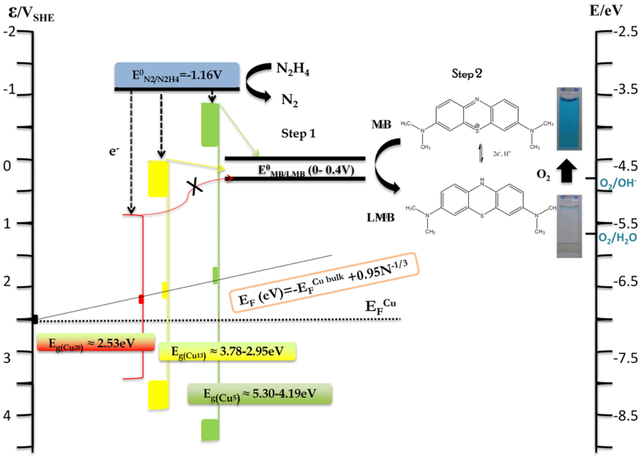
After the adsorption equilibrium between MB and Cu_{13} forming an intermediate MB-$Cu_{13\ ads}$, a posterior collision between this intermediate and the reduction agent, N_2H_4, allows two electrons to be transferred to the MB, mediated by the CuCLs, with a rate constant $k = k^0/K$. We also studied the influence of the pH on the redox reaction (see Supporting Information, Table S1- Reactions 12−16). As it can be seen in Supporting Information, Figure S7, when the pH is reduced the reaction becomes slower.

Finally, we studied the recycling properties of the catalysts. As it can be observed in Supporting Information, Figure S5-B, clusters retain their catalytic activity for, at least, 42 cycles. It is interesting to note that the catalytic activity even increases at the second and subsequent cycles with respect to the first round (see Supporting Information, Figure S6-A), which indicates that the assumed adsorption equilibrium between CuCLs and MB was not totally established when the first round was initiated. PL properties of clusters also remain constant after each reaction cycle (see Supporting Information, Figure S8).

Once we have shown that subnanometer Cu_{13} clusters are a promising and reusable catalyst for the MB reduction, we checked if the cluster size plays a role in the catalytic behavior. Small (Cu_5) and large CuCLs (Cu_{20}) were then used for the catalytic studies under the conditions summarized in the Supporting Information, Table S1. As it can be seen in Figure 3B and Supporting Information, Figure S6−B the smallest CuCLs (Cu_5) are even more efficient than the Cu_{13} clusters. However, the largest clusters (Cu_{20}) do not catalyze the reaction. These results show that the cluster's size is crucial for the catalytic activity.

The observed size-dependent catalysis with CuCLs can be explained taking into account that the previous mechanism of a cluster-mediated electron transfer from the donor (N_2H_4) to the acceptor (MB) has to proceed through the conduction band of the CuCLs, as it is schematically depicted in Scheme 1.

Scheme 1. Schematic Energy Diagram[35] Showing the Catalytic Activity of Different CuCLs (Cu_5, Cu_{13} and Cu_{20}) Used for the MB Reduction by N_2H_4[a]



[a] After finishing the catalytic reduction, MB can be recovered by shaking the sample in oxygen atmosphere, and a new catalytic reaction cycle can be carried out.

Redox potentials for N_2H_4 ($E^0_{N2H4/N2} = -1.16$ V) and MB ($E^0_{MB/LMB}$ in the range of 0 V, for pH = 7[33] to 0.4 V for basic pHs, see Experimental Section in Supporting Information) are also shown. The position of the HOMO/LUMO frontier orbitals for the three cluster catalysts depend not only on E_g, but also on the position of their Fermi levels. Previous density functional theory (DFT) studies[34] have shown that the chemical potential in Cu clusters changes with the size of the clusters, according to the following equation $\mu(\text{eV}) = -\Phi + CN^{-1/3}$, where is Φ the work function and C is a constant, which represents the different dependence of the ionization potential and the electron affinity on the cluster size. Therefore, the Fermi level of Cu clusters can be described by a similar expression: $E_F\ (\text{eV}) = -E_F\ (\text{Cu}_{\text{bulk}}) + CN^{-1/3}$. Theoretical calculated values of C for Cu clusters in vacuum are in the range 0.1 eV−1 eV.[34]

Although our clusters are in solution and protected with tetrabutylammonium nitrate, so that the change of the chemical potential with the cluster size could be different from the DFT calculations, one can clearly see that a value of C ∼1 eV nicely agrees with our experimental results.With this value of the constant C, the LUMOs of Cu_5 and Cu_{13} are located above the MB redox potential and below the hydrazine redox potential, allowing the clusters to be catalytically active, this activity being larger for the Cu_5 clusters because of their larger driving force. However, the largest Cu_{20} clusters would be inactive because their LUMO frontier orbitals are located below the MB redox potential. The observed increase of the catalytic activity of Cu_{13} CuCLs with the pH can be also interpreted on the basis of the proposed mechanism. As it was mentioned above, the redox potential of MB increases with the pH. Therefore, the driving force will increase when the pH also does, giving rise to an increase of the catalytic activity.

In conclusion, we have demonstrated the catalytic properties of novel photoluminescent CuCLs in the clock redox MB-LMB reaction. This catalytic behavior, which depends on the size of the clusters, is explained assuming an electron transfer stage mediated by the Cu cluster catalysts. Such electron transfer can only happen when the LUMO frontier orbitals of the clusters are located in the range between the redox potential of the reducing agent (hydrazine) and the MB, establishing a range of cluster sizes to be catalytic active in redox reactions. It was observed that previous DFT calculations give a good description for the expected change of the Fermi level with the cluster size. It is interesting to note that the proposed mechanism is similar to the one used in semiconductors, showing that metal clusters can be seen as a kind of *molecular semiconductors*, which could be conveniently tuned (in terms of number of atoms and materials) to catalyze specific redox reactions. It has also been observed that CuCLs show not only very significant catalytic effects, but also a high reusability efficiency, which could be used for other types of redox reactions, with important technological applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures; stability of CuCLs; XPS measurements, kinetic experimental conditions, constant rate determination, and recycling studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through equal contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

LDI-mass spectrometry, Laser Desorption Ionization mass spectrometry; CuCLs, Copper Clusters; XPS, X-ray Photoelectron Spectroscopy; NC-AFM, noncontact Atomic Force Microscope

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(35) One can note that the interpretation based in Scheme 1 can also explain the high electrocatalytic activity of CuCLs for the oxygen reduction reaction (ORR) recently reported by Wei et al.[14] One can see that only clusters with sizes ≈≥7 could catalyze the ORR because their LUMO is located below the redox potential for the ORR at basic pHs (0.4V).