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Metal ion mediated electrooxidation of organic molecules: from *in situ* UV-Vis spectroelectrochemical perspective

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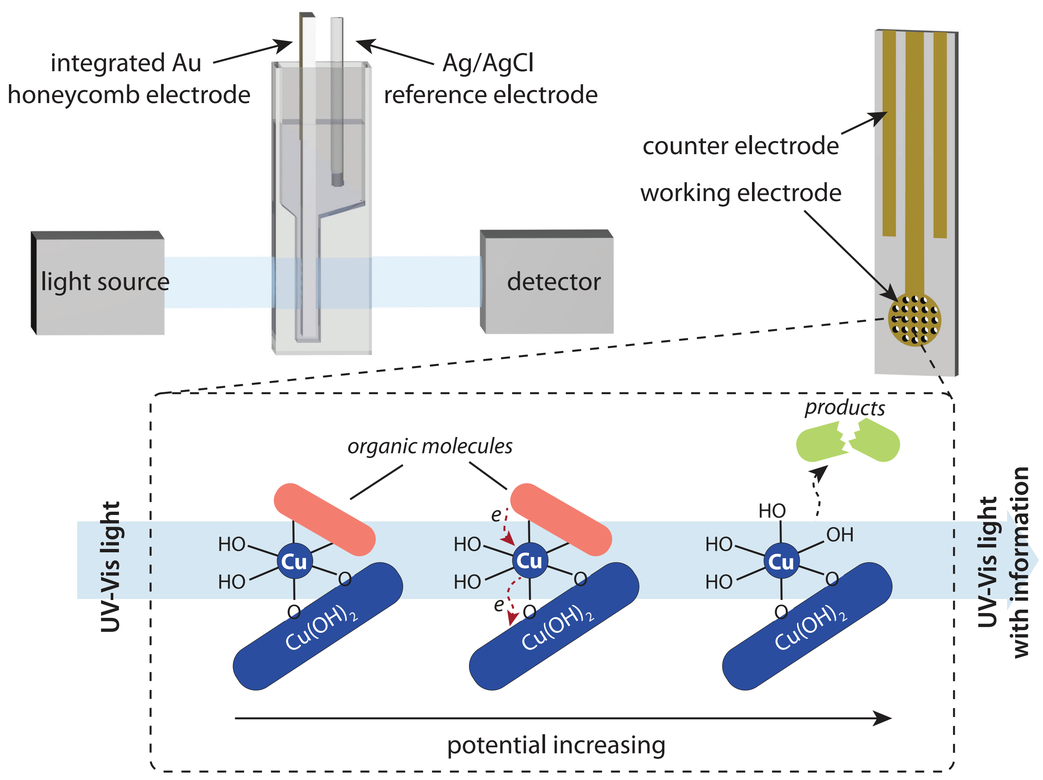
Introduction

- The electrooxidation process of small organic molecules, such as glucose and antibiotics, poses great importance in energy- and environment-related topics, yet hindered by high overpotential, involvement of noble metals, and strict requirement.
- To achieve high efficiency and low-cost of electrocatalyst, transition metal ions (for example, Cu(II)) are used in our work for both glucose and antibiotics electrooxidation, demonstrating high atomic efficiency and catalytic activity.
- Using *in situ* UV-Vis spectroelectrochemical methods, the mechanism of the metal ion mediated electrooxidation is proposed, indicating that the formed $Cu(OH)_y^{x-}$ species act as the active site *via* the formation of Cu(II)-organic molecule intermediate, which can be regenerated upon the formation and dissociation of Cu(III)-organic molecule complex.

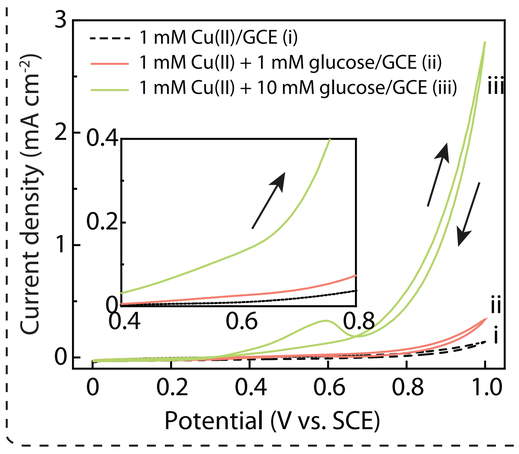
Experimental Setup



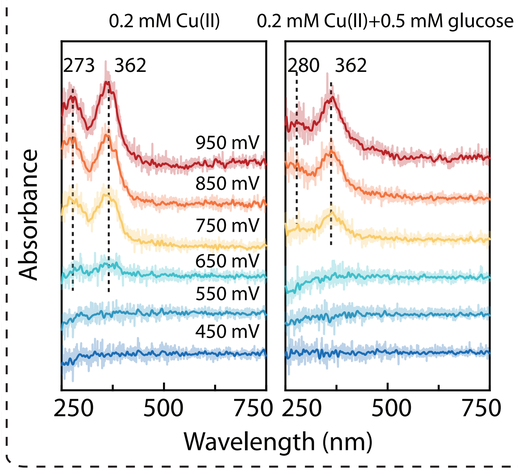
In situ UV-Vis spectroelectrochemical experiment setup (up left), integrated electrode (up right) and the simplified mechanism of Cu(II) mediated electrooxidation of organic molecules (bottom).

Glucose Electrooxidation

cyclic voltammetry in 0.1 M NaOH



***In situ* UV-Vis spectra in 0.1 M NaOH**



The 273 and 360 nm peaks indicates CuO production as a result of CuOOH formation. After adding glucose, no CuO is produced at 650 mV.

In alkaline solution with only Cu(II):

$Cu^{2+} + 3OH^- \rightarrow Cu(OH)_3^- \rightarrow CuOOH + H_2O + e^-$

with Cu(II) and glucose:

Cu^{2+} + glucose → Cu(II)-glucose complex → Cu(III)-glucose complex + e^-

Cu(III)-glucose complex → Cu(II)-gluconolactone → Cu(II) + gluconic acid

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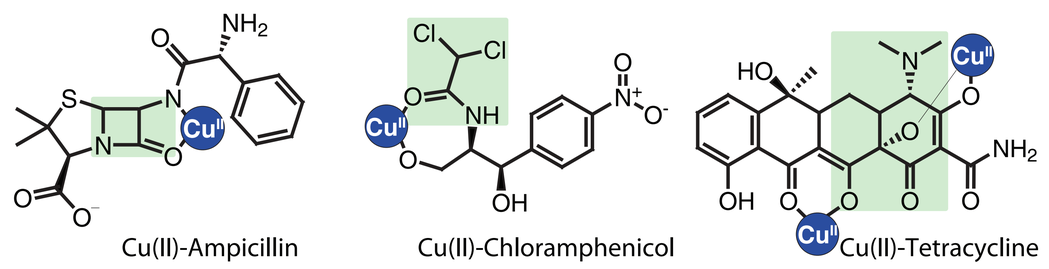
Antibiotic Electrooxidation

Cu(II)-antibiotic interaction



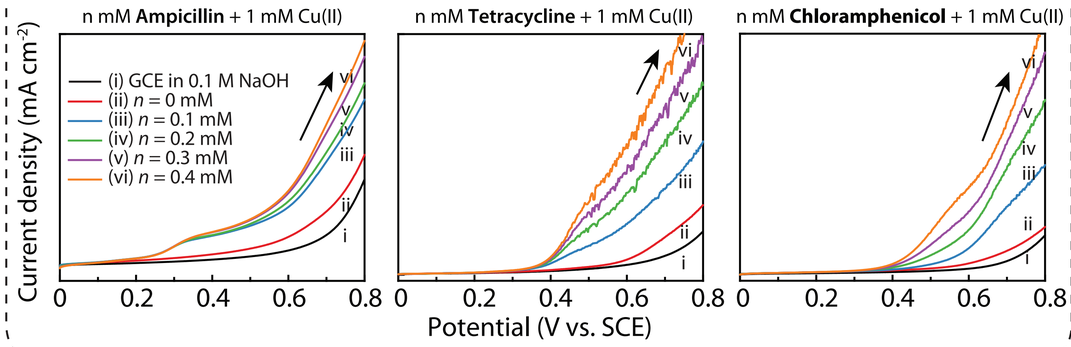
Coordination between Cu(II) and antibiotics enables the fast charge transfer from metal active sites to antibiotics.

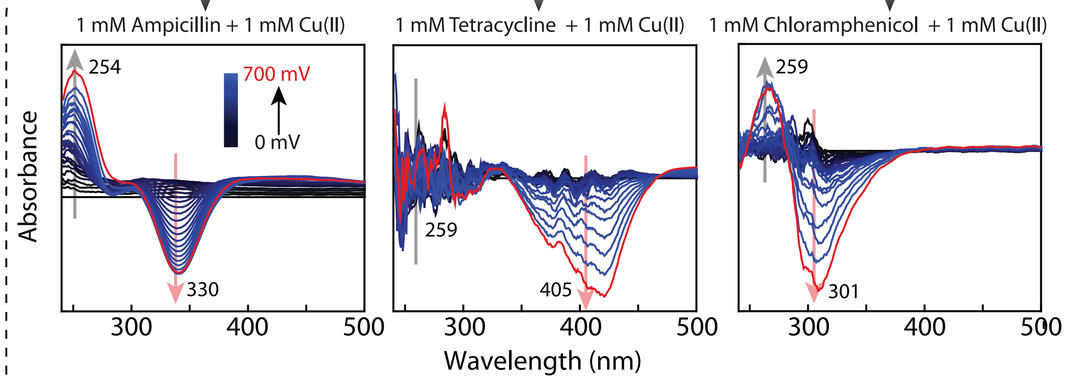
Successful degradation of antibiotics requires the destruction of fragments marked in green.

linear sweep voltammetry

In alkaline solution with Cu(II) and antibiotics:

Cu(II) + antibiotic → Cu(II)-antibiotic complex → Cu(III)-antibiotic complex → Cu(II) + degradation products

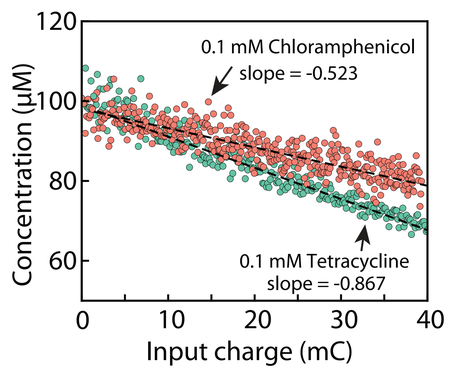


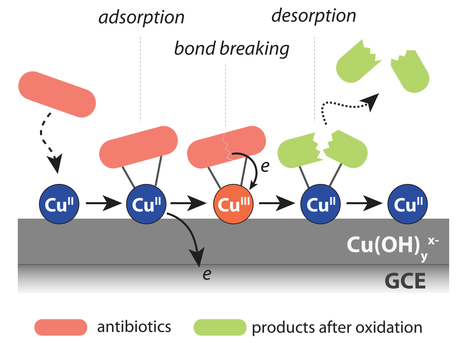


Cu(II)-antibiotic interaction is essential for antibiotic electrooxidation. For ampicillin, the concentration starts to decrease from 200 mV (vs. Ag/AgCl), a significantly lower potential than that of the other two antibiotics. The peak evolution reveals the kinetic aspects of antibiotics electrooxidation, showing multistep reaction mechanism.

***In situ* UV-Vis spectra**

Reaction kinetics





(left) Long-term electrooxidation of antibiotics monitored by *in situ* UV-Vis spectroscopy provides kinetic information of antibiotics electrooxidation.

At 0.8 V (*vs.* Ag/AgCl), the electron transfer number is 1.23 (~1) for ampicillin electrooxidation, 4.78 (~5) for tetracycline, and 7.93 (~8) for chloramphenicol.

(right) Equilibrium between surface Cu(II) species and antibiotics molecules is instantly achieved in bulk solution. During electrooxidation, electrons are transferred from antibiotics either via a Cu(III)-antibiotic intermediate or a direct route to form Cu(II)-oxidized antibiotics.

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Conclusion and Outlook

- Using metal ions in the electrolyte as the electrocatalysts for organic molecule electrooxidation shows excellent efficiency, which is comparable to metal-based nanostructure. Such route provides a more straightforward yet effective strategy toward electrocatalyst design.
- The complex intermediates formed due to coordination between active sites and substrate can be monitored by *in situ* UV-Vis spectroelectrochemistry, which benefits the mechanism discussion.

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