



4.3 Electrochemical modified electrode

4.3 Electrochemistry of Copper

The chemistry of copper is interesting and complicated and therefore is attractive to the electrochemist in the world to try making it as a sensor. Copper-plated screen printed carbon electrode (CuSPE) has been widely employed in the electrochemical analysis of o-diphenols, glucose, amino acids and oxygen etc. Its preparation is easy and fast with electrodeposition of copper on the surface of screen printed carbon electrode. The Cu particle size can be easily controlled by appropriate electrochemical parameters, and the particle size is around 100-500 nm as shown in Figure 1. The typical voltammogram of CuSPE is shown in Figure 2, the reduction peak at ~ -0.2 V (C1) is attributed to $\text{Cu}^{\text{II}}\text{O} \rightarrow \text{Cu}^{\text{I}}_2\text{O}$ and ~ -0.25 V (C2) is for $\text{Cu}^{\text{I}}_2\text{O} \rightarrow \text{Cu}^0$ (vs. Ag/AgCl), and the anodic peak (A1/A2) is the oxidation of Cu^0 to $\text{Cu}^{\text{II}}\text{O}$ and $\text{Cu}^{\text{I}}_2\text{O}$. ⁽¹⁾

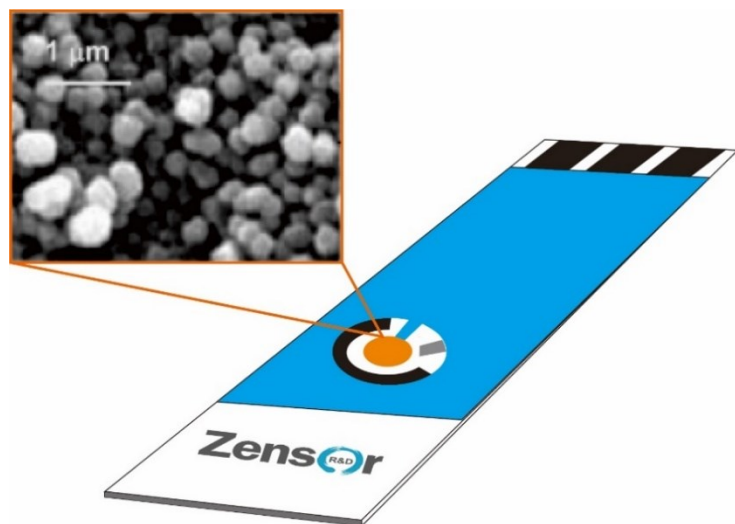


Figure 1. The CuSPE and its SEM picture

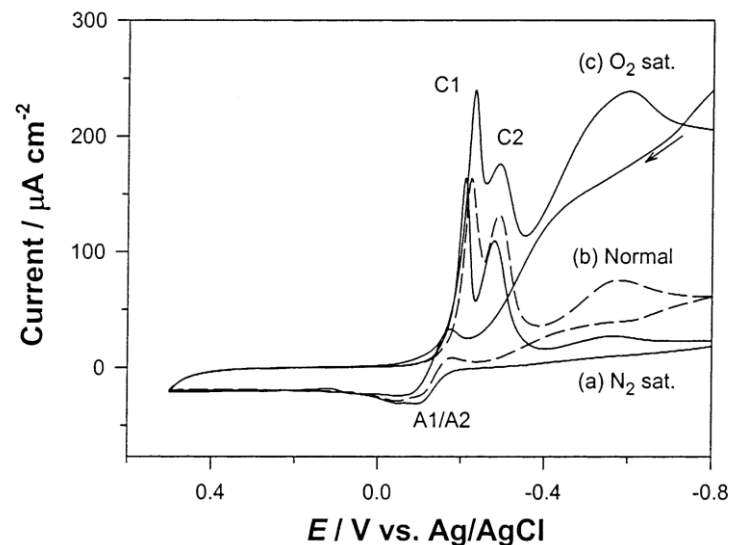


Figure 2. Typical voltammogram of CuSPE (a) N_2 -saturated, (b) normal air, and (c) O_2 -saturated pH 8 PBS.

Reference

(1) Jyh-Myng Zen, * Cheng-Teng Hsu, Annamalai Senthil Kumar, Hueih-Jing Lyuu and Ker-Yun Lin, *Analyst*, 2004, 129, 841–845

4.3.1 Photoelectrochemical oxygen sensor using copper-plated screen printed carbon electrodes

The dissolved oxygen (DO) sensor was successfully achieved by using copper-plated screen printed carbon electrode (CuSPE). The photoelectrochemical activity toward DO of the CuSPE was related to the formation of a p-type semiconductor Cu_2O . It is said that the procedure of photochemical reduction of DO goes with three steps. The first one is that H_2O_2 must be produced on CuSPE at a potential negative enough (-0.3V vs Ag/AgCl). And then the produced H_2O_2 is able to oxidize Cu^0 to Cu_2O chemically in the dark. The 3rd step is to excite the semiconductor, Cu_2O , with light to become Cu_2O^* and thus reduce DO to H_2O_2 as the signal. Therefore, the DO concentration is measured in the range of 1-8 ppm and further toward real sample analysis of groundwater and tap water.

Reference

(1)Jyh-Myng Zen,* Cheng-Teng Hsu, Annamalai Senthil Kumar, Hueih-Jing Lyuu and Ker-Yun Lin, *Analyst*, 2004, 129, 841–845

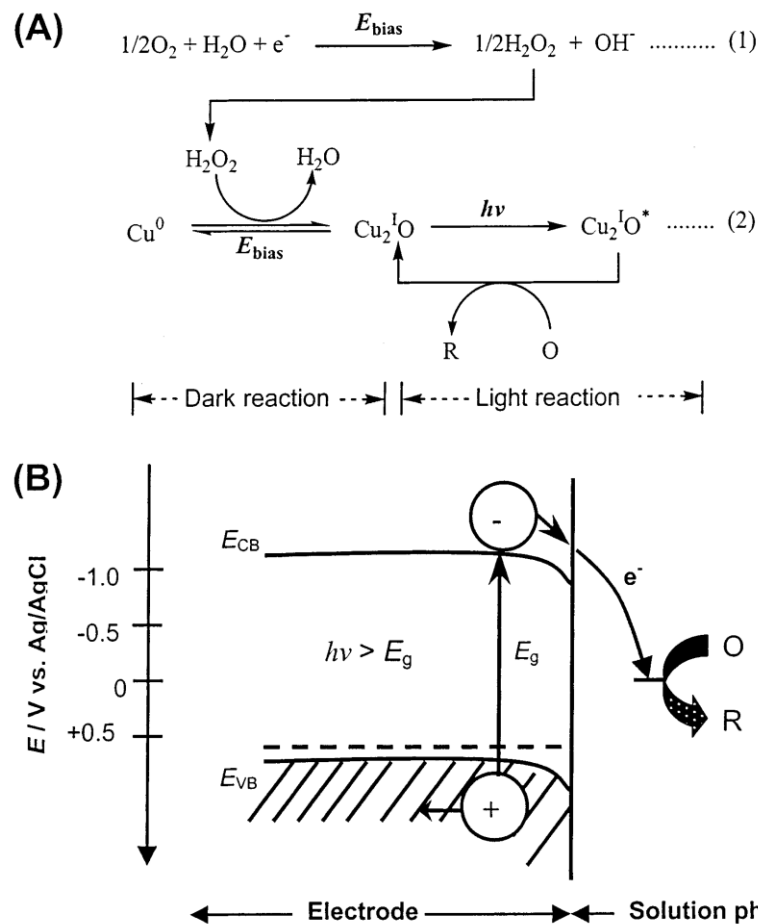


Figure 3. (A) Reaction pathway for the photoelectrochemical reduction of oxygen at the CuSPE. (B) Schematic view for the photochemical reduction of oxygen. E_{VB} , E_{CB} , and E_{g} correspond to the energy levels of valence band, conduction band, and band gap, respectively.

4.3.2 Selective detection of o-diphenols on copper-plated screen printed electrodes

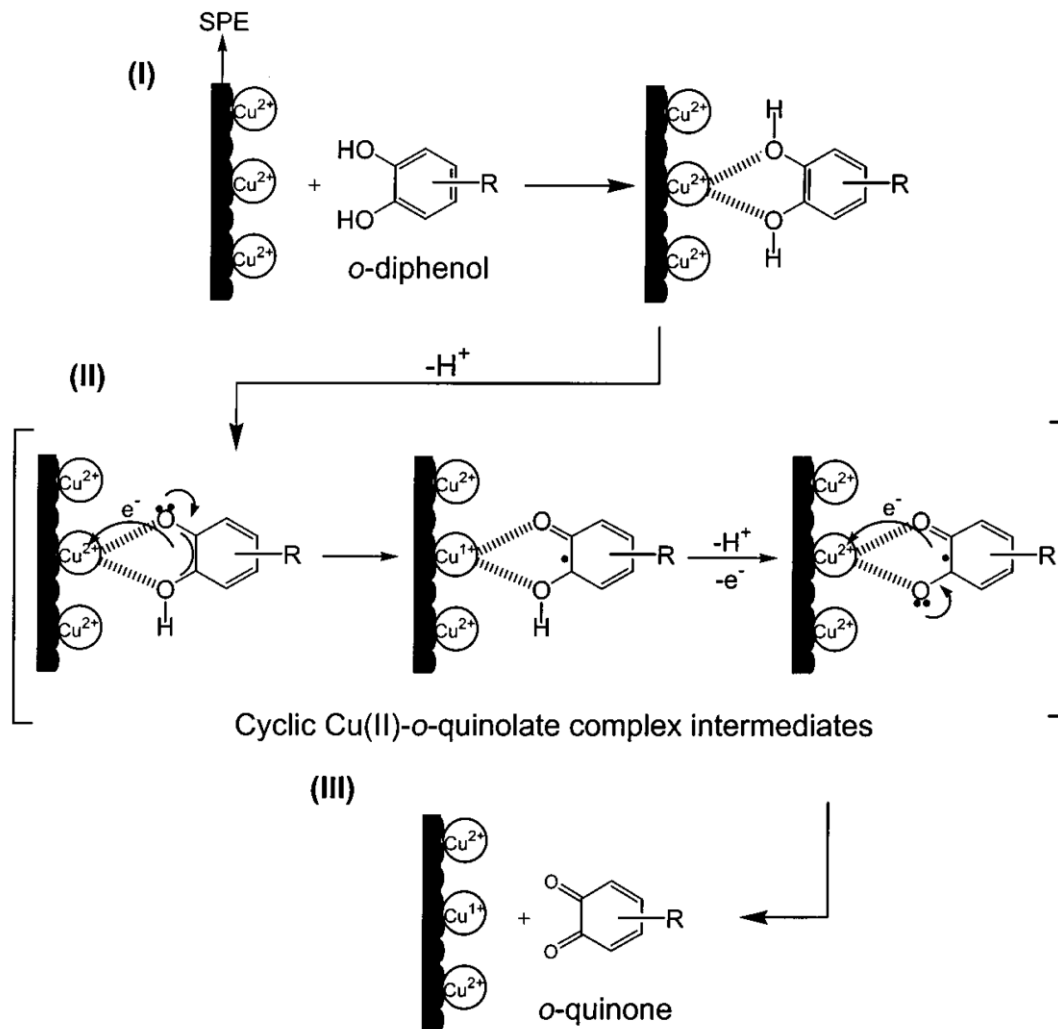


Figure 4. Reaction Mechanism for the Selective Oxidation of o-Diphenol on the CuSPE

Reference

(1) Jyh-Myng Zen,* Hsieh-Hsun Chung, and Annamalai Senthil Kumar, *Anal. Chem.* 2002, 74, 1202-1206

4.3.2 Selective detection of o-diphenols on copper-plated screen printed electrodes

It is available to selective detect the o-diphenols such as catechol, dopamine, and pyrogallol with copper-plated screen printed electrode (CuSPE) in the presence of other diphenol and ascorbic acid for clinical and biochemical examination. The possible catalytic oxidation mechanism on the CuSPE is illustrated in the Figure 4. It goes with the following 3 steps, (1) o-diphenol chelating with Cu(II) to form a weak five-member complex intermediate, (2) electron transfer and dehydrogenation reaction, and (3) formation of o-quinone derivative with reduced Cu(I), which can be further reoxidized to Cu(II). As a result, the selective o-diphenols sensor is achieved with amperometric method as shown in Figure 5. ⁽¹⁾

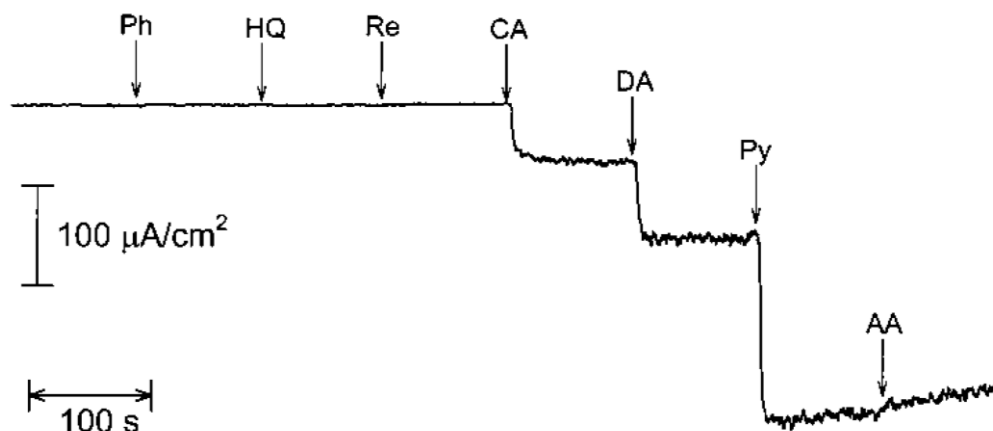


Figure 5. Typical amperometric hydrodynamic response for the CuSPE with a spike of 2 mM various phenolic and o-diphenol derivatives in pH 7.4 PBS

Reference

(1) Jyh-Myng Zen,* Hsieh-Hsun Chung, and Annamalai Senthil Kumar, *Anal. Chem.* 2002, 74, 1202-1206

4.3.3 Photoelectrocatalytic Oxidation of o-Phenols on Copper-Plated Screen-Printed Electrodes

A novel and sensitive detection method based on photoelectrocatalytic oxidation of o-diphenols was demonstrated on a copper-plated screen-printed carbon electrode (CuSPE) in pH 8 PBS. The o-diphenols can be detected amperometrically through electrochemical oxidation at a low applied potential of -0.1 V versus Ag/AgCl, where the CuSPE is much less subject to interfering reactions. The mechanism that induces good selectivity of the CuSPE is explained in terms of the formation of a cyclic five-member complex intermediate (Cu^{II} -o-quinolate). A prototype homemade flow through cell design is described for incorporating the photoelectrode and light source. Electrode irradiation results in a large increase in anodic current. The oxidative photocurrents produced by irradiation increase with light intensity presumably because of the formation of semiconductor Cu_2O .

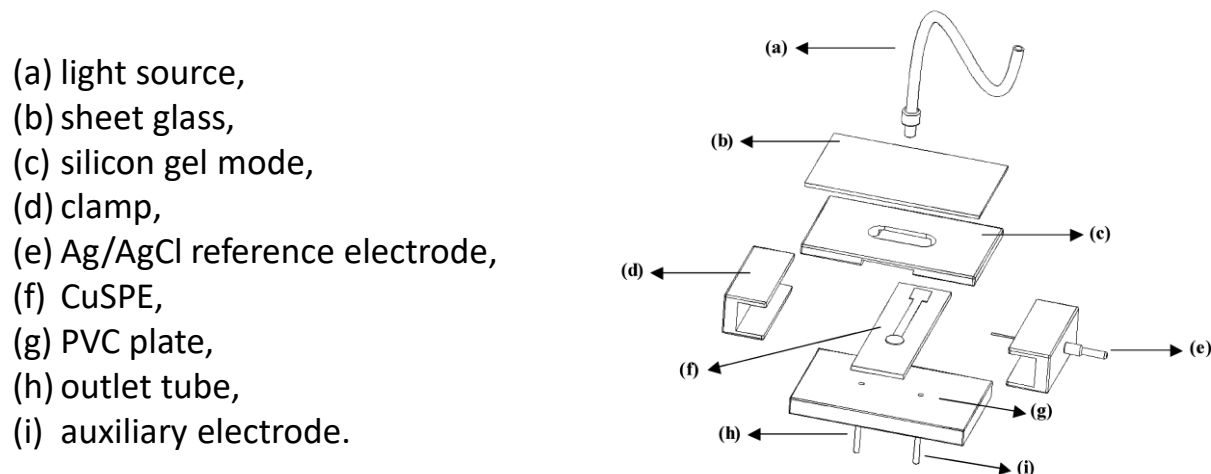


Figure 6. Light-passable flow-through cell

Reference

(1) Jyh-Myng Zen,* Hsieh-Hsun Chung, Hsueh-Hui Yang, Mei-Hsin Chiu, and Jun-Wei Sue, *Anal. Chem.* 2003, 75, 7020-7025

4.3.3 Photoelectrocatalytic Oxidation of o-Phenols on Copper-Plated Screen-Printed Electrodes

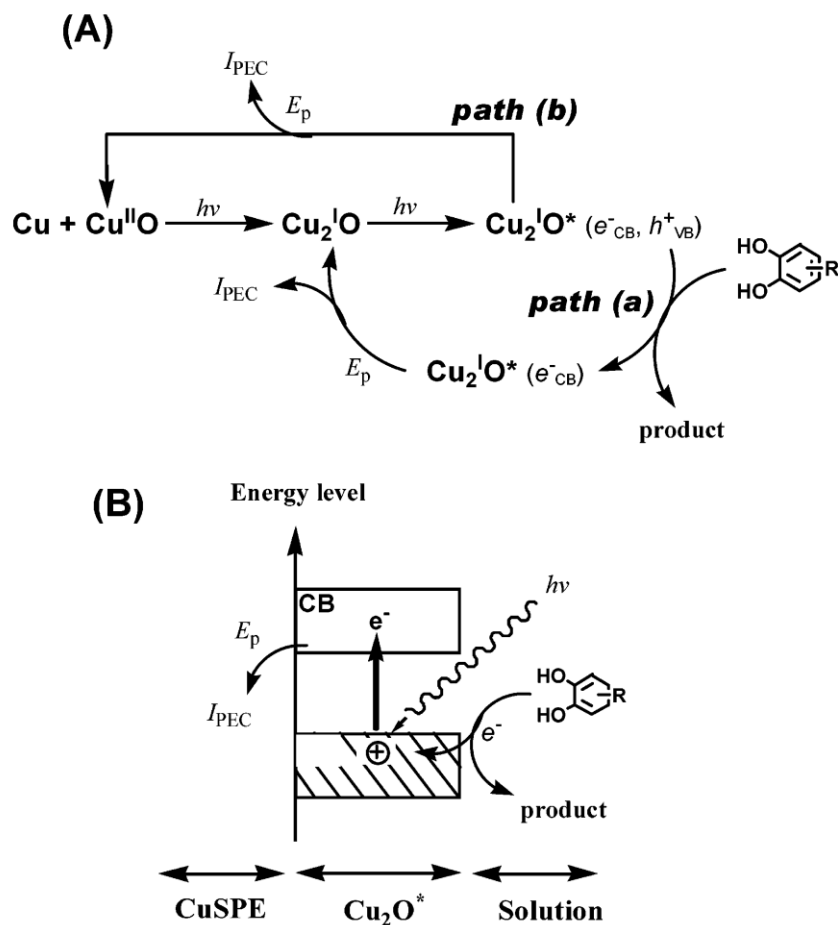


Figure 7. (A) Proposed mechanism for the photoelectrocatalytic oxidation of o-phenols. (B) An electron flow diagram based on the energy state of semiconductor Cu_2O layer on the CuSPE.

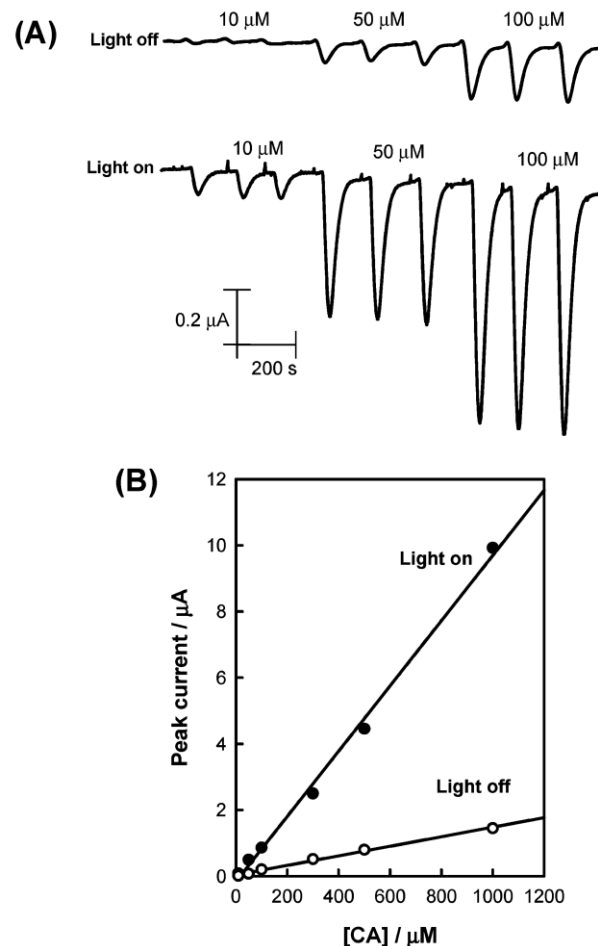


Figure 8. (A) Amperometric responses for the analysis of 10, 50, and 100 μM CA. (B) Calibration curve for CA.

Reference

(1) Jyh-Myng Zen,* Hsieh-Hsun Chung, Hsueh-Hui Yang, Mei-Hsin Chiu, and Jun-Wei Sue, Anal. Chem. 2003, 75, 7020-7025

4.3.4 Electrochemical investigation of glucose sensor fabricated at copper-plated screen-printed carbon electrodes

Copper-plated screen-printed carbon electrode (CuSPE) provides a suitable catalytic surface for the amperometric detection of hydrogen peroxide. Glucose oxidase (GOD) is immobilized on the top of the CuSPE to form a glucose sensor. The interaction of copper oxide with GOD was found to be an important factor in the glucose detection. Preliminary investigation under hydrodynamic conditions showed a linear calibration plot up to 26.7 mM glucose with a slope and regression coefficient of 4.5 $\mu\text{A}/\text{mM}$ and 0.9902, respectively. The Michaelis-Menten kinetics by nonlinear curve fitting yielded a K_m value close to that in solution indicating the ideality and suitability of the present system. Classical mixed potential mechanism is for the first time applied to the enzyme-coated CuSPE to further understand the system.

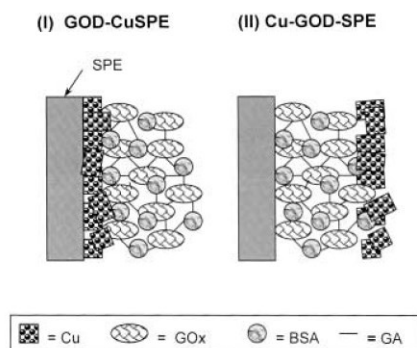


Figure 9. Electrode configurations of Type I and Type II glucose sensors.

Reference

(1) Annamalai Senthil Kumar and Jyh-Myng Zen, *Electroanalysis* 2002, 14, No. 10

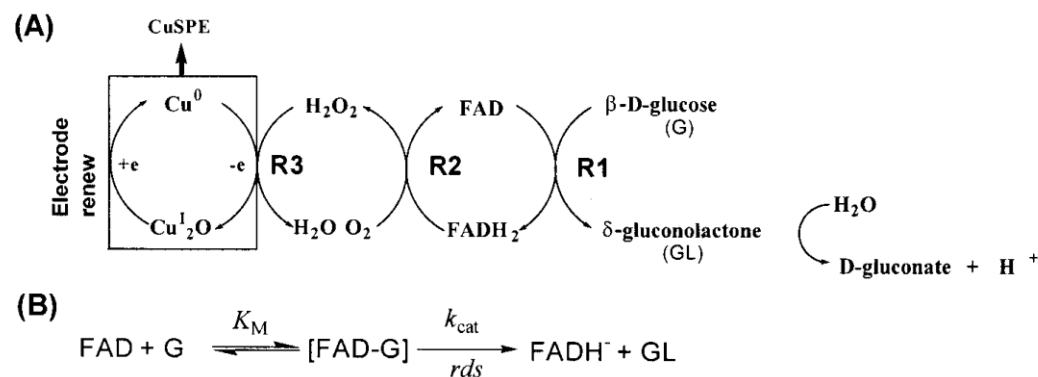
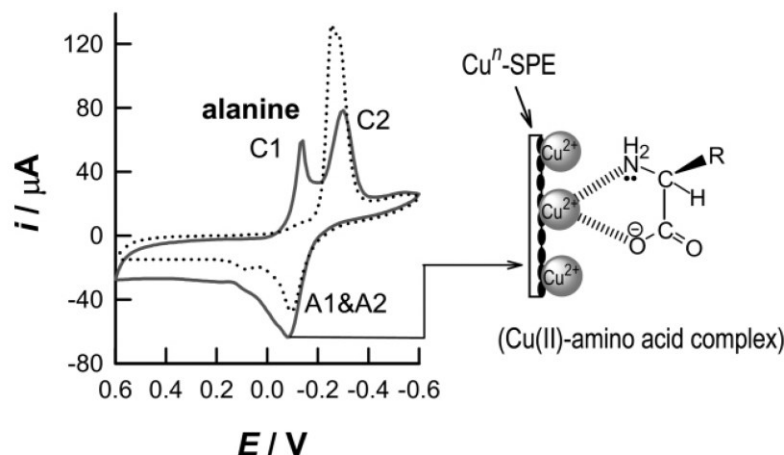


Figure 10. (A) Schematic representation of the transducing biosensor signals on the GOD-CuSPE. (B) Reaction pathway in terms of Michaelis-Menten kinetics

4.3.5 Amino acid analysis using disposable copper nanoparticle plated electrodes

A disposable copper nanoparticle-plated screen-printed carbon electrode (designated as Cuⁿ-SPE_{100-nm}) provides a new material for the determination of native amino acids. All 20 underivatized amino acids can be sensitively determined at 0.0 V vs. Ag/AgCl in pH 8 phosphate buffer solution. The precisely controlled copper nanoparticles can boost up the Cu^{II}O/Cu₂O redox signal on the working surface without any prior pretreatment procedure. The formation of a reversible 1:1 Cu^{II}O–amino acid complex on the Cuⁿ-SPE_{100-nm} was proposed to play a key role in the reaction mechanism. Stable detection responses were obtained for all amino acids by flow injection analysis with detection limits (S/N = 3) that lie in the range of 24 nM–2.7 μM. Selected amino acids from six representative chemical natures were separated by HPLC and detected at the Cuⁿ-SPE_{100-nm} with promising results.

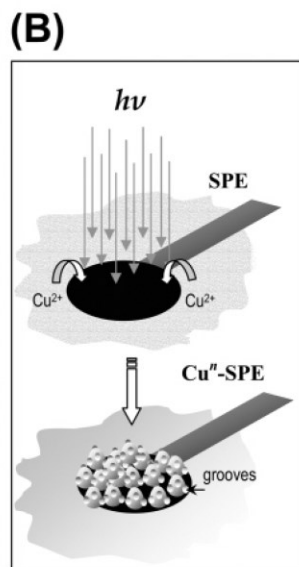
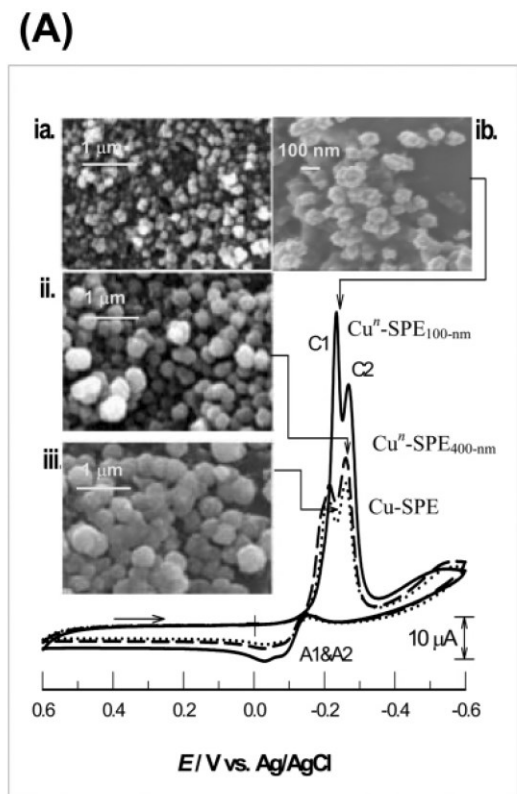
Figure 11. Typical CV responses of the Cuⁿ-SPE_{100-nm} in the absence (dotted line) and presence (solid line) of (A) 2 mM alanine



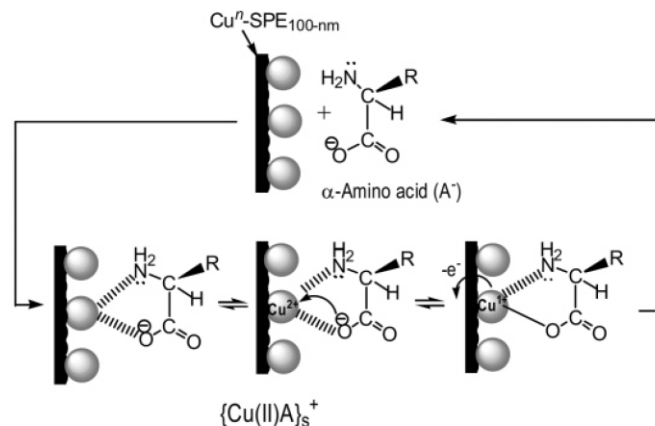
Reference

(1) Jyh-Myng Zen,* Cheng-Teng Hsu, Annamalai Senthil Kumar, Hueih-Jing Lyuu and Ker-Yun Lin, *Analyst*, 2004, 129, 841–845

4.3.5 Amino acid analysis using disposable copper nanoparticle plated electrodes



step 1:



step 2:

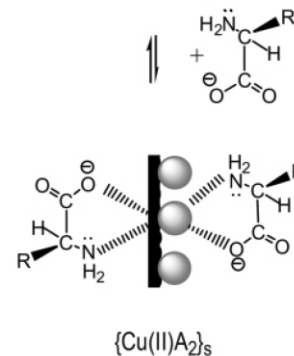


Figure 12. (A) SEM morphological view and typical CV (in pH 8 PBS) of Cu-SPE and Cuⁿ-SPE prepared without (iii) and with 49 (ii) & 399 (ia & ib) klx of light illumination. (B) Conceptual representation of the proposed plating method for the Cuⁿ-SPE.

Figure 13. Reaction mechanism for the copper(II)-amino acid complexation at the Cuⁿ-SPE_{100-nm}.

Reference

(1) Jyh-Myng Zen,* Cheng-Teng Hsu, Annamalai Senthil Kumar, Hueih-Jing Lyuu and Ker-Yun Lin, *Analyst*, 2004, 129, 841–845

4.3.6 Novel Preparation and Photoelectrochemical Properties of γ -CuI Semiconductor Nanocrystallites on Screen-Printed Carbon Electrodes

Cuprous iodide (γ -CuI) is an important semiconductor material having a band gap of 3.1 eV often used for visible light assisted photoelectrochemical and solar energy conservation systems. It is reported that the first and unique preparation of fine and precisely controlled γ -CuI semiconductor nanocrystallites on the surface of a screen-printed carbon electrode using a photoelectrochemical copper nanoparticle deposition method with tris(hydroxymethyl)-aminomethane (Tris) buffer solution as a control medium. Tris buffer helps to split $\text{Cu}^{\text{I}}_2\text{O}$ and $\text{Cu}^{\text{II}}\text{O}$ oxidation states through specific complexation mechanism and in turn to selective iodination of $\text{Cu}^{\text{I}}_2\text{O}$ to the formation of γ -CuI on the electrode. Stable and linear photoelectrochemical response was further demonstrated against variable light intensity up to 400 Klux using the γ -CuI modified system.

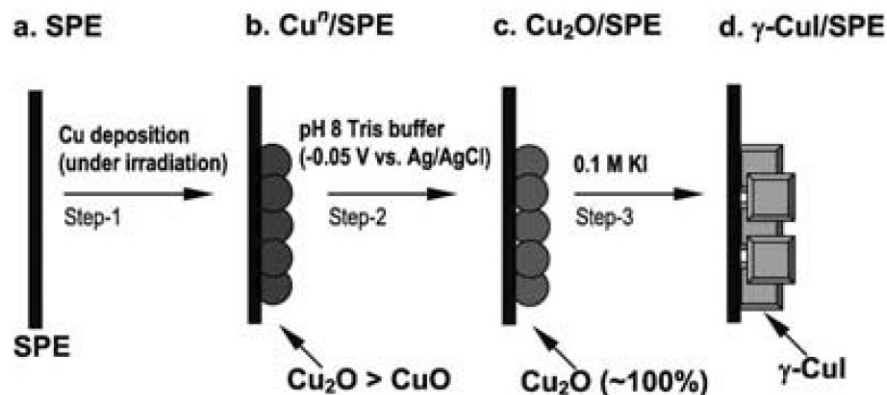


Figure 14. Preparation of γ -CuI on a disposable screen-printed carbon electrode support

Reference

(1) Cheng-Teng Hsu, Hsieh-Hsun Chung, Annamalai Senthil Kumar, Jyh-Myng Zen, *Electroanalysis* 17, 2005, No. 20, 1822 – 1827

4.3.6 Novel Preparation and Photoelectrochemical Properties of γ -CuI Semiconductor Nanocrystallites on Screen-Printed Carbon Electrodes

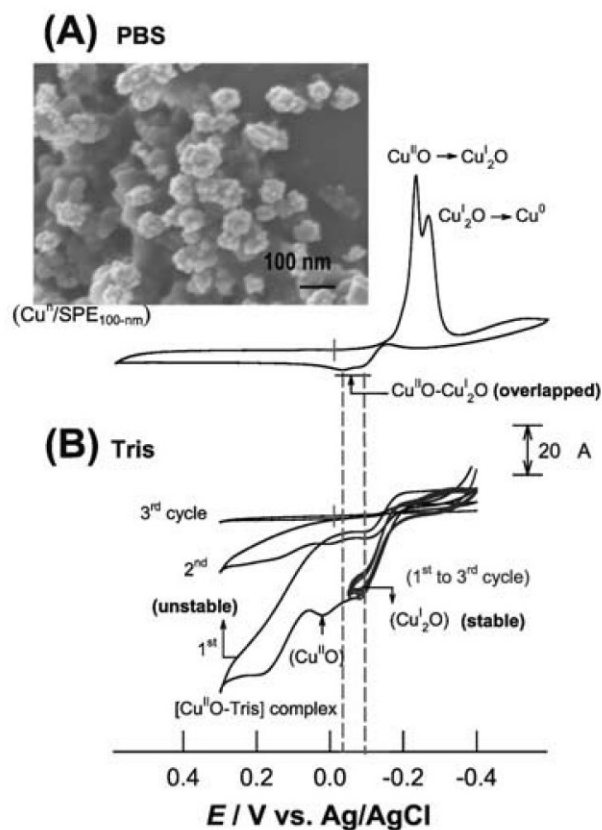


Figure 15. Cyclic voltammetric responses of the $\text{Cu}^n/\text{SPE}_{100\text{-nm}}$ in pH 8 PBS (A) and Tris buffer solution (B) at a scan rate of 5 mV/s. Insert: SEM picture corresponding the surface morphology of the $\text{Cu}^n/\text{SPE}_{100\text{-nm}}$ system prepared under photoelectrochemical deposition method.

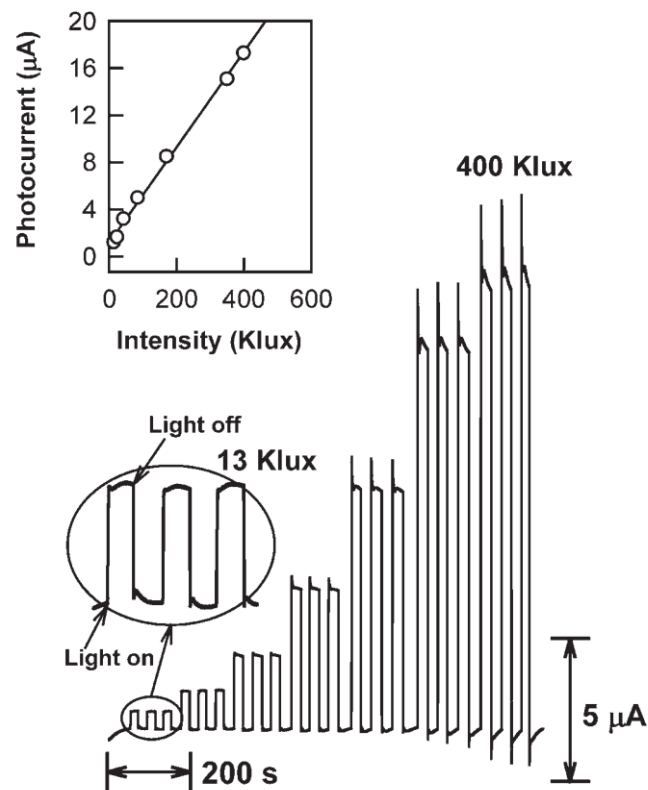


Figure 16. Typical photoresponses of the $\gamma\text{-CuI}/\text{SPE}$ under irradiation at a biased potential of 0.2 V vs. Ag/AgCl. Insert Figure is a plot of the observed photocurrent versus photo-intensity.

Reference

(1) Cheng-Teng Hsu, Hsieh-Hsun Chung, Annamalai Senthil Kumar, Jyh-Myng Zen, *Electroanalysis* 17, 2005, No. 20, 1822 – 1827

4.3.7 Multiple screening of urolithic organic acids with copper nanoparticle-plated electrode: Potential assessment of urolithic risks

There is yet to be a reliable prediction of urolithiasis. To facilitate early diagnosis, a simple and rapid high performance liquid chromatography method with electrochemical detection using disposable coppernanoparticle-plated electrodes ($\text{Cu}^n\text{-SPE}$) was developed for multiple detection of creatinine and 4 urolithic organic acids. A total of 206 normal and urolithic human and canine urines and urolith samples were collected for direct analysis of creatinine, cystine, uric acid, oxalic acid, and citric acid without sample cleanup and derivatization processes. Urinary organic acids were separated in 11 min and were devoid of ascorbic acid interference. The detection limits ($S/N > 3$) were at the nanomolar level with linear dynamic ranges spanning 2–3 orders of magnitude. Recoveries in urine ranged from 99.5% for creatinine to 86.5% for citric acid. The analytical variations (RSD) were less than 6.2% in phosphate buffer and 7.7% in urine. Important differences in organic acid levels/profiles between animal species and among normal and urolithic urines/urolith were unveiled and corresponded well (70–90%) with the urolithic risk in a retrospective assessment. The simplicity and reproducibility of this method using disposable $\text{Cu}^n\text{-SPE}$ has made routine urine analysis possible and can be of great clinical and diagnostic potential in the screening of urolithiasis and abnormal states related to excess secretion of organic acids and amino acids in humans and animals.

Reference

(1) Chung-Wei Yang, Jyh-Myng Zen, Yu-Lin Kao, Cheng-Teng Hsu, Tung-Ching Chung, Chao-Chin Chang, Chi-Chung Chou, *Analytical Biochemistry* 395 (2009) 224–230

4.3.7 Multiple screening of urolithic organic acids with copper nanoparticle-plated electrode: Potential assessment of urolithic risks

Figure 17. Differential chromatographic profiles of organic acids between urine (solid line) and urolith extractions (dotted line) in the same human and canine subject. Urolith is subjected to organic acid extraction as described under Materials and methods. Samples A and B represent characteristic chromatograms rich in distinctive organic acids. Peak identification: (a) cystine, (b) creatinine, (c) oxalic acid, (d) uric acid, and (e) citric acid. The possible presence of ascorbic acid is pointed out by arrows.

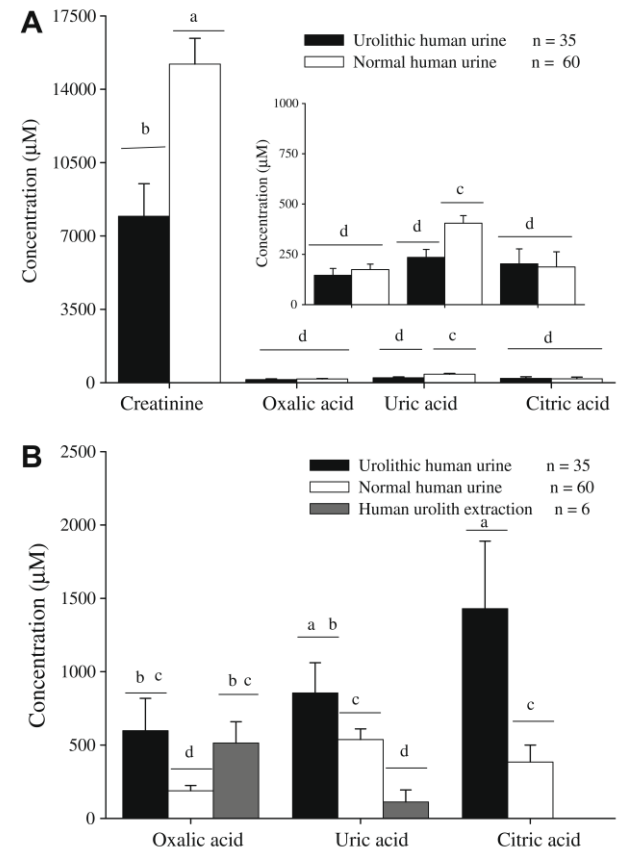
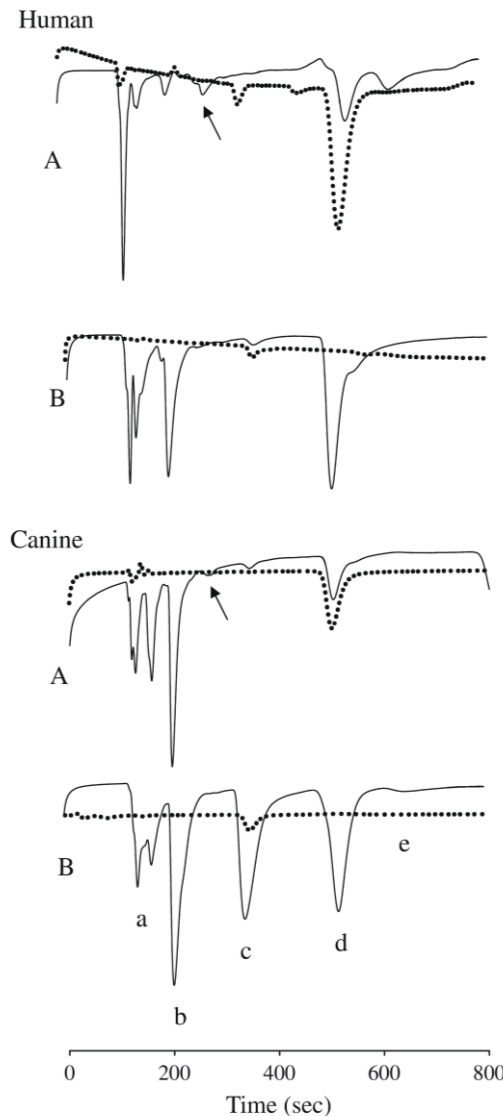


Figure 18. Average concentrations of creatinine, oxalic acid, uric acid, and citric acid in normal and urolithic human urines and in uroliths are shown in panel A. Creatinine-corrected organic acid concentrations are shown in panel B. Columns with the same letter and bar were not statistically different at $P < 0.05$ level.