Determination of Chemical Oxygen Demand (COD) Using Nanoparticle-Modified Voltammetric Sensors and Electronic Tongue Principles

GRUP DE SENSORS I BIOSENSORS

Qing Wang, Manel del Valle*
Group of Sensors and Biosensors, Department of Chemistry,
Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain
E-mail: manel.delvalle@uab.es

UAB Universitat Autònoma de Barcelona

Abstract

This research focuses on the use of nanoparticle-modified voltammetric sensors for the rapid and green determination of Chemical Oxygen Demand in river waters and waters from agricultural waste. Four different variants of modified electrodes have been prepared: CuO nanoparticles electrogenerated over Cu and covered with Nafion film (CuO/Cu-Nf), and graphite–epoxy composites modified with Cu, CuO, and Cu–Ni alloy nanoparticles. The response features of these electrodes were assessed by calibrating them vs. glucose, glycine, ethylene glycol, and potassium hydrogen phthalate in alkaline media, as samples providing different difficulty in their (bio)degradation characteristics. The most sensitive electrode was demonstrated to be the (CuO/Cu-Nf) electrode, with an LOD of 12.3 mg $O_2 \cdot L^{-1}$. The joint information provided by the sensor array showed the ability of estimating both the organic load and the type of sample in terms of difficulty of degradation, in what can be named an intelligent sensor assembly.

Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is defined as the amount of molecular oxygen (in milligrams of O_2) required to decompose all the organic compounds in 1 L of aqueous solution to carbon dioxide and water. There are many methods reported for COD determination, such as the conventional dichromate titration method. Electro-oxidizing the organic contaminants to completely transform them into CO_2 and H_2O using sensors is considered the best method for COD estimation [1-3].

Fabrication of Electrodes

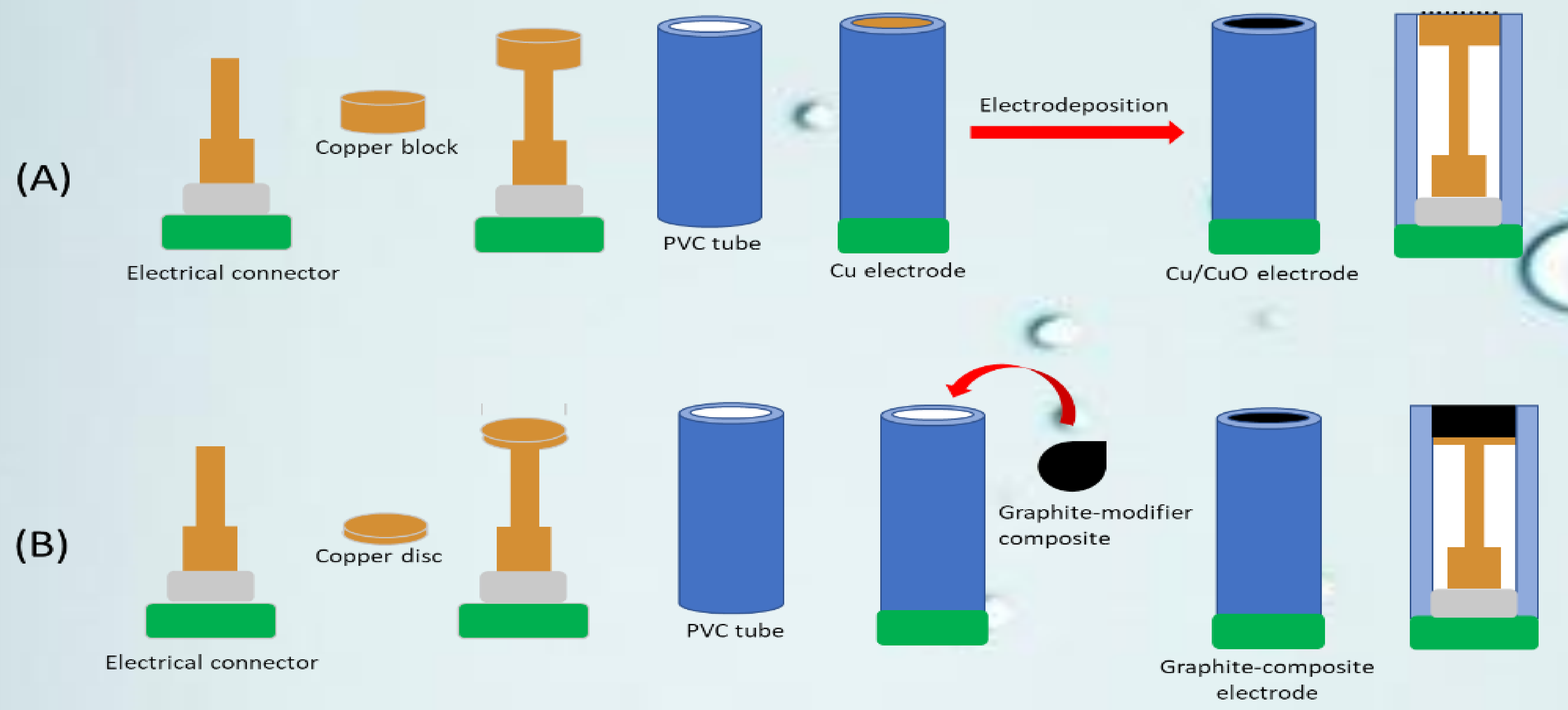
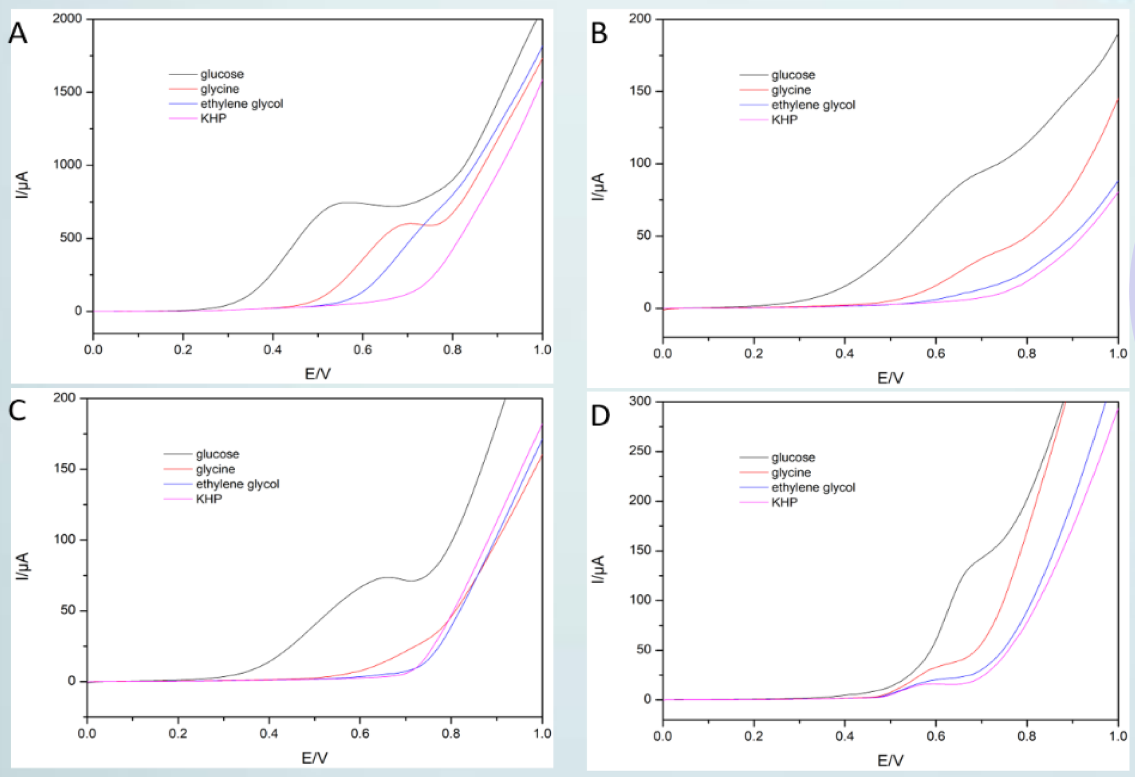


Figure 1. Diagram of the fabrication procedures of (A) the deposited Cu/CuO electrode and (B) the graphite–epoxy electrodes (**E2**, **E3** and **E4**) modified with metal nanoparticles (Cu, CuO and Ni Cu alloy, respectively)

Response Tests on Standard Compounds

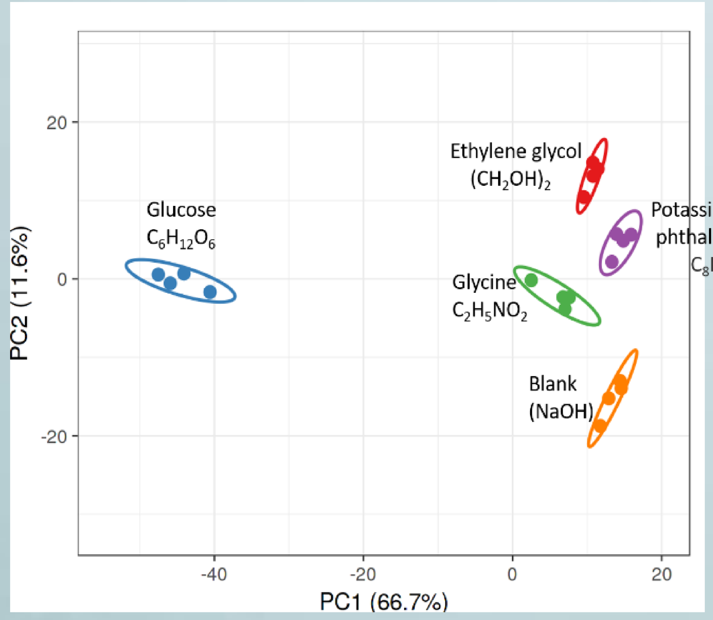
1. Voltammetric Responses of Electrodes to Standard Compounds



Different sensors show different cyclic voltammogram shapes and indicates the potential for distinguishing the main components and multivariate analysis

Figure 2. Oxidation curves of cyclic voltammetric responses of electrodes **E1** (A), **E2** (B), **E3** (C), and **E4** (D) to four standard chemical oxygen demand (COD) substances: 2.15 mM glucose; 2.15 mM glycine; 2.15 mM ethylene glycol; 2.15 mM KHP.

2. PCA on Standard Compounds



The level of degradation difficulty:
More easier, more left;
More difficult, more right.

Figure 3. Score plot of the first two components obtained after principal component analysis (PCA). A total of 20 samples were analyzed corresponding to quadruplicate determinations of glucose (blue), glycine (green), ethylene glycol (red), potassium hydrogen phthalate (purple), and blank (orange).

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Real Samples Analysis

1. Calibration

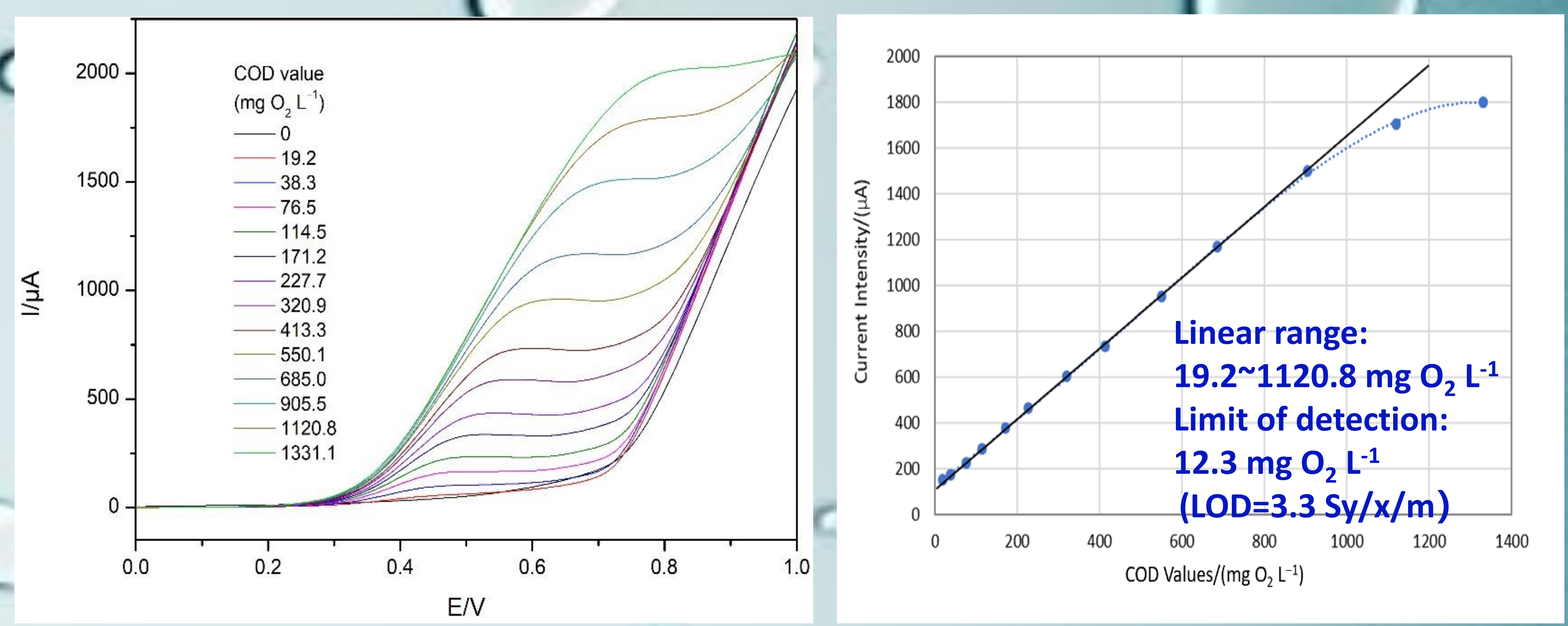


Figure 4. (A) Oxidation curves of cyclic voltammetric responses of electrode **E1** with the increase of addition of glucose in 0.05 M NaOH solution. (B) Calibration plot of intensity of current at E=0.7050 of electrode **E1** as a function of COD values (glucose as standard substance). Potential scan window, -1.0 to +0.7 V vs. Ag/AgCl (3.0 M KCl). Scan rate, 50 mV/s.

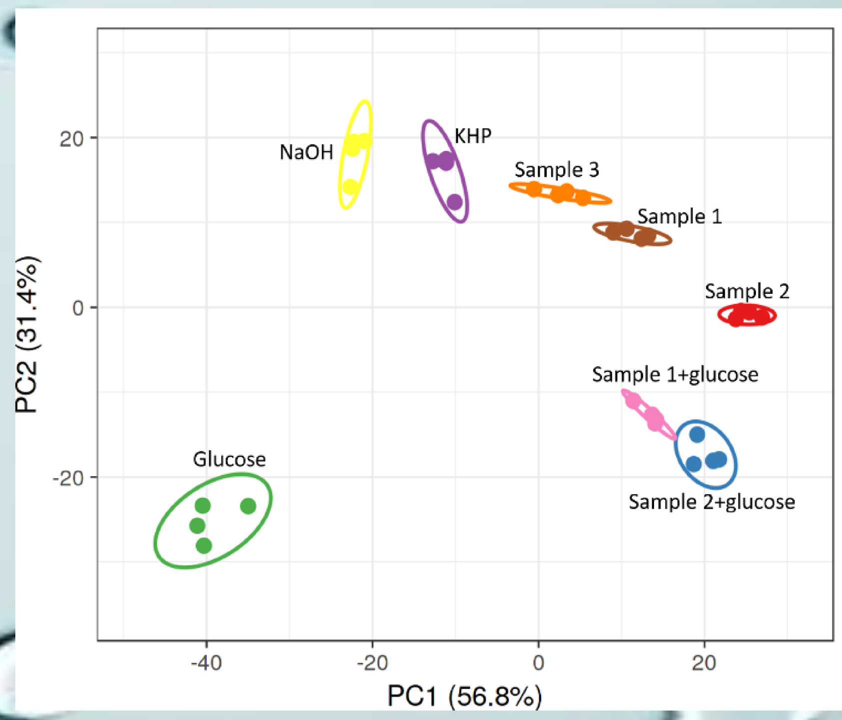
2. Spiking Tests

Table 1. Recovery yield of spiked glucose detected by electrode E1 towards Sample 1, 2 and 3.

	Sample found (mg O_2 L^{-1})	Added glucose (mg O_2 L^{-1})	Spiked sample found	Recovery yield (%)
Sample 1	<LOD	38.32	27.11	109.5
Sample 2	<LOD	38.32	27.67	108.6
Sample 1nd	33.76	95.52	112.11	82.02
Sample 2nd	17.10	95.52	101.64	88.51
Sample 3nd	18.56	95.52	97.37	82.50

nd Spiking tests of real samples with fewer dilution.

3. PCA on Real Samples and Standard Compounds



Sample 2, which contains lots of pesticides, is on the right. Sample 1 contains fewer pesticides than Sample 2, more left. Sample 3 also contains some organic compounds that are difficult to be degraded.

Figure 5. Score plot of the first two components obtained after PCA analysis to real samples and standard substances. These samples are glucose (green), NaOH (yellow), potassium hydrogen phthalate (purple), Sample 1 (brown) and its spike with glucose (pink), Sample 2 (red) and its spike with glucose (blue), and Sample 3

Conclusion

This work developed an easy method of analyzing wastewaters quantitatively and qualitatively by combining the electrochemical electrodes with the electronic tongue technique. The COD values were calculated based on the calibration and the PCA technique can be used to evaluate the main component of a river sample, which is easy or difficult to be degraded. The resulting sensor-based method demonstrates great potential not only for estimating the precise value of organic load but for predicting the difficulty behavior in its degradation.

References

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