Ionic Liquid of a Gold Nanocluster: A Versatile Matrix for Electrochemical Biosensors

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INTRODUCTION

- ❖ Ionic liquids are room-temperature molten salts that are typically composed of organic cations (e.g., N-alkylpyridinium, N,N' dialkylimidazolium) with a variety of anions and exhibit high ionic conductivity, nonflammability, and electrochemical and thermal stability and biocompatibility.
- ❖ They are increasingly used in electrochemical devices, such as batteries, fuel cells, and sensors, where their intrinsic ionic conductivity is exploited.
- ❖ A variety of biosensors and biofuel cells have been developed by immobilizing enzymes in ionic liquid matrices.
- ❖ A significant challenge in the development of such devices is to facilitate electron transfer between enzymes and electrodes because the redox center of the enzyme is surrounded by a thick protein layer.
- ❖ Innovative approaches have been developed to establish electrical communication between the redox center of the enzyme and the electrode by introducing redox mediators or electrical conductors to the ionic liquid matrix.

- Nonetheless, efficient wiring of redox enzymes still remains unaccomplished mostly because of the problems associated with the instability or non-optimal positioning of these electron relays in the heterogeneous mixtures.
- Electrochemical and computational investigations have revealed that these molecular clusters display unique redox properties that can be tuned effectively by controlling the core size.
- The Au25 clusters entrapped in a silica solgel matrix showed excellent electrocatalytic activity toward the oxidation of dopamine, ascorbic acid and uric acid.

In this work…………..

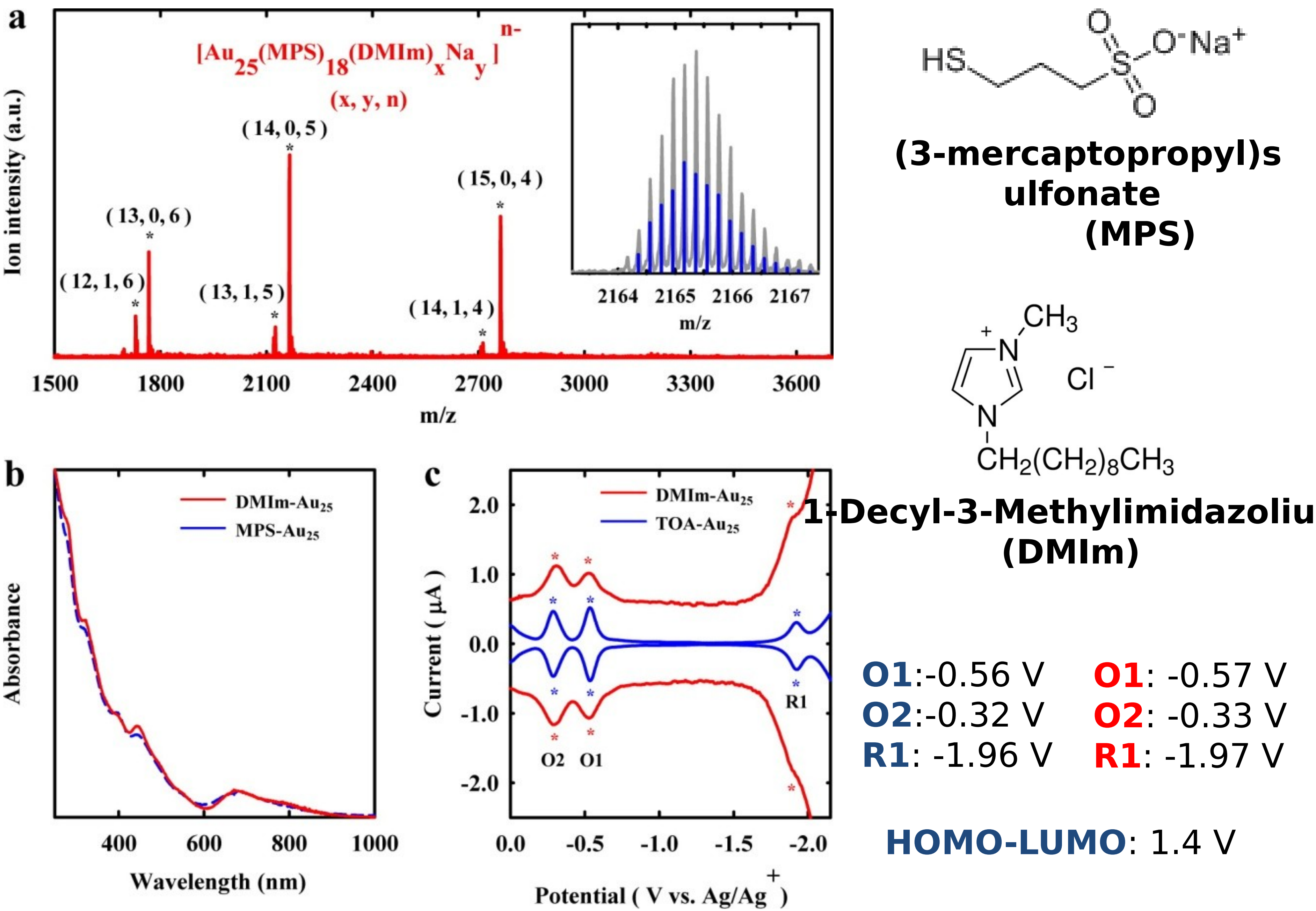
- Combined these two unique materials to produce a multifunctioning matrix that can be utilized in a variety of electrochemical applications.

- An ionic liquid of a quantum-sized gold nanocluster was prepared by ion-pairing of anionic Au25 clusters stabilized with (3-mercaptopropyl)sulfonate (MPS-Au25) with 1-decyl-3 methylimidazolium (DMIm) cations.

❖ The ion-paired form of Au25 (DMIm-Au25) is a highly viscous ionic liquid and readily forms a film on an electrode. Voltammetric investigation has revealed that the Au25 film is electrically conductive and the electron transport occurs via a diffusion-like electron hopping process.

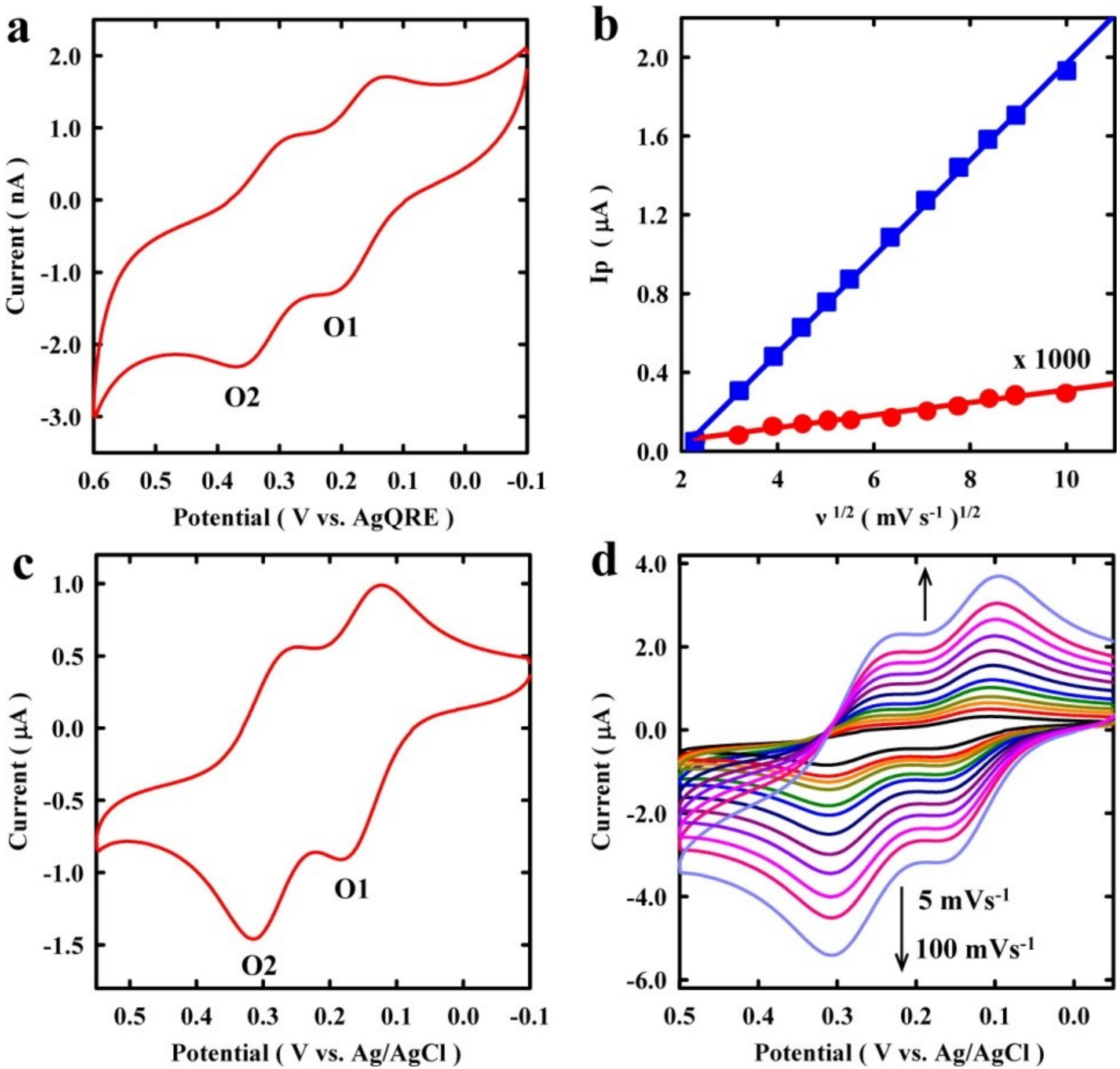
❖DMIm-Au25 can be used as an effective matrix for the fabrication of electrochemical glucose biosensors based on glucose oxidase (GOx), the most widely studied assays for the management of diabetes.

❖ The enzyme electrodes prepared by incorporating GOx in the DMIm-Au25 show excellent electrocatalytic activity toward the oxidation of glucose and high glucose binding affinity, demonstrating the great potential of the DMIm-Au25 in the development of enzyme-based biosensors



a
$[Au_{25}(MPS)_{18}(DMIm)_xNa_y]^{n-}$
(x, y, n)
(12, 1, 6)
(13, 0, 6)
(13, 1, 5)
(14, 0, 5)
(14, 1, 4)
(15, 0, 4)
Ion intensity (a.u.)
1500 1800 2100 2400 2700 3000 3300 3600
m/z
2164 2165 2166 2167
m/z
HS
O
O⁻Na⁺
S
O
(3-mercaptopropyl)sulfonate
(MPS)
CH3
N
Cl⁻
N
CH2(CH2)8CH3
1-Decyl-3-Methylimidazoliu
(DMIm)
b
DMIm-Au25
MPS-Au25
Absorbance
400 600 800 1000
Wavelength (nm)
c
DMIm-Au25
TOA-Au25
Current (μA)
2.0 1.0 0.0 -1.0 -2.0
O2 O1
R1
0.0 -0.5 -1.0 -1.5 -2.0
Potential (V vs. Ag/Ag+)
O1:-0.56 V
O2:-0.32 V
R1: -1.96 V
O1: -0.57 V
O2: -0.33 V
R1: -1.97 V
HOMO-LUMO: 1.4 V

CYCLIC VOLTAMMETRY OF DMIm-Au25 FILM



O1: 0.15 V **Au250/-1**

O2: 0.28 V **Au25+1/0**

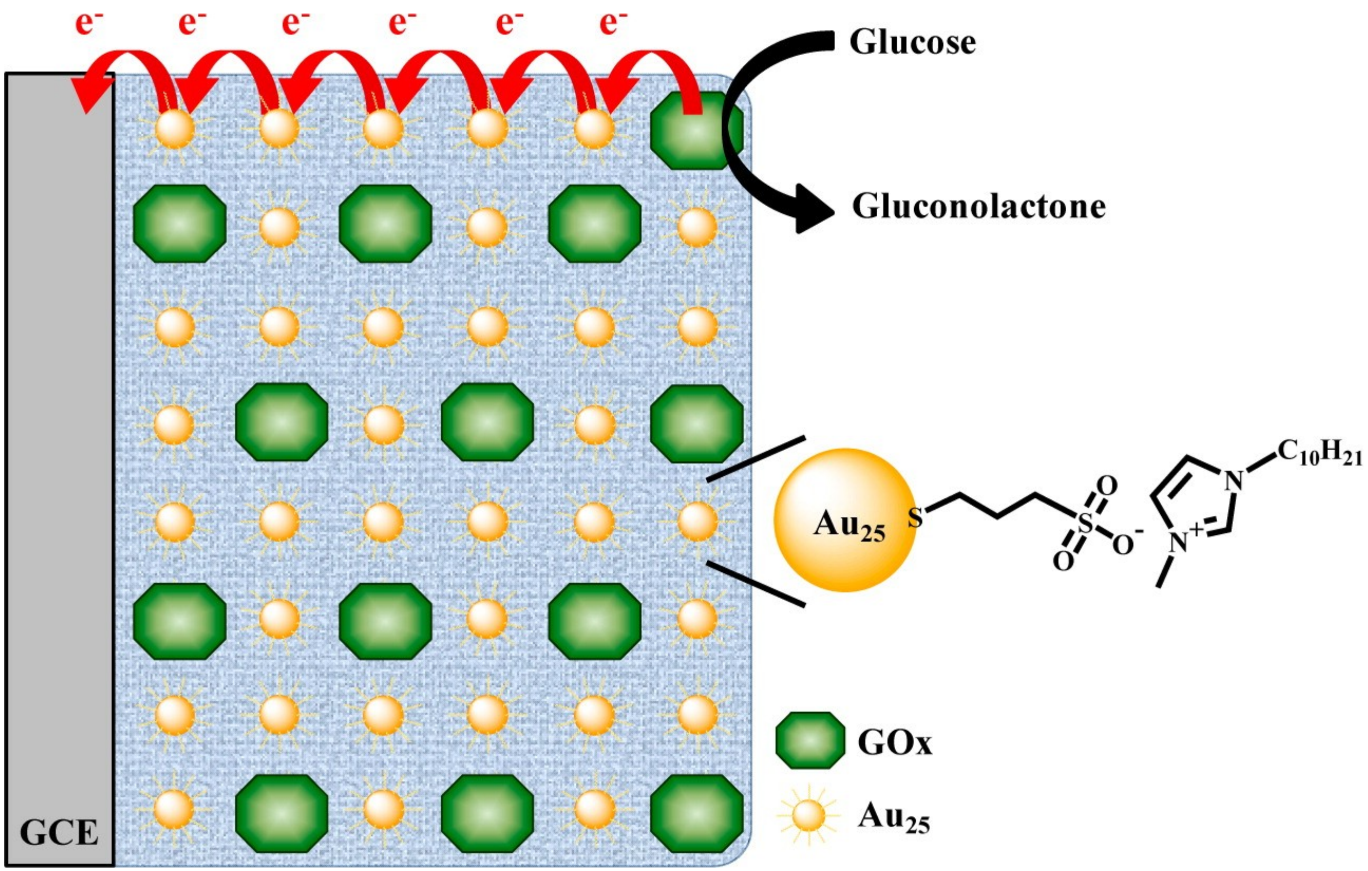
R1: -1.96 V

Electronic Diffusion Coefficients

1.3 X 10-8 (without S. E.)

4.2 X 10-12 cm2/s (with S. E.)

SCHEMATIC ILLUSTRATION OF PROCESSES OCCURING IN A GOx-DMIm-Au25 COMPOSITE ELECTRODE

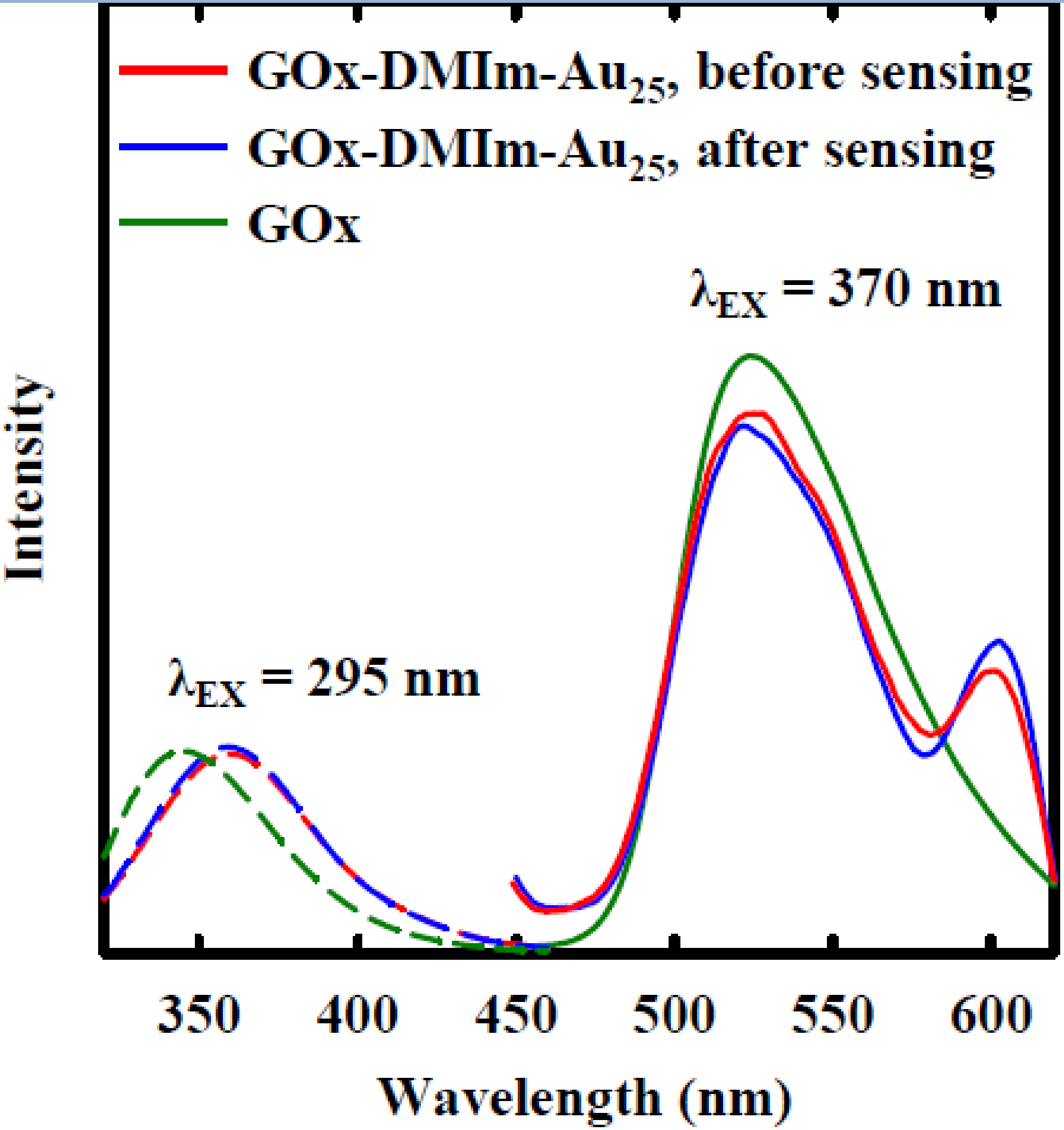


$$Au_{25}(red) \rightarrow Au_{25}(ox) \quad (1)$$

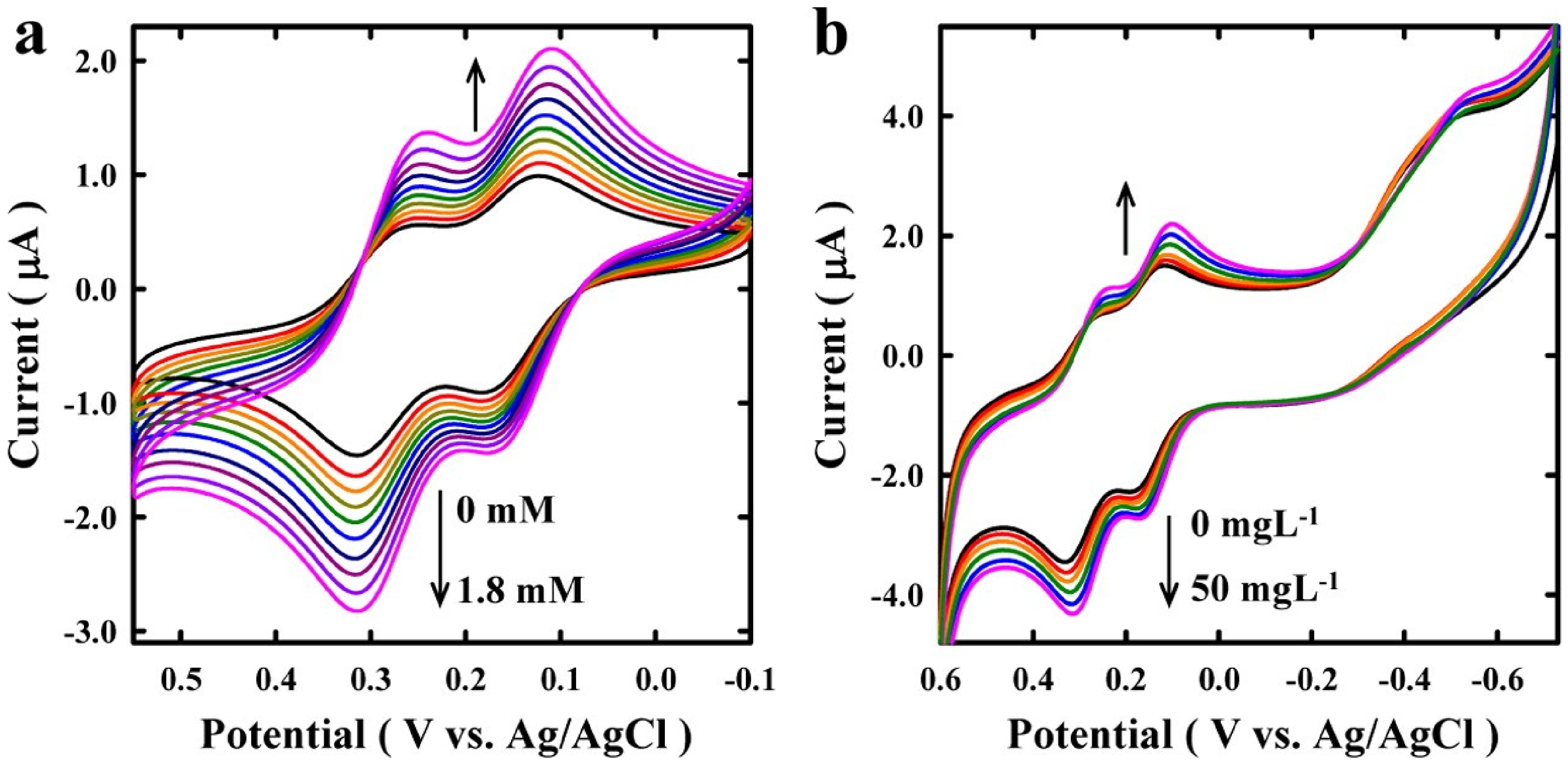
$$glucose + GOx(FAD) \rightarrow gluconolactone + GOx(FADH_2) \quad (2)$$

$$GOx(FADH_2) + Au_{25}(ox) \rightarrow GOx(FAD) + Au_{25}(red) \quad (3)$$

Fluorescence spectra of tryptophan and FAD residues in GOx, GOx in GOx-DMIm-Au25 composite films before and after the glucose sensing experiment



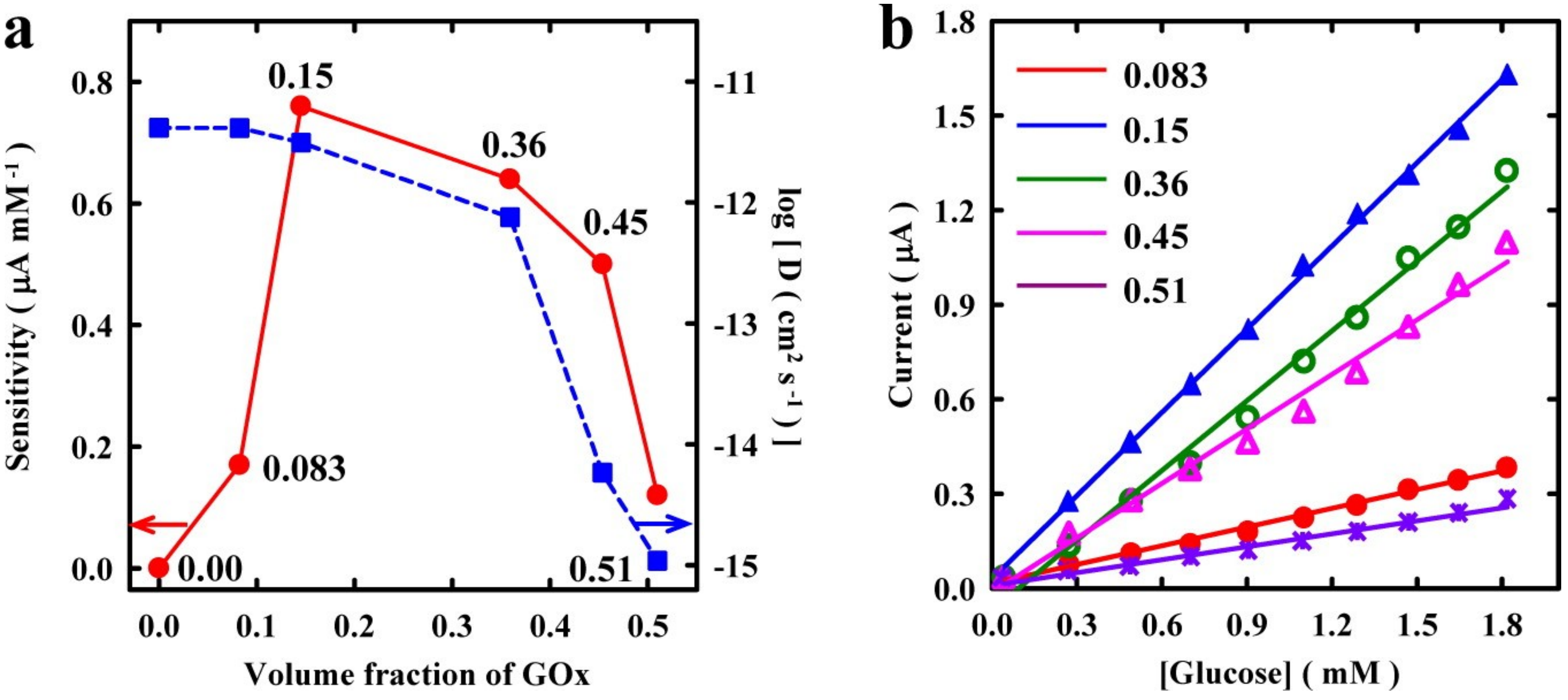
CVs demonstrating the amperometric detection of glucose in concentration range of 0 -1.8 mM using a GOx-DMIm-Au25 composite electrode



crease in anodic peak current varies linearly with concentration of gluc

Linear range: 0.028 – 2.0 mM

Sensitivity: 0.76 uA/mM

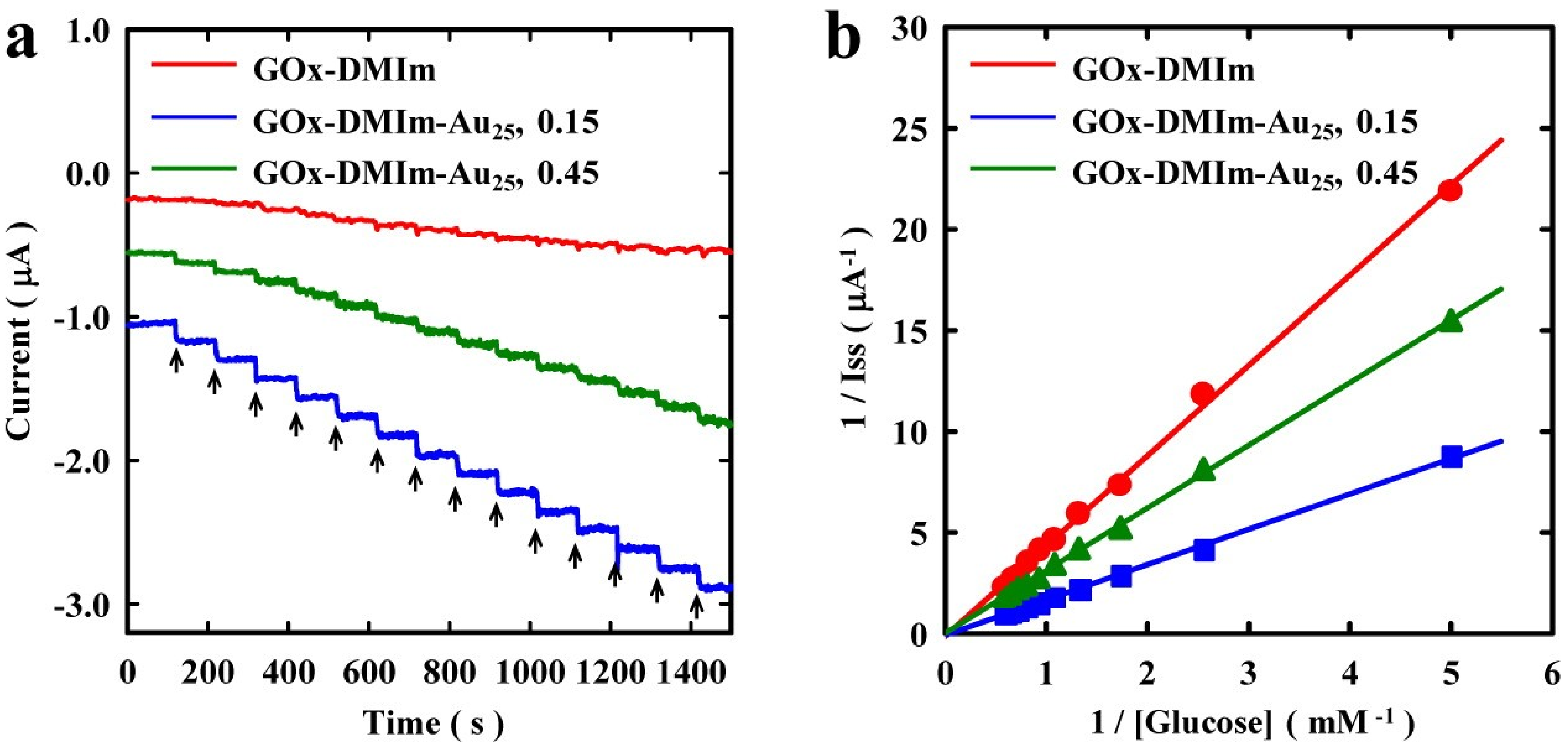


Electronic Diffusion Coefficient

&

Sensitivity

Lineweaver-Burk plots



Sensitivity	Sensitivity	Km values
0.21 uA/mM at 0.5 V	0.85 uA/mM	9.3 mM
	0.43 uA/mM	3.4 mM (< NPs
	at 0.31 V	5.1 mM

SUMMARY AND CONCLUSIONS

- ❖ A multifunctioning ionic liquid of a quantum-sized gold cluster can be prepared by ion-pairing of anionic MPS-Au25 with imidazolium cations for the first time.

- ❖ Voltammetry study of the Au25 ionic liquid film shows that it is electrically conductive, and the electron transport in the film occurs via diffusion-like electron hopping process.

- ❖ Composite enzyme electrodes fabricated easily by incorporating GOx in this homogeneous ionic liquid film exhibit excellent mediated electrocatalytic activity that can be successfully exploited for the detection of glucose.

- ❖ The Au25 clusters in the composite films act as efficient redox mediators as well as electronic conductors whose transport dynamics was found to control the sensing sensitivity.

- ❖ Combined with the unique properties of ionic liquids, these cluster ionic liquids may find important applications not only in biosensors but also in many other electrochemical devices.

FUTURE PROSPECTS

- Functional lignads to be chosen for exploring the utilities of monolayer protected clusters:

    Organic electron acceptors with Au25: TCNE ?
    Cluster based conducting polymers utilising redox properties of clusters

- Linking monolayer protected clusters of different nuclearity through

    lignad-mediated bonding
    Ionic bonding between cluster cores: $[Au25]^{-}[cluster]^{+}$

- Linking monolayer-protected clusters with other family of clusters through redox mediation and covalent bonding.

THANK YOU