

Magnetic Fe₃O₄ Carbon Aerogel and Ionic Liquid Composite Films as an Electrochemical Interface for Accelerated Electrochemistry of Glucose Oxidase and Myoglobin

Miao Li ^a, Sheying Dong ^{a*}, Nan Li ^b, Hongsheng Tang ^c, Jianbin Zheng ^c

^a *College of Sciences, Xi'an University of Architecture and Technology, Xi'an, 710055, China*

^b *Xi'an Chuanglian Huate Surface Treatment Tech. Co. Ltd., Xi'an 710055, China*

^c *Institute of Analytical Science, Shaanxi Provincial Key Laboratory of Electroanalytical
Chemistry, Northwest University, Xi'an 710069)*

*Corresponding author. Tel.: +86 29 82201203; fax: +86 29 82205332.

E-mail address: dongsyy@126.com (S.Y. Dong)

Appendix: EXPERIMENTAL SECTION

Preparation of the carbon paste electrode. Carbon paste electrode (CPE) was fabricated as follows: 3.4 g of graphite powder and 0.6 g of liquid paraffin were hand-mixed in an agate mortar and ground carefully to form a homogeneous paste. The prepared carbon paste was then tightly packed into a PVC tube (3 mm internal diameter) and a copper wire (1.5 mm external diameter) was inserted through the opposite end to establish an electrical contact. Prior to use, the bare CPE surface was first polished mechanically on a weighing paper and cleaned by distilled water.

Appendix: RESULTS AND DISCUSSION

Spectroscopic characterization of the composite film.

The FTIR spectra of CA and Fe₃O₄-CA/IL composite film were shown in Fig. S1. As we can see, the Fe₃O₄-CA/IL composite film shown obvious absorption at 576 cm⁻¹ corresponding to Fe-O bond with the forming of Fe₃O₄-CA. Two important bands at 1125 and 1100 cm⁻¹ were assigned to the stretching vibration of N₁C₂ and C₅N₁ for [BMIm]BF₄ IL, respectively. Moreover, the symmetric deformation and bend stretching vibration peak of -CH₃ was appeared at 1428 and 1467 cm⁻¹. It is also clearly observed that the situation at 1600 cm⁻¹ consistent with the skeletal vibration of benzene ring in CA, and 2870 and 2935 cm⁻¹ were corresponded to symmetric and asymmetric stretching vibration of -CH₃ and -CH₂-, respectively. In addition, the stretching vibration peaks of C₄H, C₅H and C₂H for N-methylimidazole were appeared at 3105 and 3145 cm⁻¹. The strength peak at 3400 cm⁻¹ was ascribed to the vibration of -OH in CA. The combination between Fe₃O₄-CA and IL leads to an

apparent increase of the intensity of the O-H peaks, which could form numerous hydrogen bond and would be benefit to the association of GOx and Mb.

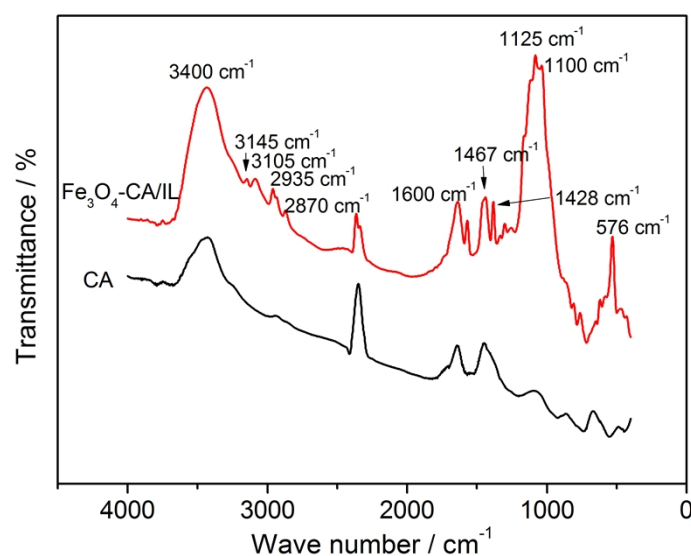


Fig. S1 FTIR spectra of CA and Fe₃O₄-CA/IL composite film

UV-Vis adsorption spectroscopy is also an effective method to probe the structure change of proteins. The shape and location of the Soret absorption band of GOx could provide structural information about possible denaturation of protein, especially the conformational change around the flavin adenine dinucleotide (FAD). As supported by the results in Figure S2A, the absorption peak of native GOx (curve a) at nearly 279 nm was ascribed to the characteristic of polypeptide chains. The positions and shapes of adsorption bands for IL/GOx and Fe₃O₄-CA/IL/GOx were almost the same as pure GOx, indicating that GOx immobilized in Fe₃O₄-CA/IL nanocomposite film indeed retained its native structure. FT-IR spectroscopy was further conducted to provide additional information for the secondary structure of GOx in the presence of Fe₃O₄-CA and IL. As shown in Figure S2B, the two characteristic peaks of Fe₃O₄-

CA/IL/GOx appeared at 1635 and 1435 cm^{-1} , which were slightly shifted as compared to those of native GOx of 1641 and 1438 cm^{-1} attributed to amide I and II bands of enzyme, respectively.

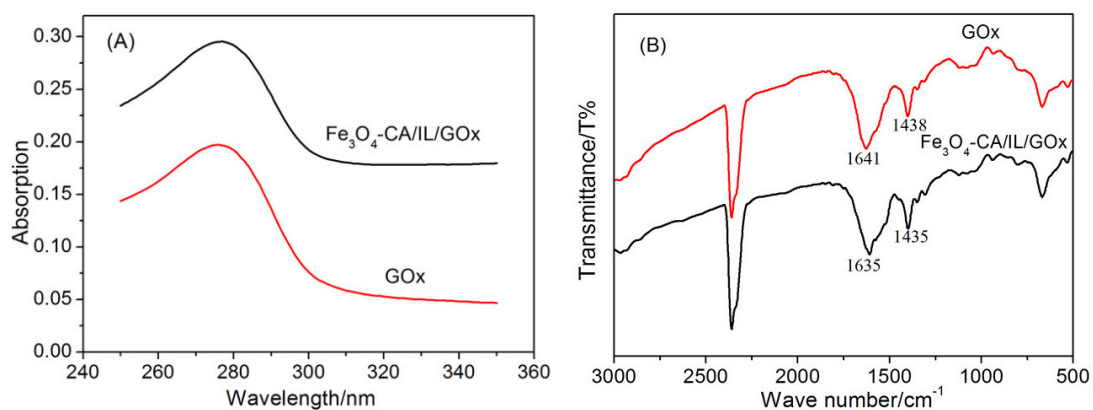


Fig. S2. (A) UV-vis spectra of GOx and Fe₃O₄-CA/IL/GOx in 0.1M pH 7.0 PBS solution. (B) FT-IR spectra of GOx and Fe₃O₄-CA/IL/GOx film.

Similarly, the UV-Vis spectra of Mb in the solution of Fe₃O₄-CA and IL were shown in Figure S3A, the Soret band also appeared at about 409 nm without apparent changes compared with pure Mb, which indicated that Mb molecules kept its native structure in the mixture Fe₃O₄-CA/IL. Moreover, the secondary structure of Mb could be investigated by FT-IR. As shown in Figure S3B, the amide I and II bands of Mb in Fe₃O₄-CA/IL (1645 and 1528 cm^{-1}) were similar to the free Mb (1650 and 1525 cm^{-1}).

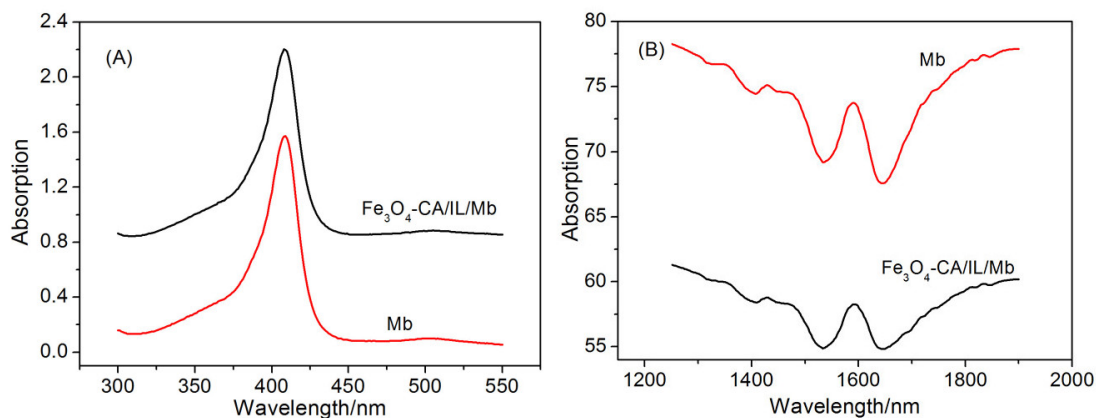


Fig. S3. (A) UV-vis spectra of Mb and $\text{Fe}_3\text{O}_4\text{-CA/IL/Mb}$ in 0.1M pH 7.0 PBS solution. (B) FT-IR spectra of Mb and $\text{Fe}_3\text{O}_4\text{-CA/IL/Mb}$ film.

The aforementioned results confirmed that the native structure of GOx/Mb had been retained because of the convenient microenvironment provided by the excellent biocompatible $\text{Fe}_3\text{O}_4\text{-CA/IL}$ composite. The small difference between native GOx/Mb and GOx/Mb immobilized in nanocomposite film might result from the intermolecular interaction between enzyme and $\text{Fe}_3\text{O}_4\text{-CA/IL}$ film. On the basis, $\text{Fe}_3\text{O}_4\text{-CA/IL}$ membrane could provide a new channel to realize the direct electrochemistry of GOx/Mb.