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#### ACCEPTED MANUSCRIPT

# Three-dimensional molecularly imprinted electrochemical sensor based on Au NPs@Ti-based metal-organic frameworks for ultra-trace detection of bovine serum albumin

Dingding Duan <sup>a</sup>, Hua Yang <sup>a</sup>, Yaping Ding <sup>1</sup>\*, <sup>a</sup>, Daixin Ye <sup>b</sup>, Li Li <sup>2</sup>\*, <sup>a</sup>, Guohong Ma <sup>a</sup> College of Sciences, Shanghai University, Shanghai 200444, PR China

<sup>b</sup>Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg S-41296, Sweden

Abstract: A novel three-dimensional molecularly imprinted electrochemical sensor (MIECS) was fabricated for ultra-trace detection of biomacromolecules bovine serum albumin (BSA), which was based on 3D porous electrocatalytic framework materials (AuNPs@NH<sub>2</sub>-MIL-125(Ti) composites) and graphene modified glassy carbon electrode. The AuNPs supported amino-functionalized Ti-benzenedicarboxylate porous metal-organic frameworks (Au/NH<sub>2</sub>-MIL-125(Ti)) was prepared by a simple and rapid ultrasonic method. The stable proteins molecularly imprinted polymers (MIPs) films were fabricated by electropolymerization using L-cysteine (L-Cys) as functional monomers and BSA as templates. The monomer L-Cys interact with AuNPs by Au-S bonds and interact with BSA by hydrogen bonding and electrostatic interaction, which was characterized with UV-vis spectra. The morphology of the MIP modified electrode was characterized by scanning electron microscopy, transmission electron microscopy and atomic force microscope. Under the optimal conditions, the 3D MIECS exhibited a wide linear range of  $10^{-18}$  g ml<sup>-1</sup> to  $10^{-12}$  g ml<sup>-1</sup> of BSA and a extremely low detection limit of 4.147×10<sup>-19</sup> g ml<sup>-1</sup>. The 3D MIECS has been applied to the assay of BSA in liquid milk samples with satisfying results.

*Key words:* Molecularly imprinted electrochemical sensor; Au nanoparticles; metal-organic frameworks; bovine serum albumin; L-cysteine

E-mail address: wdingyp@sina.com (Y.P. Ding), lilidu@shu.edu.cn (L. Li)

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<sup>\*</sup> Corresponding author: Tel: +86-21-66134734; Fax: +86-21-66132797

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