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## **ACCEPTED MANUSCRIPT**

## Visual electrochemiluminescence ratiometry on bipolar electrode for

### bioanalysis

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#### Abstract

In this work, we developed a visual ECL ratiometry on a closed bipolar electrode (BPE) for the detection of prostate specific antigen (PSA), prostate cancer biomarker. High efficient CdTe QDs was synthesized which emitted visualized red light at BPE cathode. Integrating with the anodic ECL emitters, luminol, visual emission of red-blue ratiometric ECL was achieved in BPE array chips. As a sensing probe, Au NRs nanocomposite was assembled on the surface of the cathode and acted as both the quencher of the CdTe QDs ECL and the promoter of the luminol ECL. After incubated with PSA, the Au NRs nanocomposite was peeled off from the electrode surface due to the specific recognition between PSA and aptamer. Consequently, the cathode ECL partly recovered and the anode ECL turned off. By measuring the ratio of visual ECL intensity at two poles of BPE, sensitive detection of PSA was achieved with a linear range from 1.0 ng/mL to 1.0 µg/mL and detection limit of 0.5 ng/mL (S/N=3). This strategy combining the BPE-ECL and visual ratiometry provided an accurate and intrinsic way for the sensing of PSA and showed good perspective in the clinical diagnosis.

Keywords: Visual; Ratiometry electrochemiluminescence; Bipolar electrode; Prostate specific antigen; CdTe quantum dots; DNA-modified gold nanorods

#### 1. Introduction

Electrochemiluminescence (ECL) is a light emission process triggered by electrochemical excitation of molecules or quantum dots (QDs) (Ding et al. 2002; Kim et al. 2005; Zanarini et al. 2009). It is remarkably sensitive, which has been widely used for immune assay in the clinical

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