Electronic Supplementary Information

An electrochemiluminescent microRNA biosensor based on hybridization chain reaction coupled with hemin as the signal enhancer

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S1. the SEM image of the Au NPs

As shown in the Fig. S1., Au NPs were electrodeposited on the surface of the electrode rather than a Au thin layer film, which provided valuable data about the real shapes of the nanoparticles.



Fig. S1. SEM image of Au NPs.

S2. ECL comparison of hemin and HRP for miRNA detection

Both hemin and HRP showed peroxidatic activity on luminol/H₂O₂ system through catalyzing the decomposition of H₂O₂. In order to further investigate the effect of hemin and HRP, we detected the ECL intensity with hemin (7 μ M) and HRP (7 μ M) modified GCE in 2 mL PBS (pH 7.4) with 1.00×10⁻⁴ M luminol and 3.50×10⁻⁵ M H₂O₂, respectively. As can be seen from Fig. S2, HRP/GCE showed a lower ECL intensity, indicating the poor catalytic efficiency to H₂O₂ (curve blue). However, an obviously amplified ECL signal of hemin/GCE was achieved (curve red). Such results indicated the excellent amplified property of the proposed biosensor with hemin, which may ascribe to the following reasons: hemin, which is enable to maintain high catalytic activities, showed remarkable catalyzing performance towards H₂O₂. Besides, hemin was introduced by intercalating into the grooves of the dsDNA, so there were

amounts of hemin to catalyze the decomposition of H_2O_2 . The biocompatible dsDNA could not only improve the amount of immobilized hemin but also efficiently maintain its catalytic activity and improve the stability. However, there were a small number of HRP immobilized on the surface of the electrode. Based on the above advantages, application of hemin modified electrode is becoming a commonly used method to sensitize and amplified the ECL signal¹⁻².



Fig. S2. ECL intensity of the biosensor in 2 mL PBS (pH 7.4) with 1.00×10^{-4} M luminol and 3.50×10^{-5} M H₂O₂ by using different catalysts: the blue one is the biosensor with 7 μ M HRP as the enhancer, the red one is the biosensor with 7 μ M hemin as the enhancer.

Reference:

- 1 P. Kara, D. Ozkan, K. Kerman, B. Meric, A. Erdem, M. Ozsoz, *Analytical and Bioanalytical Chemistry*, 2002, **373**, 710-716.
- 2 R. L. Af, G. C. Mueller, *The journal of biological chemistry*, 1983, **258**, 12069-12072.