supplemental information

Ultrasensitive electrochemiluminescence detection of lengthy DNA molecules based on dual signal amplification

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Preparation of CdTe QDs

The preparation of the water-soluble CdTe QDs was reported previously [1]. Herein, we took a method similar to that involved in the article mentioned above. In brief, 0.1980 g of $CdCl_2 \cdot 2.5 H_2O$ was dispersed in 50 mL of water, and then 160 μL of TGA was added. The pH of the turbid suspension was adjusted to 11 by NaOH solution (1.0 M) to get the clear solution. The resulting solution was bubbled with highly pure N_2 for 30 min to form the CdTe precursors, and a 10.0 mL of the NaHTe solution (obtained by the reaction of 0.1190 g $NaBH_4$ and 0.0492 g Te powder in oxygen-free water) was injected into the vigorously stirred solution immediately. The obtained QDs solutions were refluxed for different time to form different sizes of QDs by refluxing at 100 ℃.

Optimization of experimental conditions

Figure S1

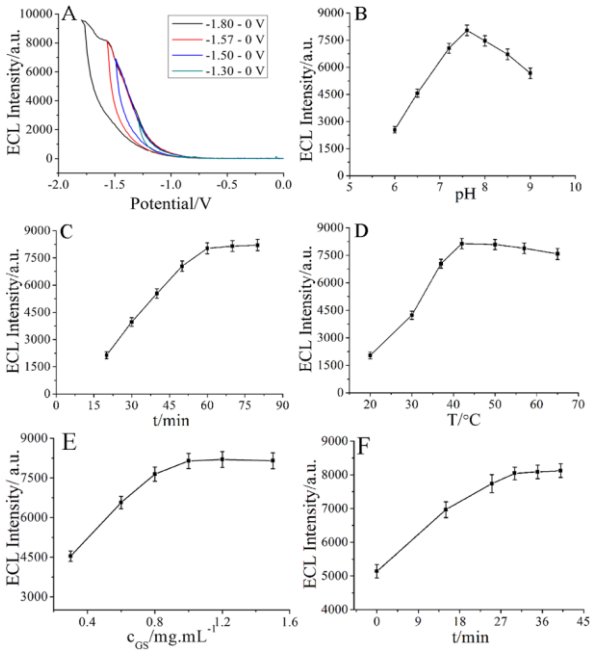

Figure S1. Effect of potential (A), pH (B), incubation time (C), hybridization temperature （D）, the concentration (E) and dispersity (F) of graphene on the ECL intensity.

To obtain the best detection sensitivity and selectivity for the DNA assay, some factors, such as applied potential, pH value, hybridization time, hybridization temperature and the concentration and dispersity of graphene have been systematically investigated and optimized.

The effect of applied potential over the different ranges in Tris-HCl solution (10 mM) containing 0.05 M $K_2S_2O_8$ as the coreactant at pH 7.8 was studied (Figure S1A). In the view of high intensity and good ECL peak shape, the optimal scanning potential of -1.56 - 0 V was employed for the following experiments.

It is well known that the ECL performance of CdTe QDs was dependent greatly on the pH of the solution. The influence of pH in the range of 6.0 - 9.0 (10 mM Tris-HCl) on the ECL intensity was examined. As shown in Figure S1B, the maximum ECL intensity was obtained at pH 7.8.

The effect of the hybridization time has also been investigated. The target DNA was incubated with an immobilized probe at 42 °C for different times from 20 to 80 min. The signal responses of the assay to the different hybridization times were shown in Figure S1C. It can be seen from this figure that the signal increased rapidly when the hybridization time increased from 20 to 60 min and then inclined to a constant value from 60 to 80 min, indicating that the hybridization reaches equilibrium at 60 min. As a result, a reaction time of 60 min was selected for the DNA hybridization.

Figure S1D shows the effect of the hybridization temperature on the efficiency of DNA hybridization. In this study, a 10^{-16} M complementary target DNA was incubated with the CdTe/ZnO labeled S_3 at pH 7.8 for 60 min at a series of temperatures ranging from 20 to 65 °C. As shown in Figure S1D, the highest signal was obtained at 42 °C. Therefore, a hybridization temperature of 42 °C was selected in the following experiments.

Effect of the concentration and dispersity of graphene on the ECL intensity was also researched. From Figure S1E, it was observed that the ECL response increased with the increasing of the concentration of graphene, and increased little when the concentration was higher than 1 ng·mL^{-1}. So the concentration of 1 ng·mL^{-1} was selected for graphene. Different dispersity of graphene was obtained by changing the ultrasonic time of graphene solution. From Figure S1F, we can see that signal increases when the ultrasonic time increased from 0 to 30 min and then inclined to a constant value from 30 to 45 min. As a result, we choose 30 min of ultrasonic time to obtain the optimal dispersity of graphene.

Figure S2

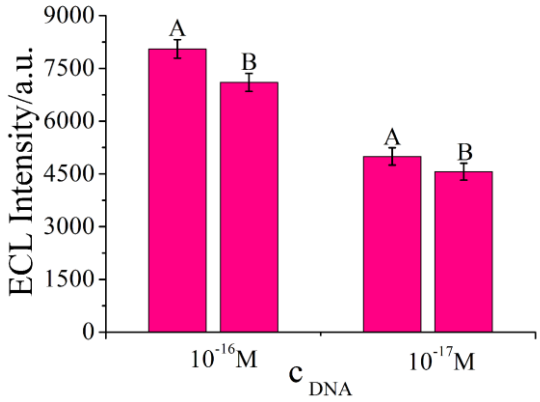

Figure S2. Comparison of ECL signals for unheated electrode (A) and heated (95 ℃ for 3 min) electrode (B) hybridized with a series of target DNA for 10^{-16} M and 10^{-17} M, respectively. Error bars showed the standard deviations of measurements.

Figure S3

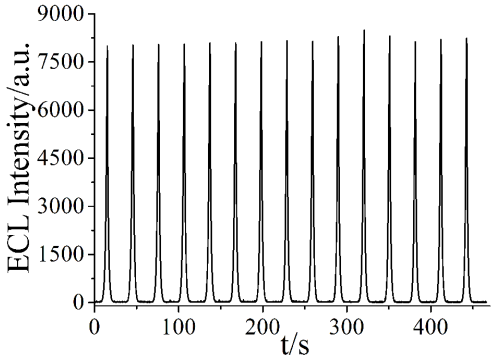

Figure S3. ECL emission of the DNA biosensor. Scan rate: 0.1 $V \cdot s^{-1}$. The voltage of the PMT was set at 800 V.

Figure S4

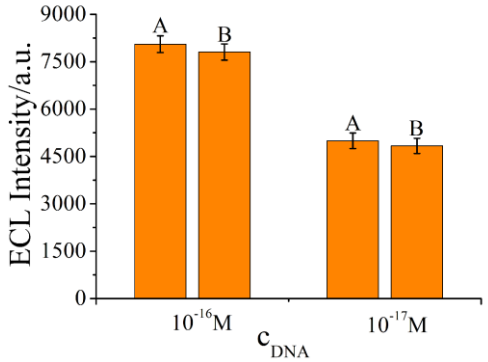

Figure S4. Comparison of ECL signals for first prepared DNA biosensor (A) and two weeks later (B) hybridized with a series of target DNA for 10^{-16} M and 10^{-17} M, respectively. Error bars showed the standard deviations of measurements.

Figure S5

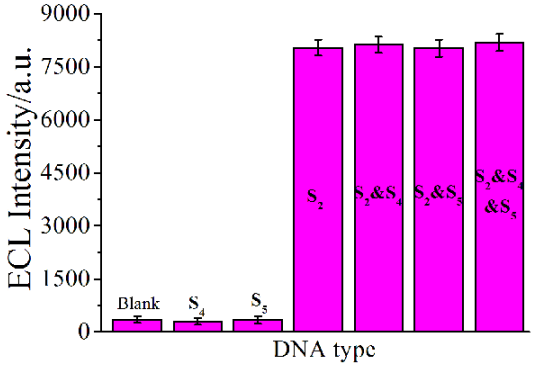

Figure S5. Specificity of the DNA sensor.

References

[1] N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski, A. Eychmüller, H. Weller, *J. Phys. Chem. B.*, 2002, **106**, 7177.