Supplementary material (ESI) for Journal of Materials Chemistry

Supporting information

Sunlight-induced formation of silver-gold bimetallic nanostructures on DNA-template for highly active surface enhanced Raman scattering substrates and application in TNT/tumor markers detection

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Experimental

Electrical measurements

Two-terminal two-probe currents measurements were taken using a picoammeter/ voltage source (Keithley 6487) in the range 0–500V, the dc current sensitivity of the system is in the range 10^{-14}A. Timed data acquisition was performed using a LabView® program and the current sampling frequency was set at two samples per second. Bias voltage was set at V=0.1V in all of the experiments. The electrical measurements were repeated many times until the signal is stable.

Synthesis of silver nanowires in DNA

An aqueous solution of $AgNO_3$ (100 μL, 1 mM) was added to a solution of λ-DNA (20 μL, 300 ngμL^{-1}, the diluted DNA solution is 50 ngμL^{-1}), and the solution was mixed thoroughly and kept for 3 h at room temperature. Then photoreduction was performed directly by exposure to the sunlight. The solution changed from colorless to yellow, and to gray gradually, indicating the formation of silver nanoparticles. The

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exposing time was controlled from several minutes to several hours. The samples for electrical measurement were prepared by depositing a drop (3 μL) of the Ag-DNA solution onto the surface of comb-like gold electrodes.

Results and Discussion

To test the electrical transport capabilities of the Ag-DNA networks, electrically contacted networks of wires were fabricated by dropping Ag-DNA solutions onto 15 nm thick comb-like gold electrodes which were setup on silicon (400 nm oxide) substrate.

Figure S1

The electrical characterization of nano-networks of the metallized DNA is investigated and a typical time response of the output currents to CEA solution under different concentration is shown in Figure S1, indicating that the output current increases rapidly and converges after about 2 seconds in the CEA solution, due to possible increase of the electric charge density on the electrode surface. Furthermore, this result indicates that the reaction between the immobilized Ag-DNA and free CEA is a dynamic equilibrium process. Additionally, the real-current obviously increases when the concentration of CEA solution is increased towards 40 ngμL^{-1}; in contrast, the real-current decreases with the increase of the concentration of CEA solution beyond 40 ngμL^{-1}. Unfortunately, the reasons for this phenomenon have not been clarified yet. Influence from irradiation time of Ag-DNA networks for detecting CEA is also considered. Compared to the current intensity (10.1μA) from curve 2 in Figure S2A, the current intensity (14.1μA) of Ag-DNA network (refer to curve 1) at long irradiation time is high. Also, different mesh sized Ag-DNA network for detection of CEA is investigated and the result reveals that current intensity (6.94 μA) of the sparse Ag-DNA network (see curve 3 in Figure S2A) is remarkably weaker than that (10.1μA) (refer to curve 2 in Figure S2A) of the thick Ag-DNA network. In addition, real-time detection for human sera of healthy persons without CEA is carried out and the background current (0.594μA) in Figure S2B is obtained, suggesting that the presence of CEA in solution play a crucial role in influencing the value of current. It

should be mentioned that the reproducibility of the Ag-DNA network is excellent on the basis of repetitive measurements or regeneration cycles performed at 5, 10, and 20 ngμL^{-1} CEA.

Figure S2

In order to further assess the nature of the observable alteration, a series of control experiments have been carried out. The current (*ca.* 10μA referring to Figure S1 and Figure S2A) of gold electrode covered with metallized Ag-DNA networks in the 10 ngμL^{-1} CEA solution is much higher compared to those of the blank electrode (1.29-1.57 nA, see Figure S3) and the gold electrode covered with DNA (3.15-3.56 nA, see Figure S4) in the 10 ngμL^{-1} CEA, respectively, indicating that the Ag-DNA networks are very important in detecting CEA. In addition, a control experiment is carried out to investigate the interaction between Ag-DNA network and Alpha Fetal Protein (AFP). A typical time response of the output currents to AFP solution under different concentration is shown in Figure S5. The data show that the value of current is very small and change a little.

In summary, this methodology could be satisfactorily applied to the clinical determination of the CEA level in humans in that the sensor fabricated by this approach is very stable and no obvious change can be observed after two-week storage in dry air at 4 ^{0}C .

Figure S3, Figure S4 and Figure S5

Although the formulation of a detailed mechanism is premature at this stage, it seems reasonable to assume that silver nanoparticles and biomolecule DNA are synergistic in detecting CEA. In this study, a nontoxic biomimetic interface of reaction with CEA on a gold electrode surface could be constructed by biocompatible silver nanoparticles. Consequently, more freedom in orientation of the biomolecule CEA can be allowed in the analogous natural environment. Thus the activity of proteins can be efficiently retained and leakage of protein from the electrode interface is effectively prevented, which is similar to Yuan's report, *i.e.*, the sensor based on the combination of a magnetic core and an Ag metallic shell showing good adsorption

properties for the attachment of the CEA. [1] With the aid of the opinion of identification of cancer markers from antibody-antigen interaction,[1-8] nano-Ag/DNA are immobilized onto the sesnor's surface and CEA molecules can bind to these molecules.

References

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Figure captions

Figure S1. Real-time detection of different concentration of CEA (DNA network: 50 ngμL^{-1}, irradiation times: 30 min).

Figure S2(A). Real-time detection of the current for different Ag-DNA networks. curve 1 (DNA network: 50 ngμL^{-1}, irradiation times: 10 min); curve 2 (DNA network: 50 ngμL^{-1}, irradiation times: 30 min); curve 3: (DNA network: 30 ngμL^{-1}, irradiation times: 10 min). The concentration of CEA is 5 ngμL^{-1} in all the experiments.

(B). Real-time detection of the current for sera of healthy persons (DNA network: 50 ngμL^{-1}, irradiation times: 30 min).

Figure S3. Real-time detection of 10 ngμL^{-1}CEA using blank comb-like Au electrode.

Figure S4. Real-time detection of 10 ngμL^{-1} CEA using comb-like Au electrode

placed DNA.

Figure S5. Real-time detection of different concentration of AFP (DNA network: 50 ngμL^{-1}, irradiation times: 30 min)

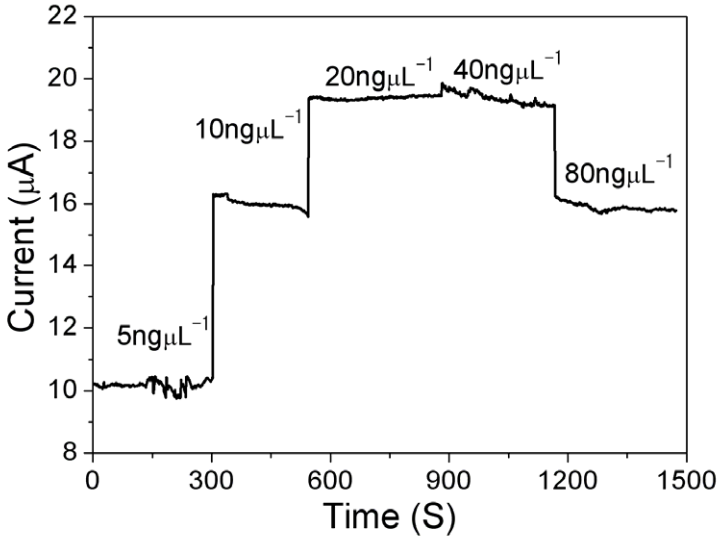
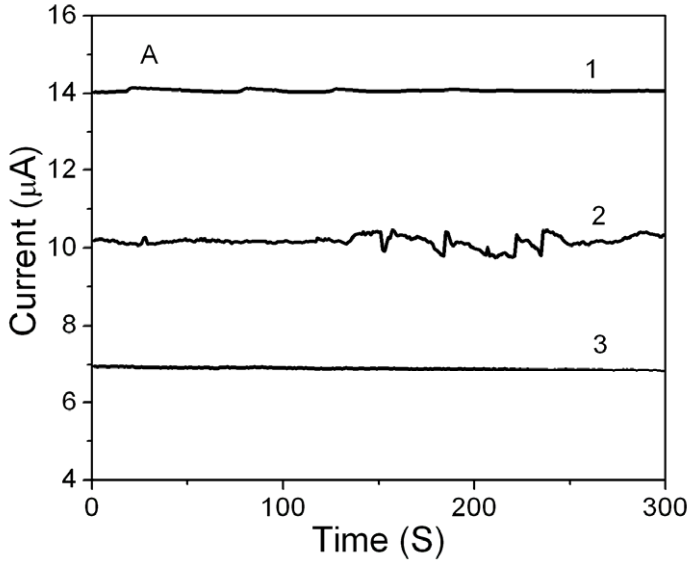


Figure S1



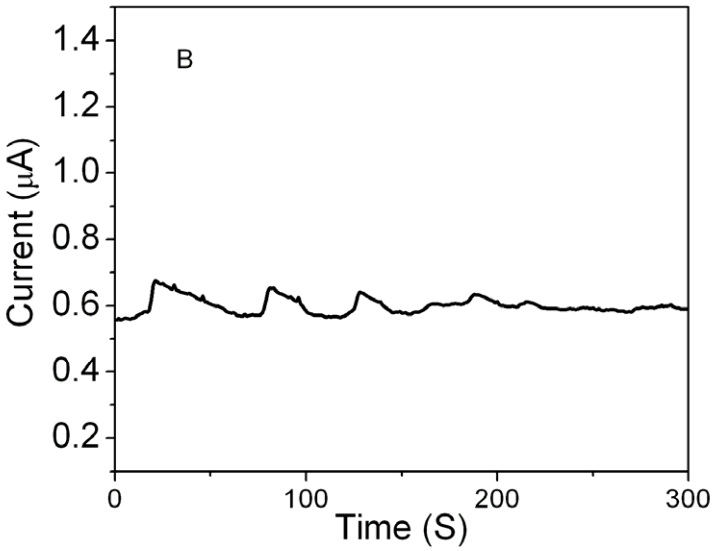


Figure S2(A) and S2(B)

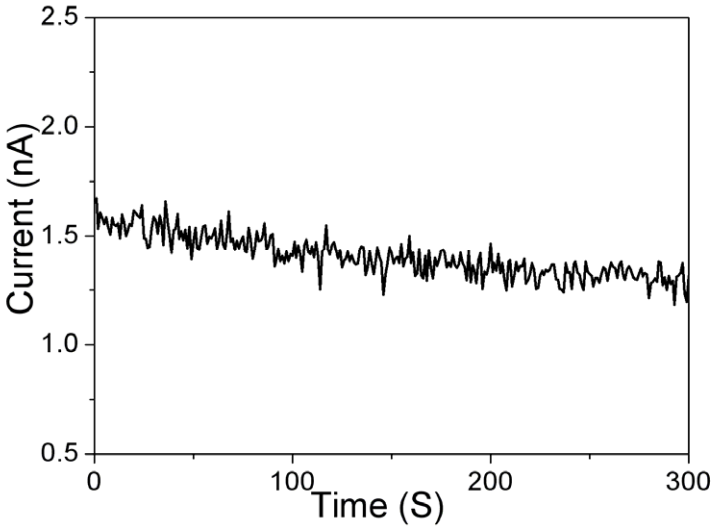


Figure S3

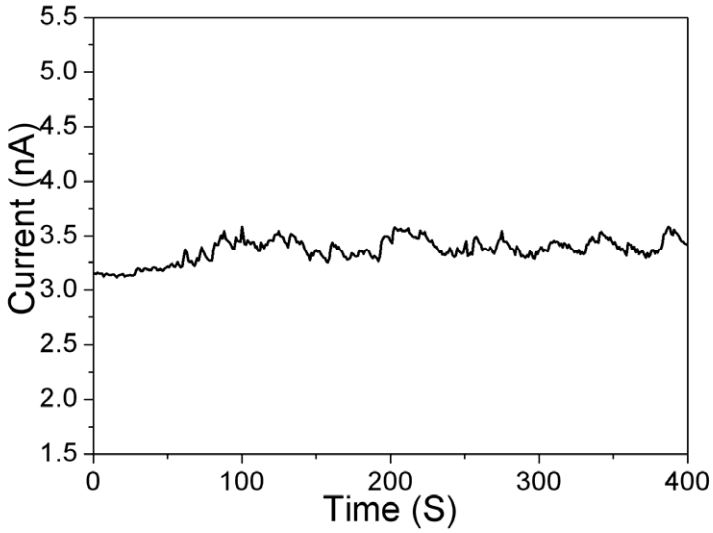


Figure S4

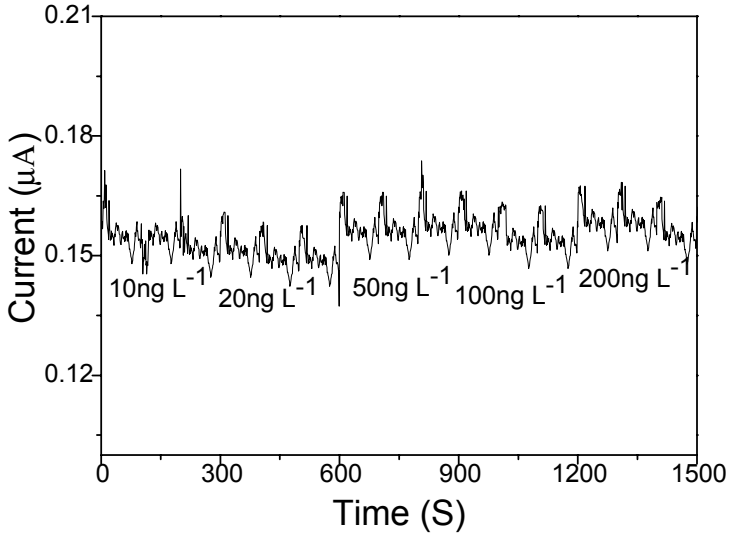


Figure S5