Electronic Supplementary Material (ESI) for Analyst.

SUPPLEMENTARY INFORMATION

Gold Nanoparticles/Polymer Nanocomposite for Highly Sensitive Drug-DNA Interaction

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Experimental

2.1. Apparatus

Electrochemical studies were carried out with CH Instruments System, Model 660 B. A platinum (Pt) (Aldrich) disc working electrode (area: 7.85×10^{-3} cm^2), an Ag/AgCl reference electrode (BAS, USA) and a Pt (Aldrich) counter electrode were used. Atomic force microscopy (AFM) (Nanomagnetics, UK) was used for the surface characterization.

2.2. Chemicals

Vinylferrocene was purchased from Aldrich (USA). Gold nanoparticles (AuNPs) (particle size: 20 nm) were from Sigma-Aldrich (USA). Fish sperm DNA (fsDNA) was obtained from Serva (Germany). Mitomycin C (MC) was purchased from Sigma (USA). Other chemicals were in analytical reagent grade and they were supplied from Sigma and Merck.

2.3. The preparation of solutions

Phosphate buffer solution (50 mM, pH 7.4) containing 0.1M $NaClO_4$ was prepared from $NaH_2PO_4.2H_2O$ and $Na_2HPO_4.2H_2O$ using distilled water. Acetate buffer solution (50 mM, pH 4.8) was prepared from $NaCH_3COO$ and CH_3COOH using distilled water. DNA and MC stock solutions were prepared with ultrapure tri-distilled water. The diluted solutions of DNA and MC were prepared by using PBS containing 20 mM NaCl.

Poly(vinylferrocene) (PVF) was prepared by the chemical polymerization of vinylferrocene with AIBN initiator [1]. 1.0 mg mL^{-1} PVF polymer solution was prepared in methylene chloride/tetra-n-butyl ammonium perchlorate (TBAP) solvent/supporting electrolyte system. AuNPs/PVF solution was prepared in methylene chloride/TBAP using 1:10 diluted form of AuNPs and 1.0 mg mL^{-1} PVF.

2.4. Procedure

All the experiments were done at room temperature. Each test was repeated three times.

The preparation of AuNPs/poly(vinylferrocenium) (PVF^+) coated electrode: The AuNPs/PVF^+ coated Pt electrode was prepared by electrooxidation in AuNPs/PVF solution using Pt electrode at +0.7 V vs. Ag/AgCl. The PVF^+ coated Pt electrode was prepared by electrooxidation in AuNPs/PVF solution using Pt electrode at +0.7 V vs. Ag/AgCl. The thicknesses of the films were controlled by the charge passed during the electroprecipitation step. Thickness value corresponding to the passage of a charge of 1.0 mC during the elecropolymerization was used.

Immobilization of DNA onto the coated electrode: The preparation of DNA immobilized electrode was accomplished by immersing the coated electrode into DNA solution for 30 min by stirring. After immobilization of DNA onto the coated electrode, the electrode was washed with PBS.

Interaction of MC with DNA at PVF^+ coated electrode: MC solution was dropped onto the DNA immobilized coated electrode. After interaction of MC with DNA on the coated electrode, the electrode was washed with PBS.

Voltammetric transduction: Cyclic voltammetry experiments were performed in the potential range of +0.0 V to +1.0 V vs. Ag/AgCl at a scan rate of 100 mV s^{-1}. Differential pulse voltammetry studies were performed between +0.0 V and +1.4 V vs. Ag/AgCl at a pulse amplitude of 50 mV.

Impedance measurements: Electrochemical impedance spectroscopy measurements were controlled at the open-circuit value of +0.4 V and the frequency was varied over the range 10^5-10^{-2} Hz with an amplitude of 5 mV in 0.1 M KCl solution containing 5 mM $Fe(CN)_6^{3-/4}$.

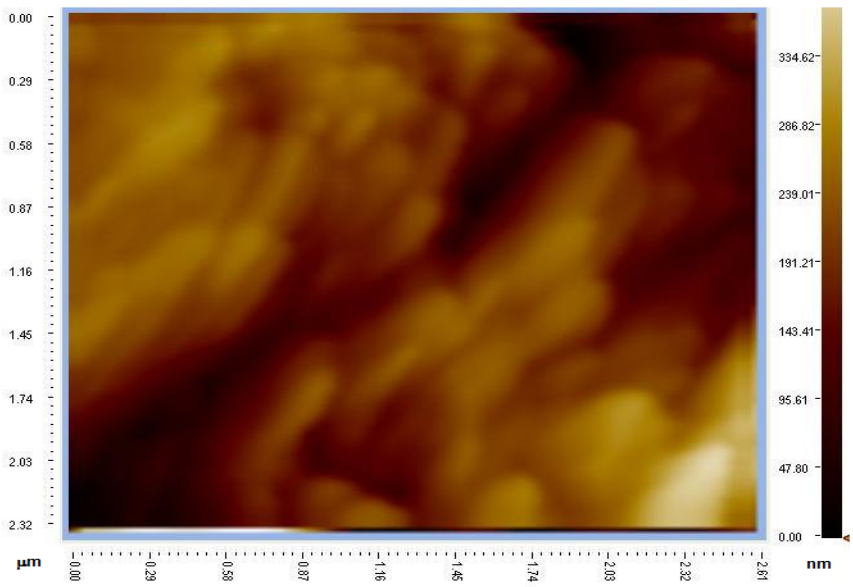

Figure S1. AFM image of AuNPs/PVF^{+}/Pt.

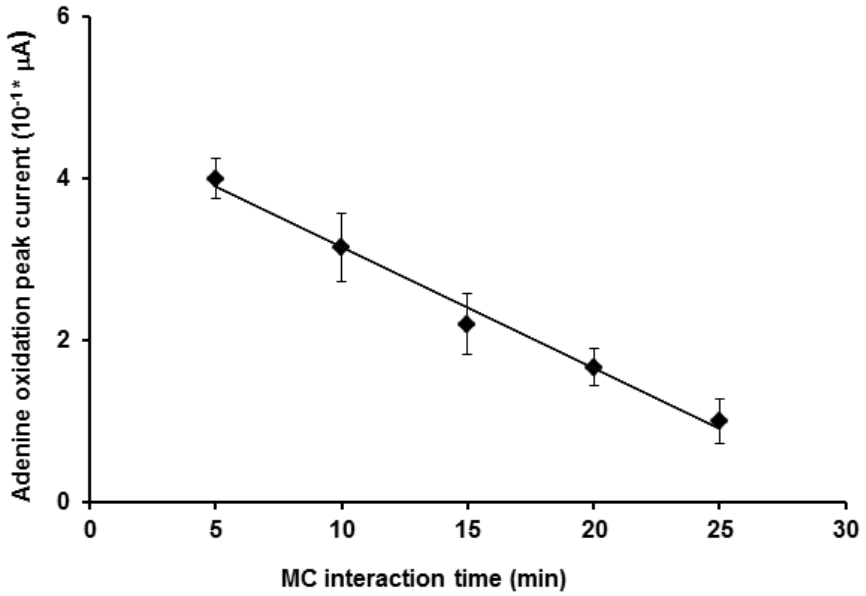

Figure S2. The changes in the oxidation peak currents of adenine after interaction of dsDNA/AuNPs/PVF^{+}/Pt with 100 ppm MC at different interaction times (n=3) (R^2=0.9910).

Reference

1. F. Kuralay, A. Erdem, S. Abacı, H. Özyörük, A. Yıldız, *Anal. Chim. Acta* 2009, **643,** 83.