Electronic Supplementary Material (ESI) for Analytical Methods.

Femtomolar determination of an ovarian cancer biomarker (miR–200a) in blood plasma using a label free electrochemical biosensor based on L–cysteine functionalized ZnS quantum dots

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S1. Equivalent circuit components to fit the Nyquist plots

Electrochemical impedance is considered as the sum of imaginary and real resistance. An electrical circuit is designed according to the conditions and results of each reaction process in the impedance, which includes resistors, capacitors or constant phase elements that are combined in series or in parallel. The best electrical circuit for a simple electrochemical process is the Randles circuit that includes R_S, C_{dl}/CPE, R_{ct} and W. $\mathbf{R_S}$ is the electrical resistance of the solution, which depends on the conductivity and cross-sectional area of the electrode and the distance to the solution. $\mathbf{C_{dl}}$**/CPE** indicates the electrostatic interaction between the electrode and the electrolyte, which depends on the electrode area and ionic strength. $\mathbf{R_{ct}}$ and **W**, these two represent the charge transfer kinetics in the reactions and were known as the charge transfer resistance at the distance between the electrode /electrolyte and the Warburg impedance, respectively.

Impedance spectra are represented by Nyquist plot and Bode plot. Nyquist plot usually consist of a semicircle related to the electron transfer process (at high frequencies) and a straight line corresponding to the diffusion process (at low frequency) as shown in Fig. S1.

In this work, Nyquist plots were used to evaluate the results of the proposed genosensor. As discussed in Section 3.2, the diameter of the semicircle (R_{ct}) in each step is larger than the previous step, which indicates an increase in resistance. Table S1 shows the results of fitting the Randles circuit corresponds to the Nyquist plots in Fig. 2.

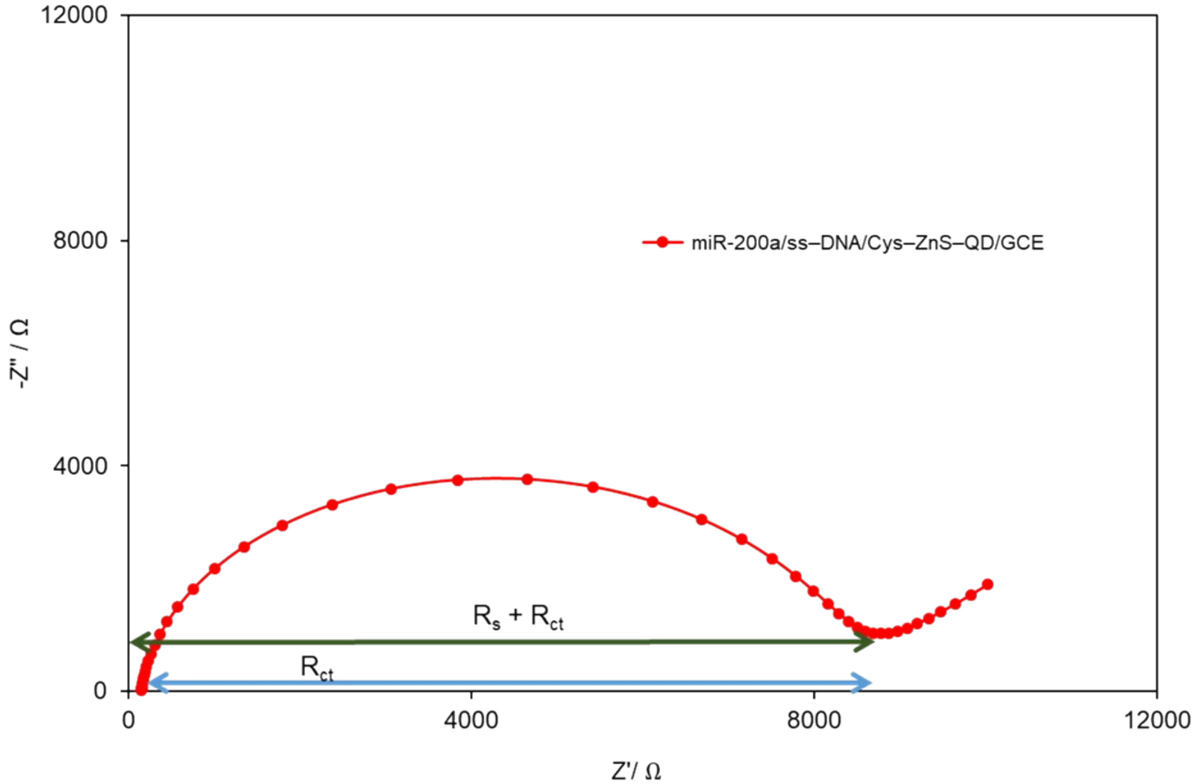

Fig S1. Nyquist plot arising from the Randles circuit

Table S1. The results of fitting the Randles circuit corresponding to the Nyquist plots of Fig. 2.

Electrode	R_S / Ω	CPE / µMho	R_{ct} / kΩ	W / µMho
Bare GCE	153±9.6	1.67±0.13	0.50±0.02	556±18
Cys–ZnS–QD/GCE	162±10.5	1.65±0.12	2.10±0.10	727±25
ssDNA/Cys–ZnS–QD/GCE	168±8.5	1.26±0.10	4.34±0.13	455±21
MiR-200a/ssDNA/Cys–ZnS–QD/GCE	159±6.5	1.11±0.09	8.08±0.13	488±23

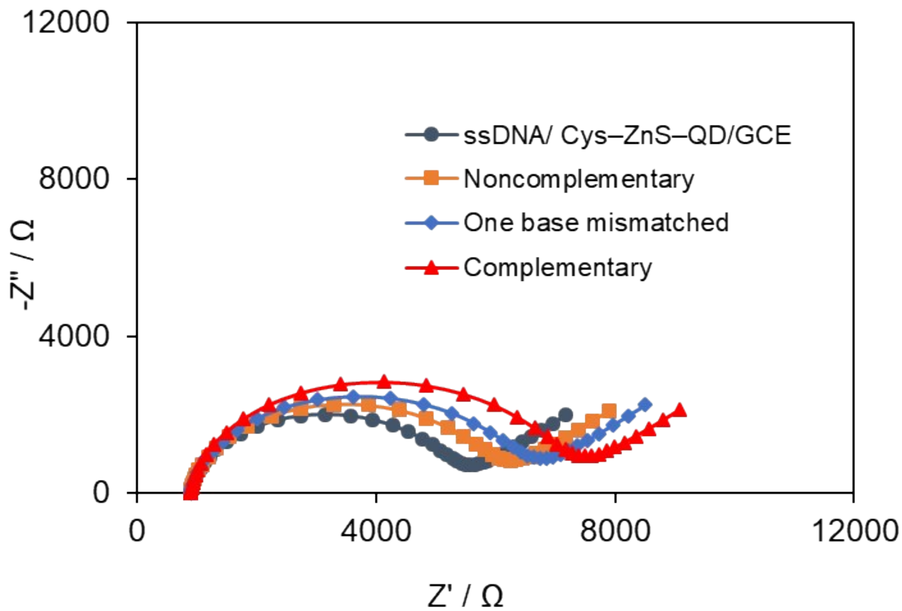

Fig S2. Nyquist plots of the ssDNA/Cys–ZnS–QD/GCE before and after hybridization with a 1.0×10^{-11} M of miR–200a (as a complementary sequence), one–base mismatch and noncomplementary sequence in a 0.1 M phosphate buffer (pH 7.0) containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl.

Table S2. The results of fitting the Randles circuit corresponding to the Nyquist plots of Fig. 4.

Electrode	R_S / Ω	CPE /µMho	R_{ct} / kΩ	W / µMho	X^2
ssDNA	924.7±15.1	1.26±0.10	4.34±0.13	455±23	0.02
1×10^{-14}	901.6±16.6	1.28±0.11	5.05±0.12	333±15	0.04
1×10^{-13}	895.2±15.1	1.03±0.10	5.42±0.15	470±20	0.09
1×10^{-12}	930.1±12.8	1.24±0.11	5.77±0.17	630±23	0.02
1×10^{-11}	919.8±17.7	1.78±0.13	6.19±0.16	618±25	0.09
1×10^{-10}	875.5±13.2	1.43±0.12	6.65±0.14	321±23	0.04
1×10^{-9}	864.2±17.4	1.58±0.13	6.94±0.15	336±21	0.01
1×10^{-8}	938.1±15.4	1.27±0.10	7.19±0.14	309±25	0.06
1×10^{-7}	845.5±15.5	1.90±0.14	7.69±0.16	350±24	0.05
1×10^{-6}	942.6±13.5	1.08±0.13	8.08±0.18	487±22	0.09