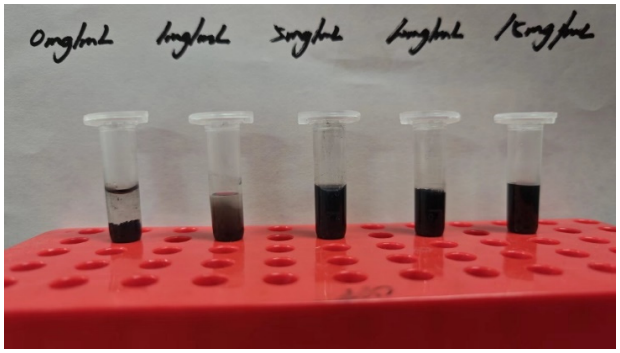

**Figure S1.** Comparation of BSA/Graphene nanocomposites with different BSA concentrations. The concentration of BSA in the samples are 0 mg/mL, 1 mg/mL, 5 mg/mL, 10 mg/mL, and 15 mg/mL, respectively.

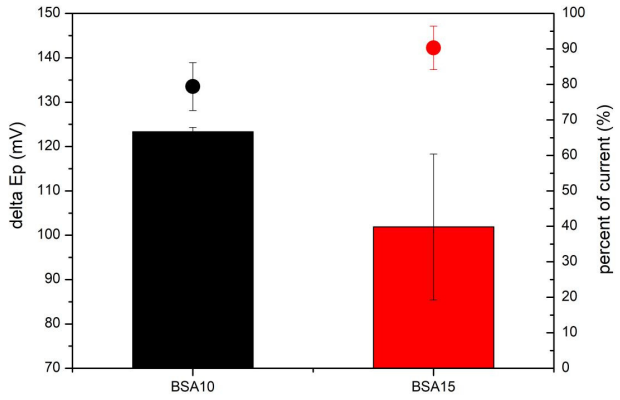


**Figure S2.** Statistical results of delta $E_P$ and current change after BSA-Graphene-GA modification of AuEs. Columns denote delta $E_p$ after modification, and dots denote the current percent.

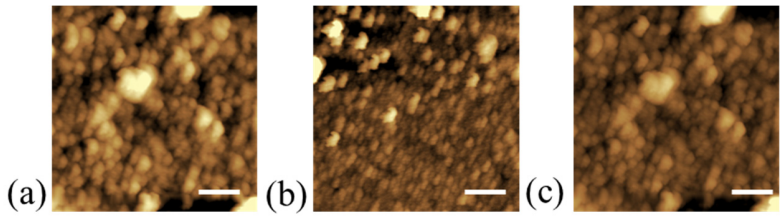


**Figure S3. AFM images of BSA/Graphene/GA modified gold electrode (a), after anti-CA19-9 antibody capture on BSA/Graphene/GA modified gold electrode (b), and after antigen (100 U/mL) capture on BSA/Graphene/GA modified gold electrode (c). Scale bar 400 nm.**

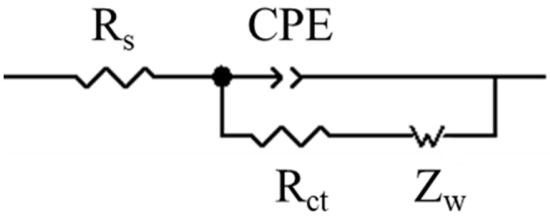


**Figure S4.** The modified Randles circuit model to fit the electrochemical impedance data.

**Table S1.** Comparison of this electrochemical immunosensor with previous reported biosensors for CA19-9 detection.

| Electrode modification | Technique | Detection range (U/mL) | LOD (U/mL） | Ref. |
|---|---|---|---|---|
| GE/anti CA19-9/TiO2-SAb19-9-MB | DPV | 1~100 | 1.6 | [31] |
| Zn-Co-S/graphene | LSV | 6.3~300 | 0.82 | [32] |
| HPR–CA19-9/Au–CPE | EIS | 2~30 | 1.37 | [33] |
| CB-polyelectrolyte/anti CA19-9 | DPV | 0.01~40 | 0.07 | [5] |
| PThi–SDS/AuNPs | EIS | 5~400 | 0.45 | [34] |
| MXene/HRP/anti CA19-9 | DPV | 0.002~30 | 0.001 | [28] |
| BSA15/Graphene/GA/anti CA19-9 | EIS | 6.25~1000 | 13.5 | This work |