Supplementary Information

A label-free electrochemical biosensor based on bimetallic organic framework for the detection of carbohydrate antigen 19-9

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Fig S1

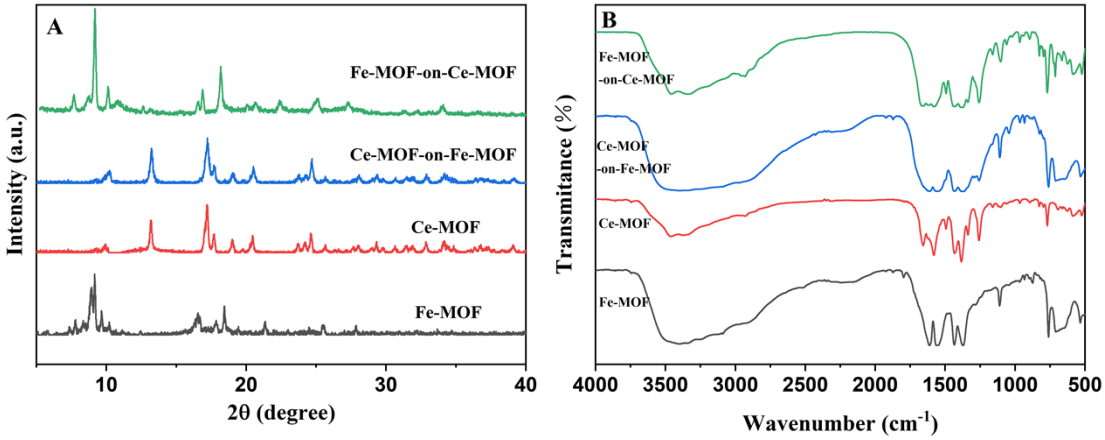

Fig. S1 (A) XRD pattern and (B) FTIR spectra of Fe-MOF，Ce-MOF，Ce-MOF-on-Fe-MOF and Fe-MOF-on-Ce-MOF.

Fig S2

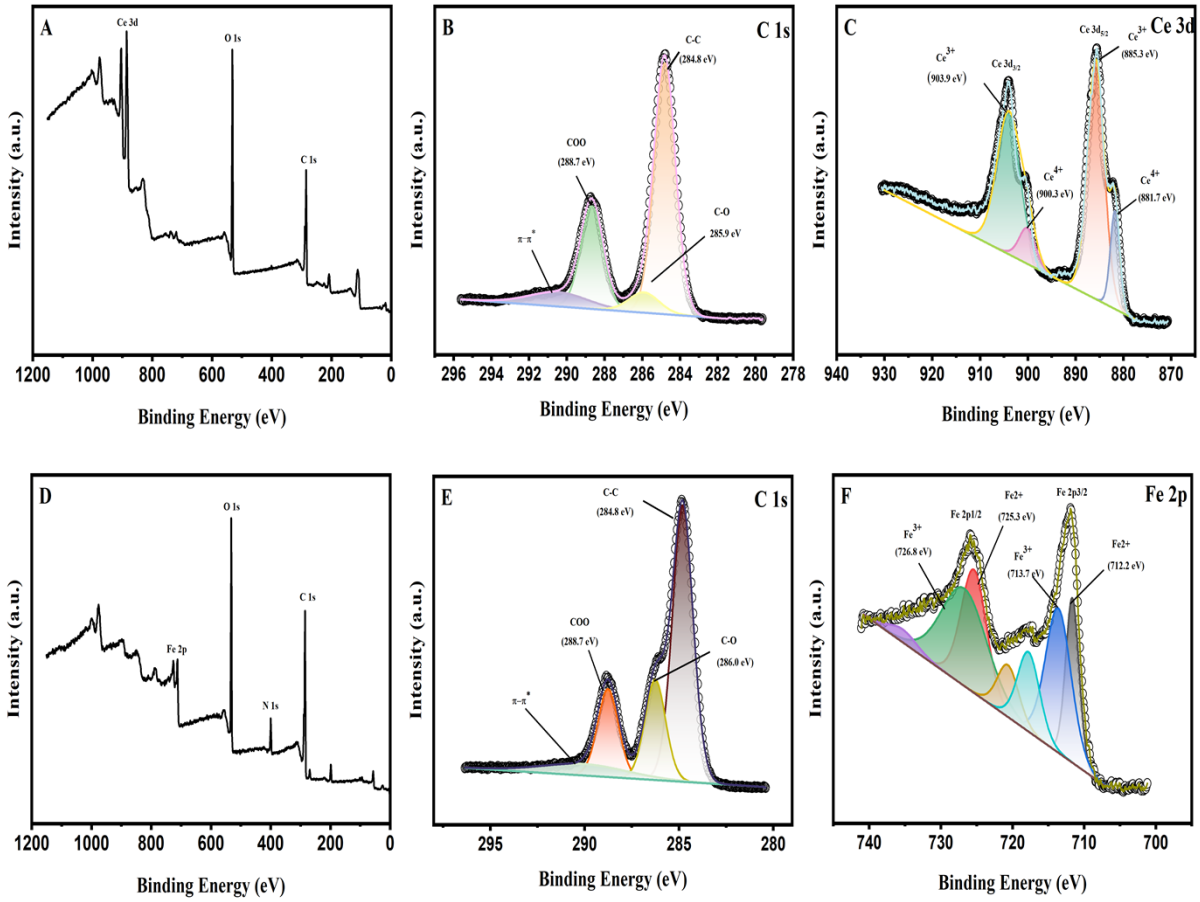

Fig. S2 (A, B, C) represent the full spectrum of Ce MOF, C 1s, and Ce 3d; (D, E, F) represent the full spectrum of Fe MOF, C 1s, and Fe 2p

Fig S3

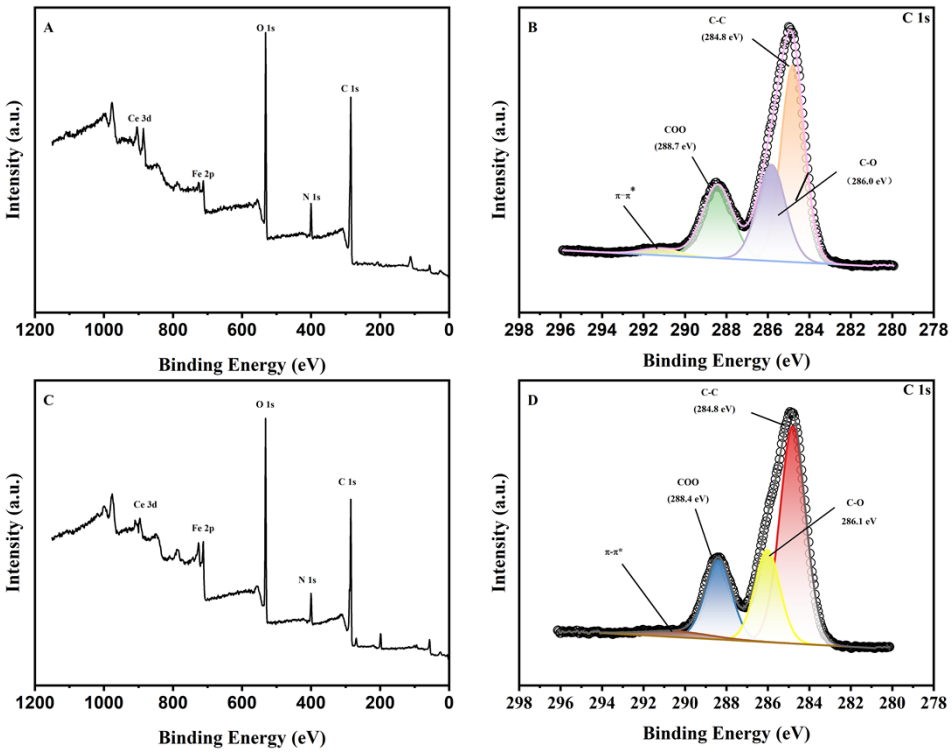

Fig. S3 (A, B) represent the full spectrum of Ce-MOF-on-Fe-MOF, and C 1s; (C, D) represent the full spectrum of Fe-MOF-on-Ce-MOF, and Fe C 1s.

Fig S4

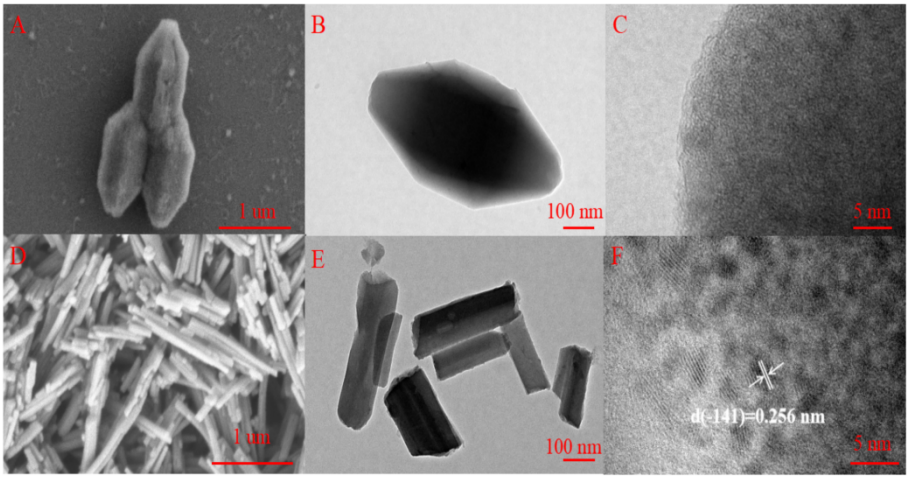

Fig. S4 SEM, TEM and HR-TEM images of (A, B, C) Fe-MOF and (D, E, F) Ce-MOF.

Fig S5

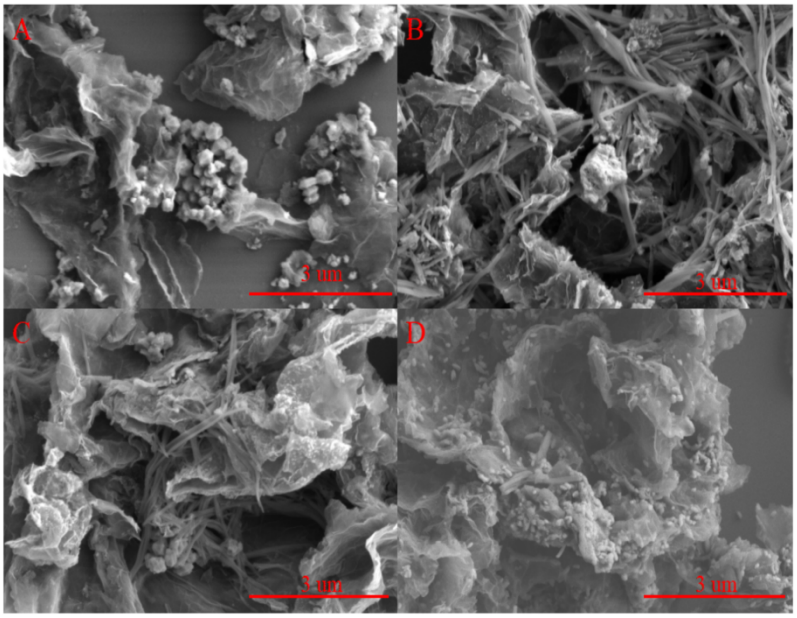

Fig. S5 SEM of (A) rGO@Fe-MOF@Tb; (B) rGO@Ce-MOF@Tb; (C)rGO@Ce-MOF-on-Fe-MOF@Tb ; (D)rGO@Fe-MOF-on-Ce-MOF@Tb.

Fig S6

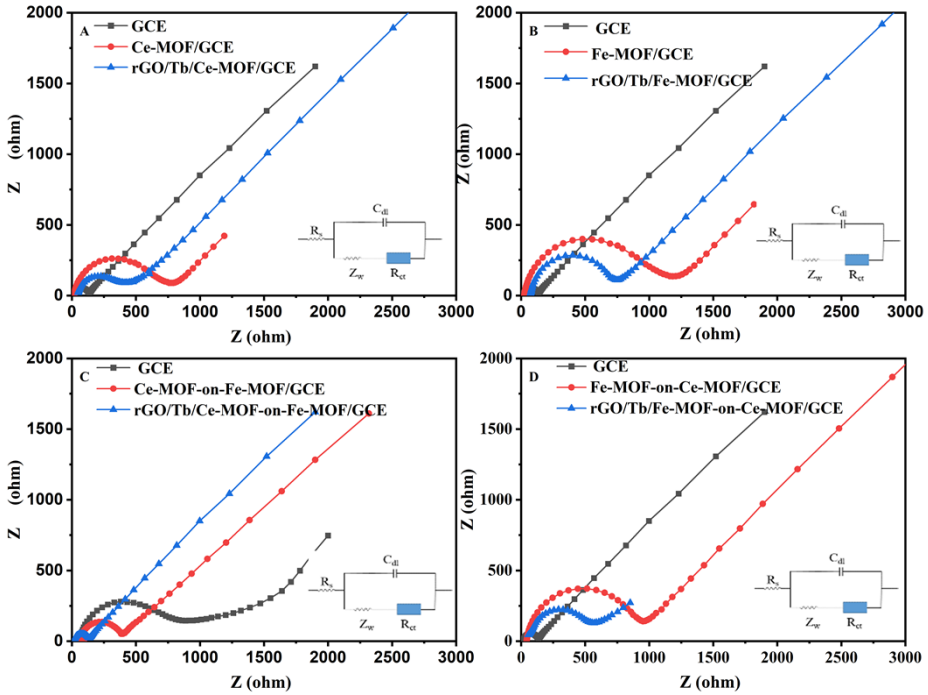

Fig. S6 EIS Nyquist plots of GCE modified by (A) Ce-MOF，(B) Fe-MOF，(C) Ce-MOF-on-Fe-MOF and (D) Fe-MOF-on-Ce-MOF in 0.01 M PBS (pH 7.4) containing 5.0 mM $[Fe(CN)6]^{3-/4-}$ redox.

Fig S7

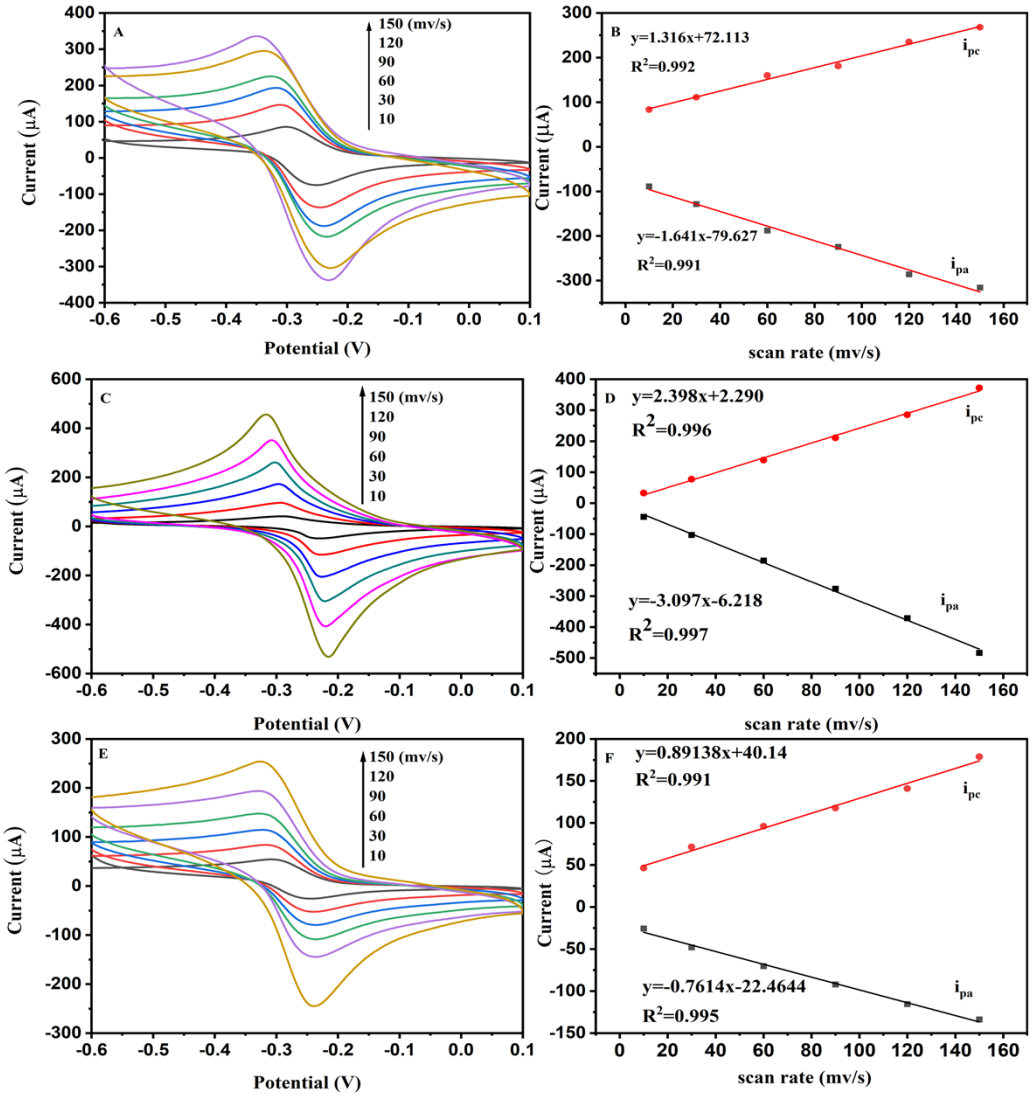

Fig. S7 CV of (A) rGO@Ce-MOF@Tb,(C) rGO@Ce-MOF-on-Fe-MOF@Tb and (E) rGO@Fe-MOF-on-Ce-MOF@Tb modified electrode at different scanning rates in 0.2 M NaCl. (D,E,F) Linear relationship between peak current and scanning rate.

Fig S8

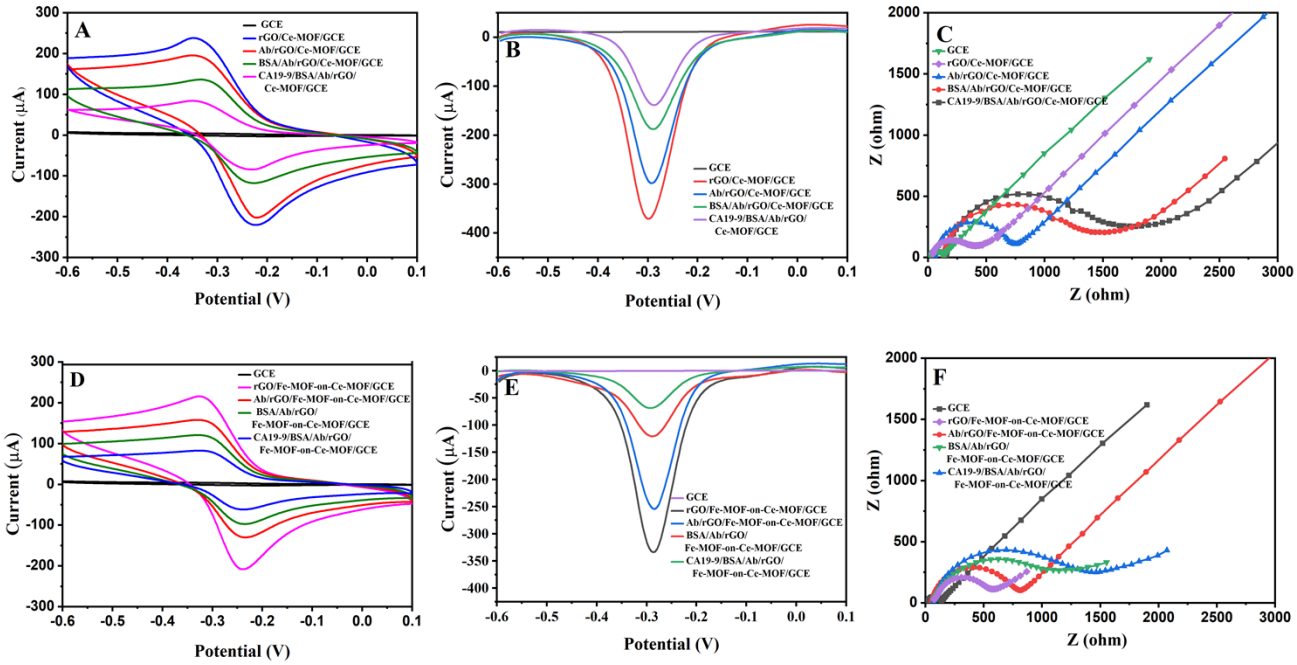

Fig. S8 (A) CV, (B) DPV and (C) EIS study for each immobilization step.CV and DPV were obtained in 0.01 M PBS (pH=7), EIS was performed in 5.0 mM $[Fe(CN)6]^{3-/4-}$ containing 0.01 M KCl electrolyte solution.

Fig S9

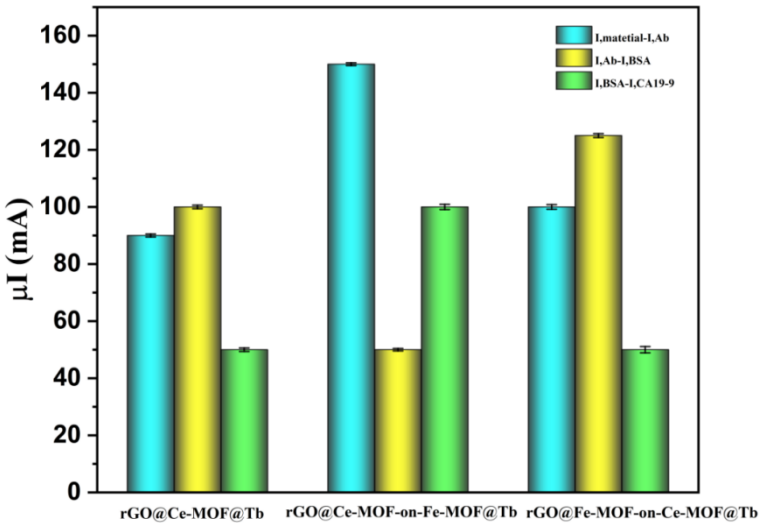

Fig. S9 The difference in peak current values at each stage of CA-199 detection using rGO@Ce-MOF@Tb、rGO@Ce-MOF-on-Fe-MOF@Tb、rGO@Fe-MOF-on-Ce-MOF@Tb immunosensors.

Fig S10

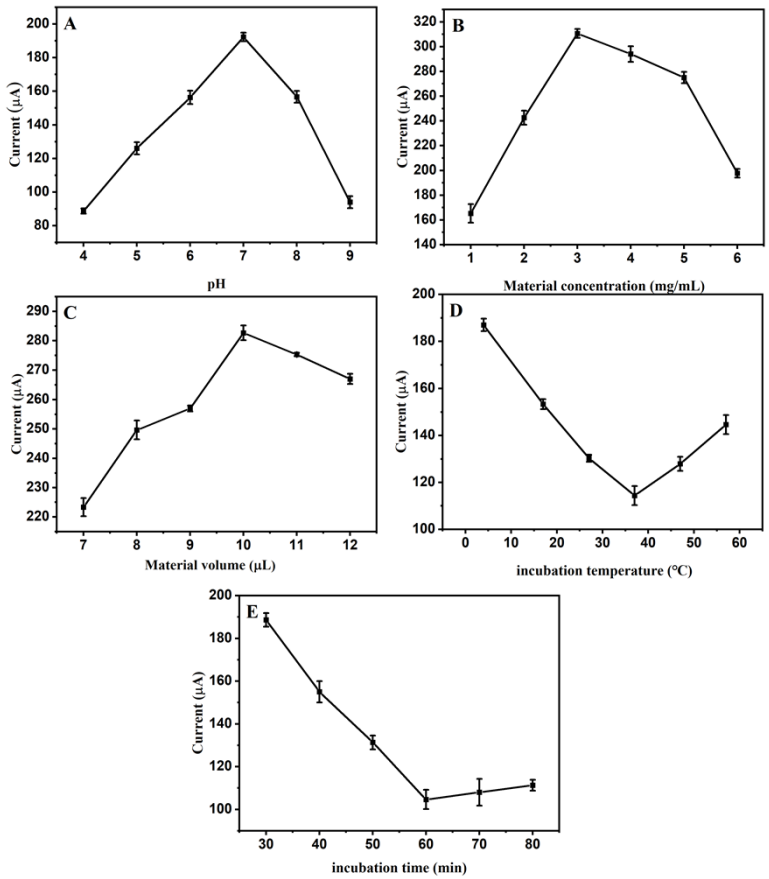

Fig. S10 Effects of the (A) pH of PBS solution, (B) material concentration, (C) material volume,(D) incubation of CA19-9 temperature, and (E) incubation time of CA19-9.

Table S1

The oxidation peak current value of each step during the detection procedures of CA199 using the immunosensors based on rGO@Ce-MOF@Tb、 rGO@Ce-MOF-on-Fe-MOF@Tb andrGO@Fe-MOF-on-Ce-MOF@Tb

electrode material	**I (uA)**				
	GCE	Modified electrodes	Ab	BSA	CA19-9
rGO@Ce-MOF@Tb	0	390	300	200	150
rGO@Ce-MOF-on-Fe-MOF@Tb	0	400	250	200	100
rGO@Fe-MOF-on-Ce-MOF@Tb	0	350	250	125	75