

Appendix

A1. Formula used for calculating recoveries of real sample analysis

For real sample analysis a standard a standard addition method was adopted where the recovery percentage was calculated by formula

$$R\% = \frac{\text{measured value}}{\text{expected value}} \times 100$$

Here, the expected value refers to the peak current of DPV plot for the standard sample of the analytes. On the other hand, measured value is the peak current of DPV plot obtained for the spiked real sample.

A2. CV and EIS during immobilization of biomolecules

For biosensing application irradiated UiO-66 samples were immobilized with antibody mouse IgG using the cross-linking agent glutaraldehyde (Gu). The modifiers Gu, antibody mouse IgG and blocking agent BSA were added in layer-by-layer manner. After addition of after each layer cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to verify the successful bioconjugation of the biomolecule, which is shown in Fig. A1. The cross-linking agent glutaraldehyde reacts with various functional groups, including the hydroxyl group present in UiO-66 coordinated with Zr nodes, allowing it to bind to the surface of the metal-organic framework (MOF) and create the necessary sites for biomolecular immobilization. This interaction leads to a decrease in the redox peak current (I_p) and an increase in carrier-transfer resistance, as the linkage of glutaraldehyde may obstruct charge transfer between the electrode and electrolyte. Similarly, the CV response decreased after the antibody was attached to glutaraldehyde (Gu), which was followed by a further decrease in CV after the BSA treatment as shown in the Fig. A1. As a consequence, the semicircle of Nyquist plot also enhanced after every step indicating a rise in the charge transfer resistance. The CV response decreased highest in UiO-66- 1×10^{12} by 68.86% as compared to samples before immobilization. The subsequent decrease in CV response in UiO-66, UiO-66- 5×10^{10} , UiO-66- 5×10^{11} are 54%, 62.8%, and 51.7%, respectively. As the Fig. A1(h) shows the UiO-66- 1×10^{12} has the highest charge transfer resistance of $\sim 6 \text{ k}\Omega$. This result is in well accordance with the CV results.

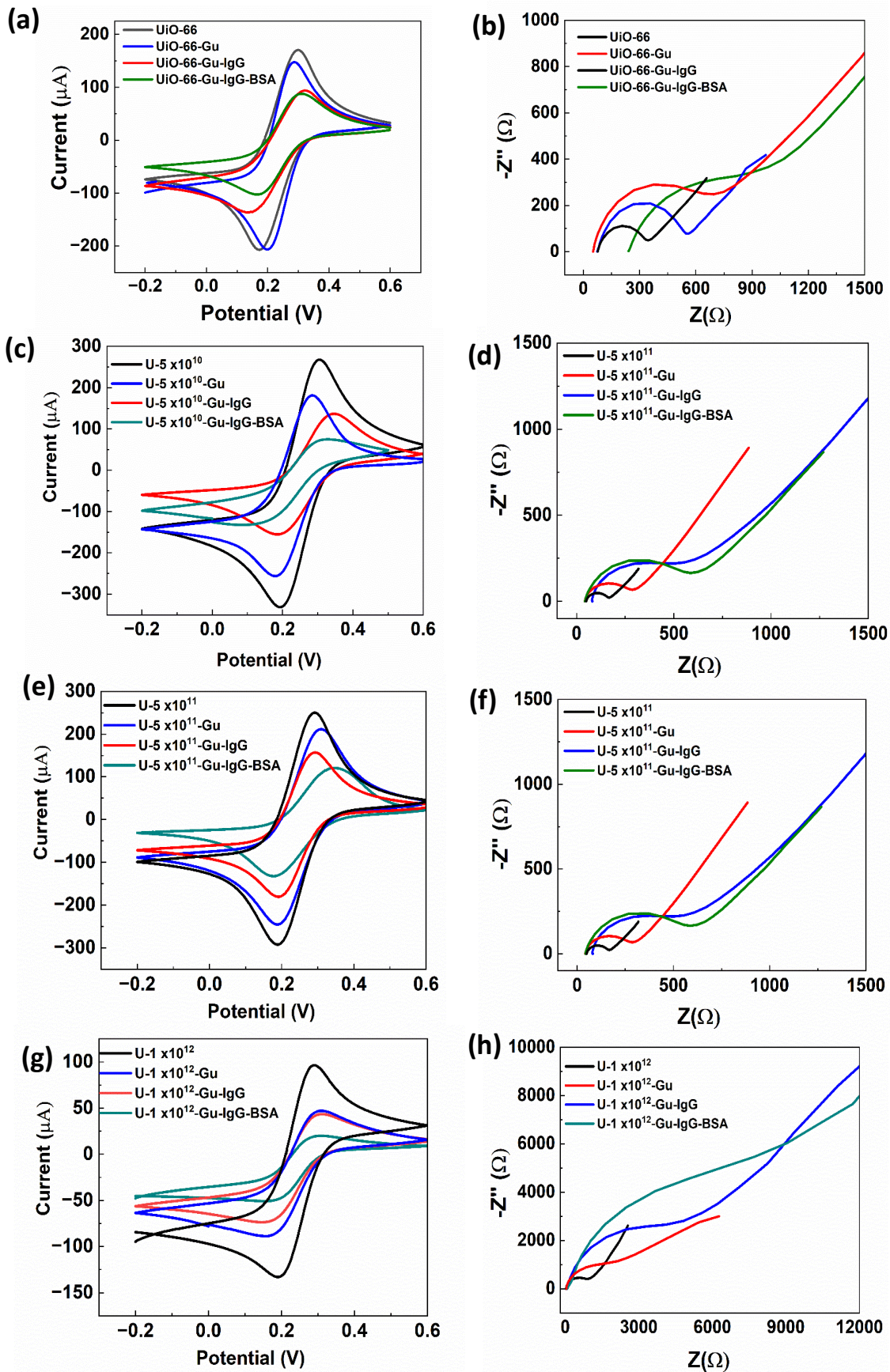


Fig.1 CV and EIS of (a), (b) UiO-66; (c), (d)UiO-66- 5×10^{10} ; (e), (f) UiO-66- 5×10^{11} and (g), (h) UiO-66- 1×10^{12} after adding glutaraldehyde, antibody mouse IgG and BSA

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