



# Highly efficient electrochemical detection of 4-nitrophenol based on electrode-modified $\text{CuInS}_2@\text{UiO-66}$ nanocomposite

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## Abstract

Owing to its extraordinary electrochemical properties, the  $\text{CIS}@\text{UiO-66}$  nanocomposite has proved to be one of the most potential materials for modifying electrode surfaces toward 4-NP detection. Herein, CIS nanomaterials are effectively combined onto UiO-66 material, aiming to achieve a unique heterostructure. In this configuration, CIS plays a role as an active material, while UiO-66 acts as an efficient framework with high specific surface area and pore volume, good chemical stability, and large electrical conductivity to uniformly decorate CIS. As expected, with such synergism of CIS and UiO-66, the electrochemical characteristics and detection performance of 4-NP are enhanced remarkably. Namely, electrochemical measurements exhibit kinetic parameters involving oxidation-reduction reactions of both the standard probe and targeted molecules (4-NP). The sensitivity, linear concentration range, LOD value, and selectivity toward the detection of the 4-NP at  $\text{CIS}@\text{UiO-66}/\text{SPE}$  are the highest compared to  $\text{CIS}/\text{SPE}$  and  $\text{UiO-66}/\text{SPE}$ , demonstrating the high applicability potential of this proposed electrode in the future.

**Keywords** Electrochemical sensor · CIS · UiO-66 · Electrode modification · Composite · Kinetic parameters

## Introduction

4-Nitrophenol (4-NP) has been known as an aromatic nitro compound—a priority toxic pollutant even at very low concentrations, which was listed in the US Environmental Protection Agency because of low degradability and good solubility in most aqueous solutions [1, 2]. Unfortunately, 4-NP still is widely found in the production process of chemicals, pharmaceuticals, dyes, wood preservatives, explosives, pesticides, and leather products. Particularly, its presence is recorded in agricultural products (vegetables, nuts, fruits, and grains) or water sources from gardens and farms. Therefore, several available analytical methods have been investigated and developed for the rapid, direct, and efficient

determination of 4-NP. Among them, the electrochemical sensor is considered to be the most effective method owing to its unique advantages such as rapid response time, low cost, simple operation steps, high sensitivity and selectivity, continuous real-time detection, and being time-saving [3, 4]. Although to enhance sensing performance toward 4-NP detection, some approaches are proposed, in which the modification of electrode surface with various nanomaterials should be stressed. Using carbonaceous nanomaterials [5–7], metal/metal oxides [8–10], conducting polymers [11, 12], and spinel nanomaterials [13] exhibits remarkable enhancements in sensing performance and kinetic parameters in electron transfer reactions.

Copper indium sulfide ( $\text{CuInS}_2\text{-CIS}$ ) has been considered to be a promising green material when extensively utilized in many different applications, for example, photocatalyst and electrocatalyst due to high absorption capacity in the visible light region and highly tunable bandgap energy [14–16]. While, UiO-66 material owns a high surface area with large pore volume and tunable pore size, low toxicity and cost, easy modifications, and excellent chemical stability and conductivity [17–19]. CIS nanomaterials have been effectively loaded on a UiO-66 and can enhance reaction surface area, improve surface evolution kinetics and stability, decrease

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carrier diffusion lengths, and enhance carrier mobility as well as light absorption coefficient. Especially, these composited heterostructures establishing the promising heterostructure interface could significantly improve the photoinduced charge separation process and exposure/interaction with electrolytes and offer much-improved electron/charge transfer in comparison with individual materials. More importantly, such influencing factors are important keys in designing high-efficiency electrochemical sensors.

Inspired by these discoveries, herein, it is the first time a heterostructure arose from the effective combination of CIS and UiO-66, together with the electrode surface modification via a simple drop-casting aiming to create a high potential electrode in increase of electrochemical performance as well as kinetic parameters at electron transfer reactions of both the standard probe and targeted molecules (4-NP).

## Experimental section

### Chemicals

Indium(III) chloride ( $\text{InCl}_3$ , 98%), copper(I) chloride ( $\text{CuCl}$ ,  $\geq 99.5\%$ ), izirconium(IV) oxychloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ,  $> 99\%$ ), sodium dodecyl sulfate (SDS, 99%), N,N-dimethylformamide (DMF,  $> 98\%$ ), sodium hydroxide (NaOH, 99%), ethylene glycol (EG,  $> 99\%$ ), terephthalic acid (TPA,  $> 99\%$ ), ammonium fluoride ( $\text{NH}_4\text{F}$ ,  $> 96\%$ ), thioacetamide (TAA,  $> 98\%$ ), and *p*-nitrophenol (4-NP,  $> 99\%$ ) were provided from Sigma–Aldrich. The standard probe ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) and alcohol ( $\text{C}_2\text{H}_5\text{OH}$ , 95%) were purchased from Xilong Scientific Co. Ltd. The phosphate-buffered saline solution (PBS, pH 7.4) containing some salts such as KCl, NaCl,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , and  $\text{KH}_2\text{PO}_4$  were obtained from Merck KGaA, Germany, and Shanghai Chemical Reagent. All chemicals were used without any further purification.

### Synthesis of CIS nanoparticles

To synthesize CIS nanoparticles, in this study, hydrothermal method was used. Accordingly, 50 mL of ethylene glycol was used as a solvent to dissolve 5.0 mmol sodium dodecyl sulfate. This mixture was stirred vigorously at  $80^\circ\text{C}$  for 15 min. Then, a mixture of 1.0 mmol copper(I) chloride, 1.0 mmol indium(III) chloride, and 5.0 mmol thioacetamide was used to slowly add into the above solution and stirred continuously until the homogeneous solution. This solution mixture was transferred into the autoclave for crystallization for 24 h at a temperature of  $180^\circ\text{C}$ . The suspension was filtered and washed with ethanol and distilled water. Finally, the obtained powder was dried in a vacuum environment at  $80^\circ\text{C}$  for 5 h, and the product was denoted as CIS.

### Synthesis of CIS@UiO-66 composite

Firstly, the solvothermal method was used for the synthesis of UiO-66. Briefly, 30 mL of total DMF was used as a solvent for the separate dissolution of 0.35 g equimolar  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and 0.997 g of organic ligand  $\text{H}_2\text{BDC}$ . Each of these solutions was sonicated for 30 min. The two solutions were then mixed and stirred continuously to obtain a homogeneous solution. Then, 1.35 g of acetic acid and 2.0 mL of distilled water were added to this solution mixture and continued stirring for 60 min. The suspension into the autoclave for crystallization at a temperature of  $120^\circ\text{C}$  for 36 h. The product was centrifuged, filtered, washed with DMF, ethanol, and distilled water, and then dried at  $120^\circ\text{C}$  for 12 h. The produced white powder was UiO-66.

The CIS@UiO-66 composite was synthesized by mixing 0.5 g of UiO-66 dispersed in distilled water (150 mL) by ultrasound for 30 min. A certain amount of CIS (0.2 g, 40 wt%) was added to the above solution with an additional 15-min ultrasound. The mixture was hydrothermally incubated in an autoclave at  $120^\circ\text{C}$  for 24 h. Then, the solid was obtained by centrifugation, filtration, washing with distilled water, and drying at  $120^\circ\text{C}$  for 12 h to obtain the CIS@UiO-66 composite.

### Preparation of CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE

To prepare the electrochemical measurements on the modified SPEs, the first experimental step needs to be performed to be the surface modification of working electrodes with the proposed synthesized samples via a simple dropping method [15, 20, 21]. First, commercial SPEs obtained from DS Dropsens, Spain, were carefully polished with Al powder, after washing several times with DI water and alcohol, and then dried at natural condition. Five milligrams of each proposed material was homogeneously dispersed into 5 mL of DI water by keeping in an ultrasonic bath for 30 min to obtain the homogeneous suspensions having a bulk concentration of  $1\text{ mg mL}^{-1}$ . Next step, 6  $\mu\text{L}$  of each suspension was dropped cast on the working electrode surface. Finally, the solvent evaporation was carried out at  $40^\circ\text{C}$  to get the modified SPEs for the next electrochemical measurements.

### Characterization techniques

The crystalline structure, structural properties, and purity of synthetic materials were studied and evaluated through X-ray diffraction pattern (XRD,  $\lambda = 1.54\text{ \AA}$ , Cu  $\text{K}\alpha$  radiation, 40 keV–40 mA current). The morphology, surface, size, and distribution were also characterized by using a HITACHI, S-4800-3000F

scanning electron microscope (SEM). Besides, the determination of the elemental composition in CIS@UiO-66 nanocomposites was performed by using the energy-dispersive X-ray (EDX) analysis. Furthermore, UV-vis spectroscopy was recorded via a HITACHI U-3900 spectrophotometer to calculate bandgap values and evaluate/compare the optical properties of the various proposed samples.

## Evaluation of electrochemical characterizations

For evaluating the difference in the electrochemical characteristics between bare SPE and modified electrodes, a series of electrochemical measurements such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and differential pulse voltammetry (DPV) were performed by using a three-electrode electrochemical workstation (Palmsens 4, PS Trace-Netherlands) at room temperature along with the support of Palmsens 4.8 software (Metrohm, The Netherlands). Firstly, CV measurements were scanned by a rate of  $50 \text{ mV s}^{-1}$  in the potential range from  $-0.3$  to  $0.6 \text{ V}$  with the presence of  $0.1 \text{ M}$  KCl solution containing  $5 \text{ mM}$   $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  as a standard probe. Similarly, EIS measurements were measured in the frequency range from  $0.01$  to  $50,000 \text{ Hz}$ . Furthermore, to evaluate sensing performance towards 4-NP detection on these electrodes, CV and DPV measurements were also taken place in  $0.1 \text{ M}$  PBS buffer as a supporting electrolyte, containing various concentrations of 4-NP. Herein, CV measurements were scanned in the potential range of  $-1.1$ – $0 \text{ V}$  at a scan rate of  $50 \text{ mV s}^{-1}$ . Similarly, DPV measurements were carried out at a scan rate of  $6 \text{ mV s}^{-1}$ ,  $E_{\text{pulse}} = 0.075 \text{ V}$ ,  $T_{\text{pulse}} = 0.2 \text{ s}$ , and  $T_{\text{equilibrium}} = 120 \text{ s}$ .

## Results and discussion

### Characterizations of materials

X-ray diffraction (XRD) patterns of as-prepared samples are exhibited in Fig. 1 aiming to investigate their crystal structures. As can be seen, the formation of CIS crystal structure was observed via the diffraction angle ( $2\theta$ ) of  $27.4^\circ$ ,  $31.6^\circ$ ,  $44.8^\circ$ , and  $55.4^\circ$  corresponding to the well-defined diffraction peaks of the tetragonal CIS marked with the (112), (004), (200), and (312) planes [15, 22, 23]. This XRD result matched well with previous reports, demonstrating the high crystalline and good purity of the CIS sample. Similarly, the diffraction peaks of UiO-66 sample at around  $7.4^\circ$ ,  $8.34^\circ$ ,  $12^\circ$ ,  $17.04^\circ$ ,  $25.6^\circ$ , and  $43^\circ$  can be clearly indexed to the crystal planes of (111), (200), (222), (400), (442), and (440) [18, 24–26]. Particularly, for CIS@UiO-66 samples, after mixing, the copresence of characteristic peaks of both CIS and UiO-66 phases was still recorded. However, these peak

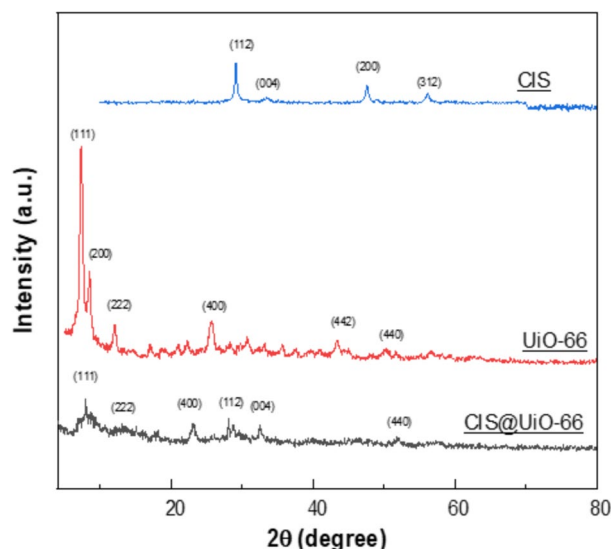


Fig. 1 XRD patterns of CIS, UiO-66, and CIS@UiO-66 samples

intensities were decreased remarkably, resulting from the efficient combination as well as the significant decoration of CIS into the UiO-66 pores.

To investigate the morphology, size, and structural characteristics of the synthesized samples, SEM measurements were used. SEM images of the CIS sample displayed spherical particles of microflower-like morphology with rough surfaces caused by the layer structure. It needs to be stressed that this structure promises to facilitate the photochemistry process occurring more effectively, in which it can create outstanding exposure and uniform dispersion of light photons to the inside interface of frameworks as well as entering deep into the photochemistry catalysts. For the UiO-66 sample, the homogeneous particle structure with the regular octahedral crystal and smooth surface was observed clearly. As described in Fig. 2c, aiming to prevent effectively the self-aggregation of both CIS and UiO-66, CIS was successfully attached to the UiO-66 surface visually, further facilitating the homogeneous distribution of CIS particles. Absolutely, the presence of both CIS on UiO-66 did not change their natural morphology; however, it led to the change of the surface roughness of CIS@UiO-66 material and contributed to the formation of a heterogeneous junction interface. The effective combination is considered to benefit the active surface area, distribution, active sites, morphology, and structural stability of CIS@UiO-66. More particularly, to further investigate the purity and component of CIS@UiO-66 composite material, the energy dispersive X-ray (EDX) analysis was used. Figure 2d illustrates the component of the synthesized composite sample including Cu, In, S, Zr, O, and C. Herein, the peaks with strong intensities were recorded at Cu, In, and S components. Besides, trace amounts of F, Cl, and N were also present on the EDX spectrum. The molar ratio of

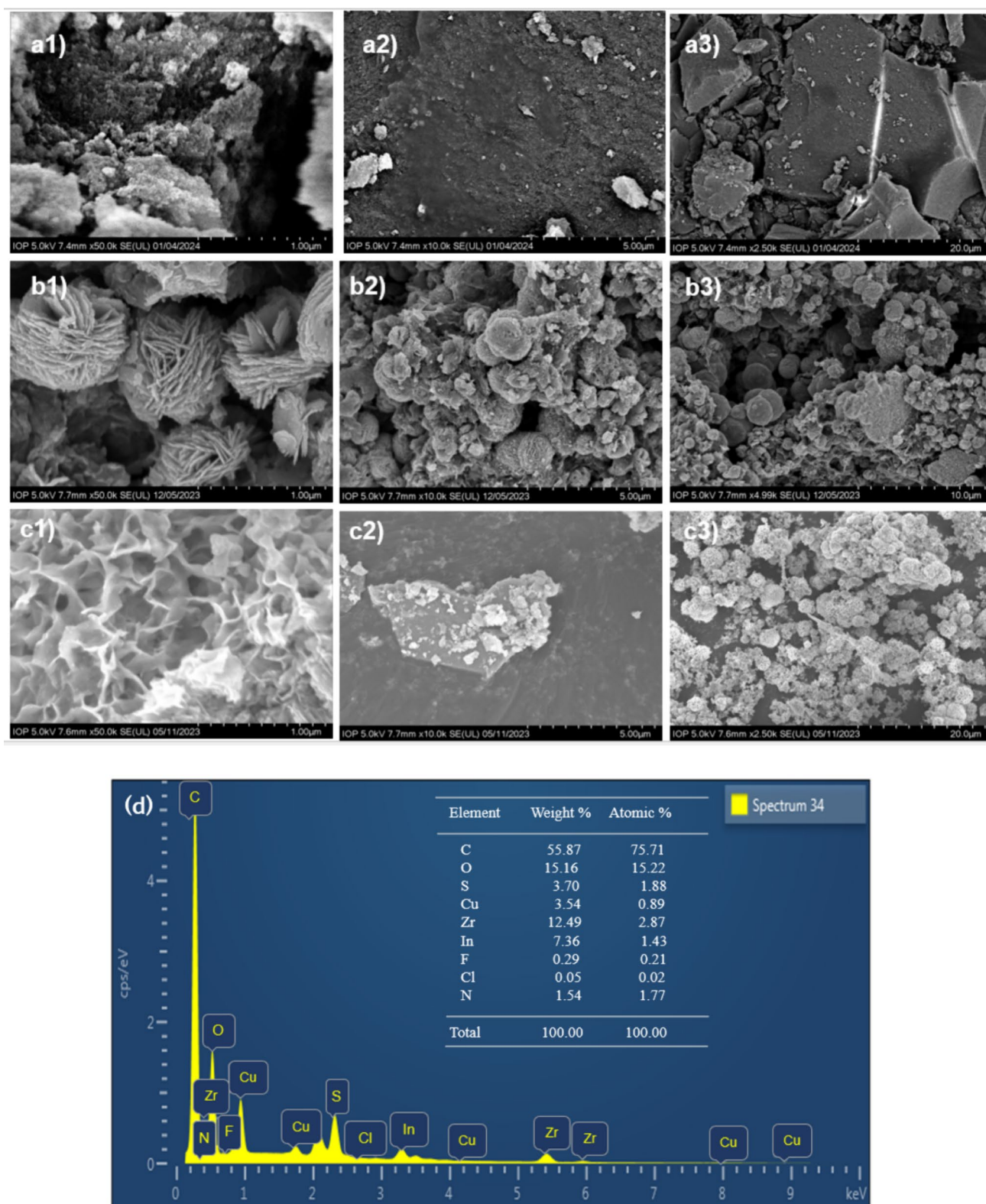
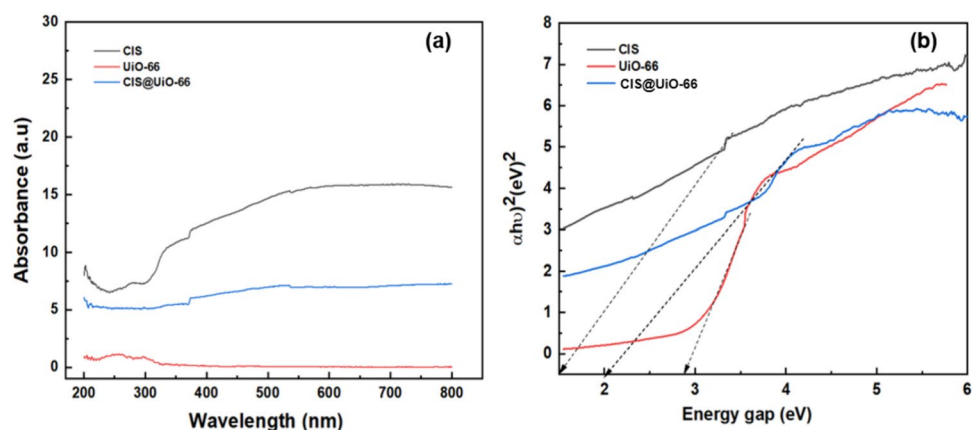


**Fig. 2** a–c SEM images of UiO-66, CIS, and CIS@UiO-66 samples. **d** Results of the energy-dispersive X-ray (EDX) analysis on CIS@UiO-66 sample

**Fig. 3** **a** UV-vis absorption spectrum of CIS, UiO-66, and CIS@UiO-66 samples; **b** the value bandgap energy by using Tauc plot of proposed samples



Cu to In and S was close to 1:1:2 as a percentage of weight which is consistent with CIS stoichiometry.

More interestingly, the optical properties of the proposed samples were also investigated by observing UV-vis diffuse absorption spectra. The obtained results pointed out that synthetic materials owned a strong absorption capacity in the UV light region ( $\lambda = 200\text{--}700\text{ nm}$ ) (Fig. 3a). Namely, UiO-66 showed a strong absorption peak at about 250 nm, corresponding to a calculated bandgap value of 2.8 eV, which can be calculated via the equation [27]:  $\alpha h\nu = A(h\nu - E_g)^{n/2}$ . Likewise, CIS showed a bandgap value of 1.48 eV. Particularly, by adding UiO-66, the light absorption at the visible region of the CIS@UiO-66 sample was remarkably increased, corresponding to the shift toward longer wavelength and higher peak intensity in the wavelength range from 400 to 700 nm. As expected, a promising bandgap value of 2.1 eV was observed (Fig. 3b). Thus, CIS@UiO-66 has low bandgap energy ( $E_g = 2.1\text{ eV}$ ) and high photostability [28], absorbs light in the visible region, and has high quantum efficiency. This may be due to the presence of

defects unsaturated by the secondary phase [29, 30]. Results from SEM images (Fig. 2b) show that microflower-shaped spherical particles were observed with an average particle size of 1.0–2.0  $\mu\text{m}$ . The rough surface of CIS caused by the layered structure provides a lot of surface area that increases visible light absorption promoting photogenerated electron exchange. This further confirms the important role of the effective combination between CIS and UiO-66 for the increase in the structural stability and optical properties, suggesting the promising potential of the CIS@UiO-66 sample for many various applications.

### Electrochemical investigation

To investigate and evaluate the electrochemical characteristics of the proposed electrodes, the CV technique was proposed in 0.1 M KCl electrolyte containing 5 mM standard redox probe ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ ). As illustrated in Fig. 4a, all CV curves of CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE possessed a pair of well-defined redox peaks, which

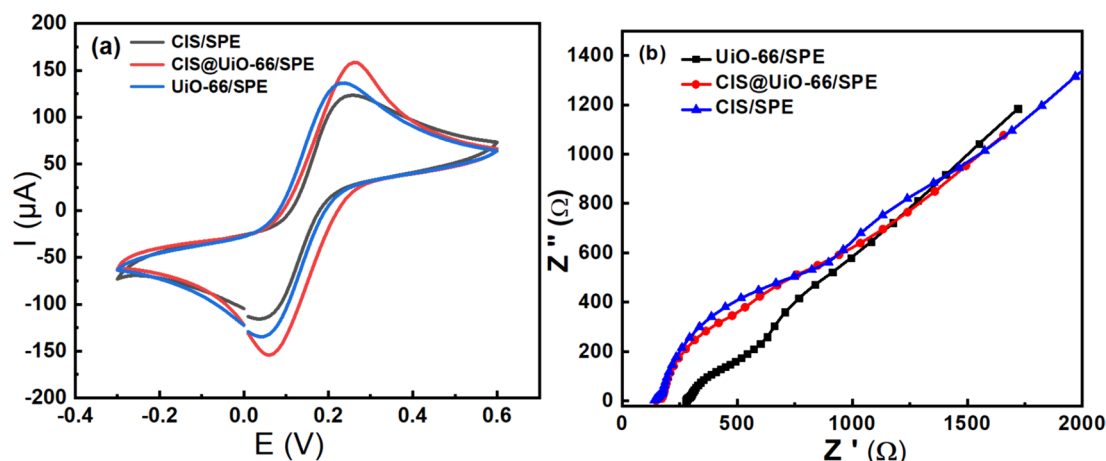


**Fig. 4** CVs response (a), EIS spectrum (b) at CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE recorded in 0.1 M KCl containing 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$

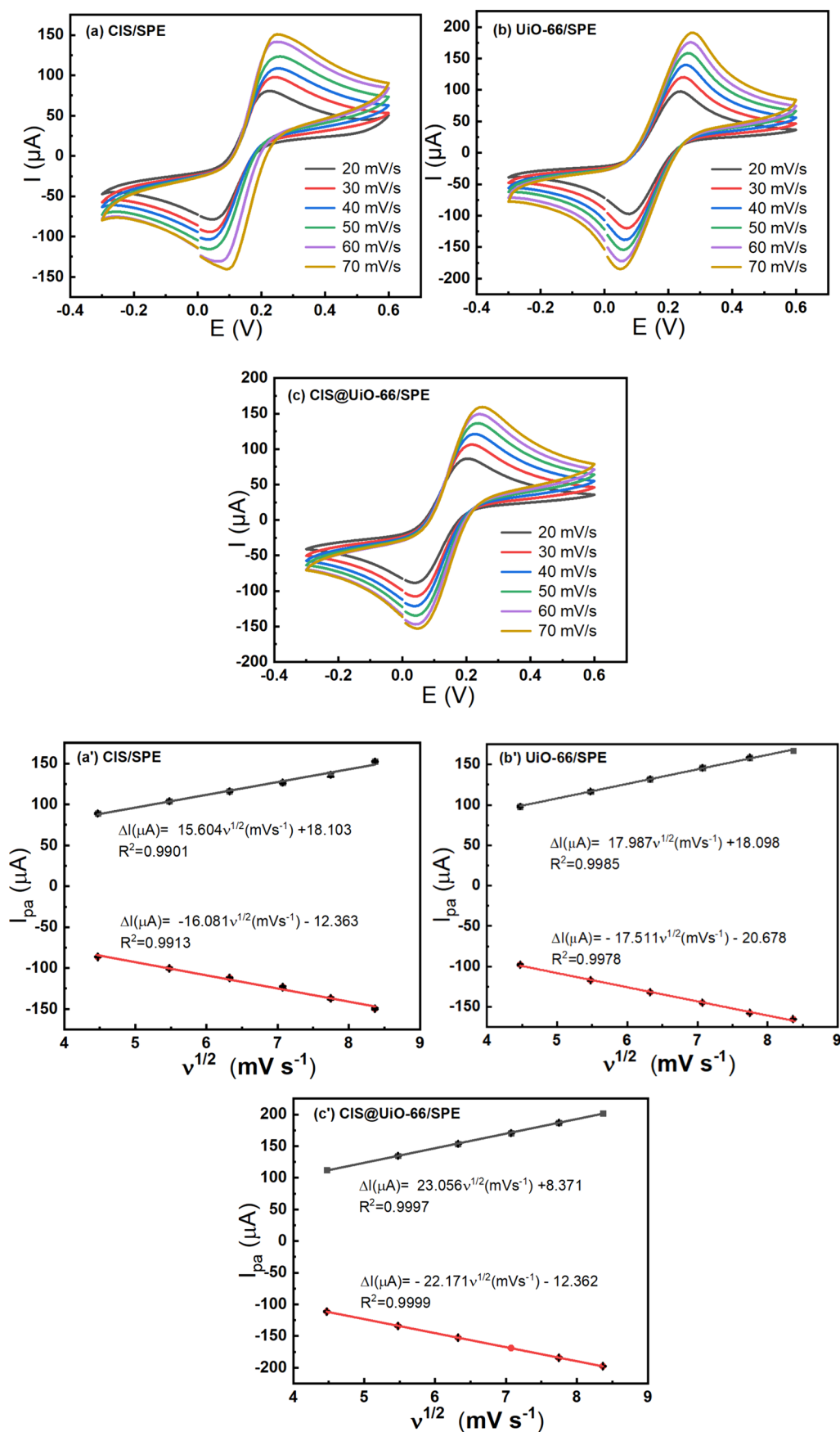


**Fig. 5** CVs response **a–c** recorded on CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE in 0.1 M KCl containing 5 mM  $[\text{Fe}]^{3+/2+}$  at various scan rates from 20 to 70  $\text{mVs}^{-1}$ , corresponding to linear plots of  $I_p$  versus  $\nu^{1/2}$  (**a'–c'**)

reflect the reversible redox reactions of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  molecules. However, the current response and redox potential at these modified electrodes were remarkably different. Namely, it was observed at about 128.4  $\mu\text{A}/0.25\text{--}0.038\text{ V}$ , 145.3  $\mu\text{A}/0.23\text{--}0.041\text{ V}$ , and 171.4  $\mu\text{A}/0.26\text{--}0.06\text{ V}$  for CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE, demonstrating CIS@UiO-66/SPE owning the best electrochemical response. More importantly, another important parameter was observed here to be peak-to-peak potential separation ( $\Delta E_p$ ). The order of this value was determined: 212 mV (CIS/SPE) > 200 mV (UiO-66/SPE) > 189 mV (CIS@UiO-66/SPE), further confirming the faster electron transfer and better electron transfer kinetic at CIS@UiO-66/SPE [26, 31, 32]. Clearly, among the proposed electrodes, modifying the electrode surface with CIS@UiO-66 nanocomposite material showed better electrochemical characteristics compared with other electrodes. Benefiting from the effective combination of CIS and UiO-66, it created a heterogeneous structure with outstanding open exposure and uniform dispersion. CIS particles were successfully attached to the UiO-66 surface, effectively preventing the self-aggregation of both CIS and UiO-66 and further facilitating the change of the surface roughness and the formation of a heterogeneous junction interface. Maybe, these characteristics contributed to promoting the electron transfer process on the electrolyte/electrode interface. An outstanding open exposure and uniform dispersion provided a better and faster diffusion of electrolytes into modified electrodes. More importantly, a rough surface and heterogeneous junction interface facilitated the wettability and charge transfer as well as the interaction between active sites and targeted analytes, which increased activity and electron transfer rate in redox reactions. Maybe, thanks to these characteristics as well as excellent synergistic effects from these two components, it provided the critical increase in the electron transfer process, active surface area, electrocatalytic activity, and electrical conductivity.

To further study the difference of electron transfer reaction at proposed electrodes, the impact of variable scan rate on the redox reaction of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  was investigated and evaluated. Figure 5 exhibits all CV curves obtained from 20 to 70  $\text{mV s}^{-1}$ . At all electrodes, the recorded current response increased linearly with the square root of the scan rate ( $\nu^{1/2}\text{-mV s}^{-1}$ ), suggesting the electro-redox reaction in a diffusion-controlled process. According to that, the active electrochemical surface area ( $\text{A-cm}^2$ ) for each modified electrode was determined by using the Randles Sevcik equation [4, 18, 33]:  $I_p = 2.69 \times 10^5 \times n^{3/2} \text{AD}^{1/2} \nu^{1/2} C$ , where  $n$

is the number of electrons transferred in the redox reaction,  $D$  refers diffusion coefficient, and  $C$  is the concentration of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  probes ( $D = 6.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ;  $C = 5 \text{ mM}$ ). Furthermore, based on the corresponding slope value of the line equations from the linear relationships between ( $I_p\text{-}\mu\text{A}$ ) and ( $\nu^{1/2}\text{-mV s}^{-1}$ ) such as:

$$I_p (\mu\text{A}) = 15.604 \nu^{1/2} (\text{mV s}^{-1}) + 18.103 \text{ for CIS/SPE}$$

$$I_p (\mu\text{A}) = 23.056 \nu^{1/2} (\text{mV s}^{-1}) + 8.371 \text{ for UiO-66/SPE}$$

$$I_p (\mu\text{A}) = 17.987 \nu^{1/2} (\text{mV s}^{-1}) + 18.098 \text{ for CIS@UiO-66/SPE}$$

Clearly, the CIS@UiO-66/SPE owned the highest  $A$  value of  $0.222 \text{ cm}^2$ , while CIS/SPE and UiO-66/SPE exhibit lower values of  $0.166$  and  $0.189 \text{ cm}^2$ . On the other hand, the EIS technique was carried out to calculate the charge transfer resistance ( $R_{ct}$ ) value, which refers to the electrical conductivity at the exposure interface between the electrode and electrolyte. Figure 4b illustrates the Nyquist plots with semicircles at high frequency and straight lines at low frequency. Using the Randles circuit model, the proposed electrodes were well-fitted and displayed the largest semicircle diameter with an  $R_{ct}$  of  $414 \Omega$  at CIS/SPE. Meanwhile, it just was about  $377 \Omega$  at UiO-66/SPE and reached the lowest value of  $199 \Omega$  at CIS@UiO-66/SPE. This result further demonstrates that CIS@UiO-66/SPE owned higher electrical conductivity, compared to other electrodes. More interestingly, from the above  $R_{ct}$  and  $A$  values obtained, the electron transfer rate constant ( $k_{et}$ ) value was also directly determined by using the equation [21, 34]:  $k_{et} = RT/n^2 F^2 A C_0 R_{ct}$ . After the surface modification with the proposed materials, the  $k_{et}$  value was increased. Significantly. Namely, it reached in turn approximately  $7.68 \times 10^{-4}$ ,  $7.45 \times 10^{-4}$ , and  $1.19 \times 10^{-3}$  for CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE, demonstrating the remarkable increase in electrochemical reaction kinetics of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  probe at the electrode/electrolyte interface of electrode.

### Electrochemical behaviors of 4-NP on modified electrodes

To gain insight into the electrochemical behaviors of 4-NP on the proposed electrodes, CV was taken place in a PBS buffer containing  $50 \mu\text{M}$  4-NP at a scan rate of  $50 \text{ mV s}^{-1}$ . Figure 6a exhibits the CV curves obtained, in which there was a strong irreversible reduction peak at around  $-0.78 \text{ V}$  at all electrodes, which reflects the reduction reaction of 4-NP occurring on the electrode surface [20, 35, 36]. More interestingly, it exhibits a considerable difference in peak current intensity. Indeed, with the presence of 4-NP in the BPS buffer, the reduction current intensity of 4-NP achieved

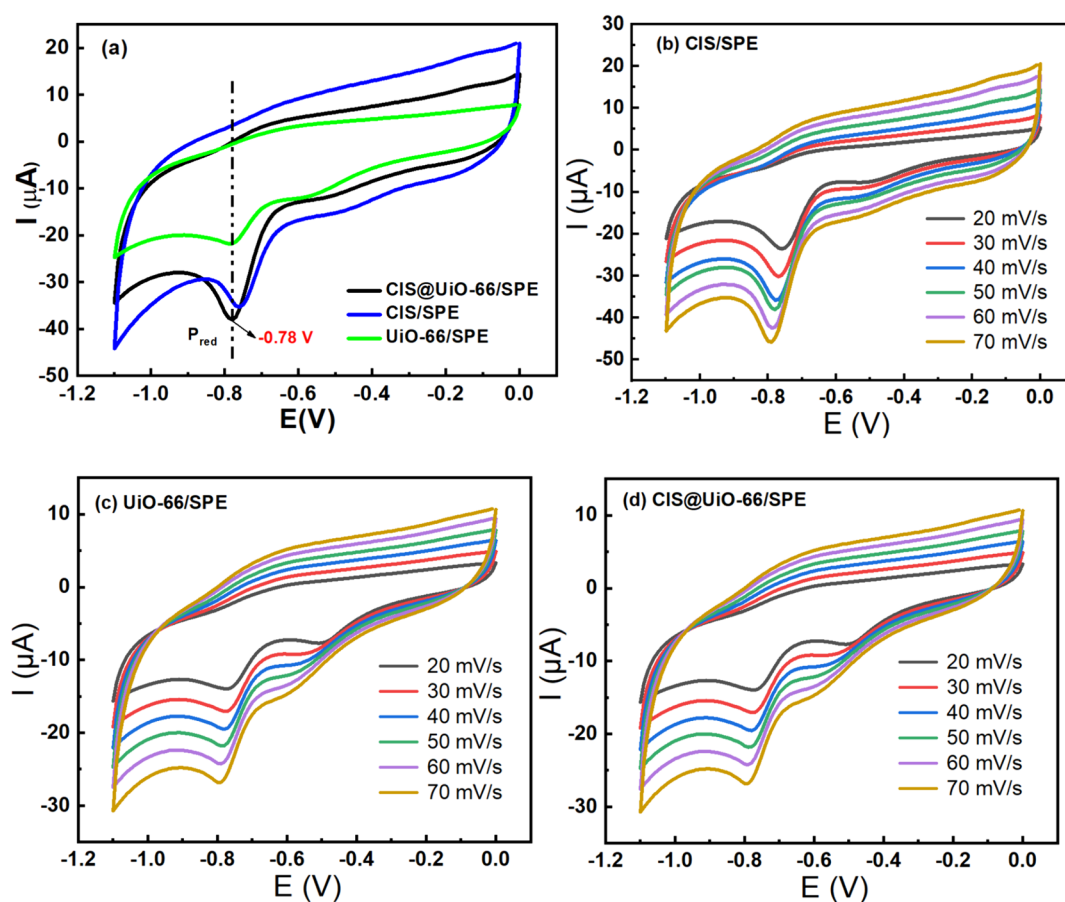


**Fig. 6** **a** A comparison of CV response at CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE in 0.1 M PBS containing 50  $\mu\text{M}$  4-NP; **b–d** CV curves at proposed electrodes at various scan rates from 20 to 70  $\text{mV s}^{-1}$  in 0.1 M KCl containing 50  $\mu\text{M}$  4-NP

approximately 11.53, 5.97, and 17.82  $\mu\text{A}$ , corresponding to CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE, respectively. Clearly, it can be concluded that the CIS@UiO-66-modified electrode significantly improved the electrochemical behaviors of 4-NP, compared with other electrodes. This result was consistent with the results observed from the electrochemical characteristics of probes.

To get a further understanding of the kinetic reactions of 4-NP on the proposed electrodes, the impact of scan rate on the electrochemical behaviors of 4-NP was also analyzed by CV technique by varying scan rates in 0.1 M PBS containing 50  $\mu\text{M}$  4-NP. As displayed in Fig. 6b–c, the linear increase of the current intensity with the change of scan rate in the range from 20 to 70  $\text{mV s}^{-1}$  was recorded. In which, the linear regression equations were expressed as  $I_{\text{pc}} (\mu\text{A}) = 0.051 \nu (\text{mV s}^{-1}) - 1.885$  ( $R^2 = 0.961$ );  $I_{\text{pc}} (\mu\text{A}) = 0.051 \nu (\text{mV s}^{-1}) + 3.418$  ( $R^2 = 0.984$ ); and  $I_{\text{pa}} (\mu\text{A}) = 0.133 \nu (\text{mV s}^{-1}) + 11.168$  ( $R^2 = 0.987$ ) for CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE, respectively (Fig. S1). According to that, it can be concluded that the redox reaction of 4-NP at all modified electrodes was a

typical surface adsorption-controlled process rather than normal diffusion processes as in the redox reaction of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  probes. Furthermore, the adsorption capacity of 4-NP on the electrode surface was determined using the equation [2, 36]:  $I_p = n^2 F^2 A \nu \Gamma / 4RT$ , where  $I_p$  is the response current obtained,  $n$  is the number of electrons transferred in the redox reaction,  $A$  is the active electrochemical surface area, and  $\nu$  refers to the scan rate. The adsorption capacities ( $\Gamma$ ) of 4-NP were approximately  $2.54 \times 10^{-10}$ ,  $6.36 \times 10^{-10}$ , and  $3.24 \times 10^{-10} \text{ mol cm}^{-2}$ , respectively. Along with that, the slight shift of the reduction potential was recorded upon varying the scan rate. It was observed that the plots of  $E_p$  vs. the natural logarithm of scan rate ( $\ln(\nu)$ ) were described as in Fig. S2, which were also estimated from the linear regression equation as follows:  $E_p(\text{V}) = -0.027 \ln(\nu) - 0.675$  ( $R^2 = 0.993$ ) for CIS/SPE,  $E_p(\text{V}) = -0.016 \ln(\nu) - 0.721$  ( $R^2 = 0.979$ ) for UiO-66/SPE, and  $E_p(\text{V}) = -0.039 \ln(\nu) - 0.603$  ( $R^2 = 0.989$ ) for CIS@UiO-66/SPE, respectively. Based on Laviron's equation for adsorption-controlled irreversible electrode processes, the kinetic parameters involving the redox reaction of 4-NP onto

the electrode/electrolyte interface were also determined [37, 38]. Namely, the number of transferred electrons ( $n$ ) was 3 at all modified electrodes; the charge transfer coefficient ( $\alpha$ ) values were 0.32, 0.55, and 0.34 for CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE, respectively. More particularly, the  $k_s$  value (electron transfer rate constant) from the reduction reaction of 4-NP was calculated to be 0.27, 0.95, and  $0.81 \text{ s}^{-1}$ , respectively.

$$E_p = E_o + (RT/\alpha nF) \times \ln(RT k_0/\alpha nF) - (RT/\alpha nF) \ln(\nu)$$

$$\ln(k_s) = \alpha \ln(1-\alpha) + (1-\alpha) \ln \alpha - \ln(RT/nFv) - \alpha(1-\alpha) \times (nF(E_p - E_{p/2})/RT)$$

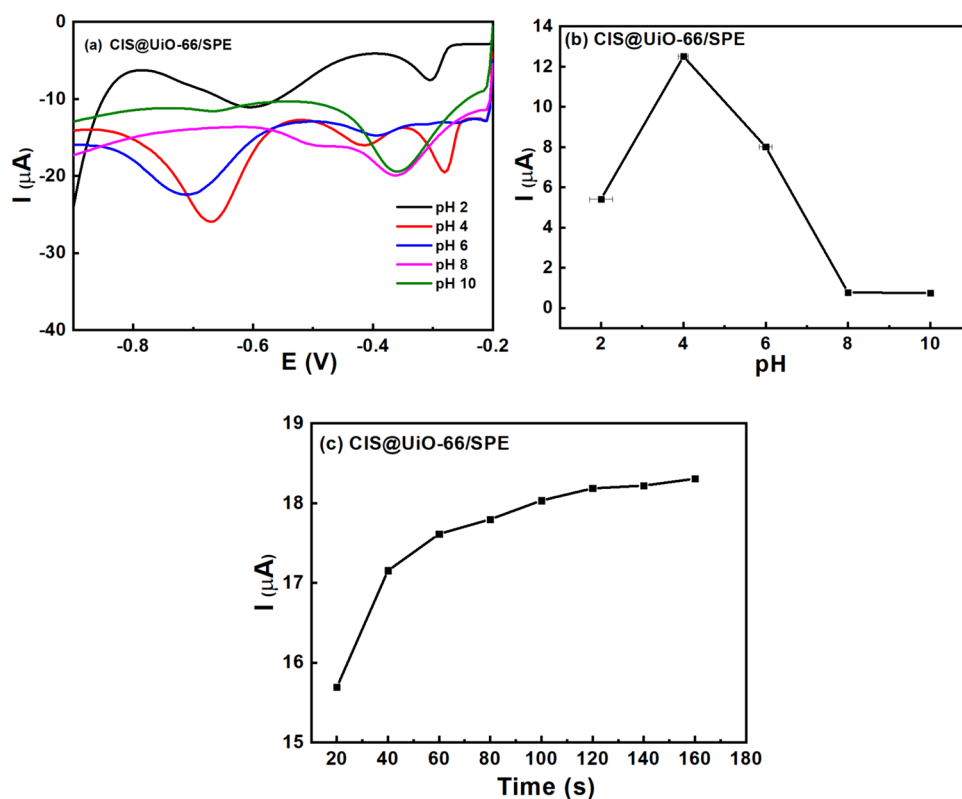
From the obtained results, it shows that the effective surface modification of the working electrode with proposed materials proved impressive enhancements in kinetic parameters of the electrochemical reaction of 4-NP. Although UiO-66/SPE showed a high potential in the increase of adsorption capacities ( $\Gamma$ ), charge transfer coefficient ( $\alpha$ ), and  $k_s$  value, CIS@UiO-66/SPE possessed a higher response current, arising from the outstanding electrocatalytic characteristics of CIS@UiO-66/SPE as well as the great structural stability and good synergistic effects of nanocomposite structure [39]. Furthermore, it further confirms that for 4-NP, the reduction reactions directly and considerably depended on the electrocatalytic ability of

electrode materials instead of only the electrical conductivity and adsorbability of the electrode.

As mentioned out in many previous reports, the optimization of pH value and accumulation time during electrochemical measurements is considered to be one of the most important factors in achieving better sensitivity and electrochemical performance. According to that, the effect of two factors on the current response of CIS@UiO-66/SPE for the 4-NP sensitive detection was investigated. DPV curves were observed in the pH range of from 2 to 10 along with the accumulation time from 20 to 160 s, respectively. Along with the increase in pH value, the current intensity gradually increased and reached the maximum intensity at around pH 4 and then decreased at higher values. Therefore, pH 4 was selected to be the best pH condition for the subsequent analytical experiments. Also, the optimal value of accumulation time was evaluated in PBS buffer with pH 4. The obtained results showed the response reached the maximum value at 120 s and decreased then. The reason is proposed due to the saturated state of the adsorption process of 4-NP onto the active electrode surface. According to these results, an accumulation time of 120 s and pH 4 were adopted as the optimal values for all subsequent experimental conditions (Fig. 7).

Returning to Fig. 8, under the optimal conditions of pH and accumulation time, to evaluate the sensing performance of 4-NP, DPV measurements in 0.1 M PBS buffer (pH 4) were carried out to determine the linear range and sensitivity

**Fig. 7** a DPVs curves; b, c the current intensity values obtained at CIS@UiO-66/SPE in 0.1 M PBS containing 4-NP when pH and accumulation time varies



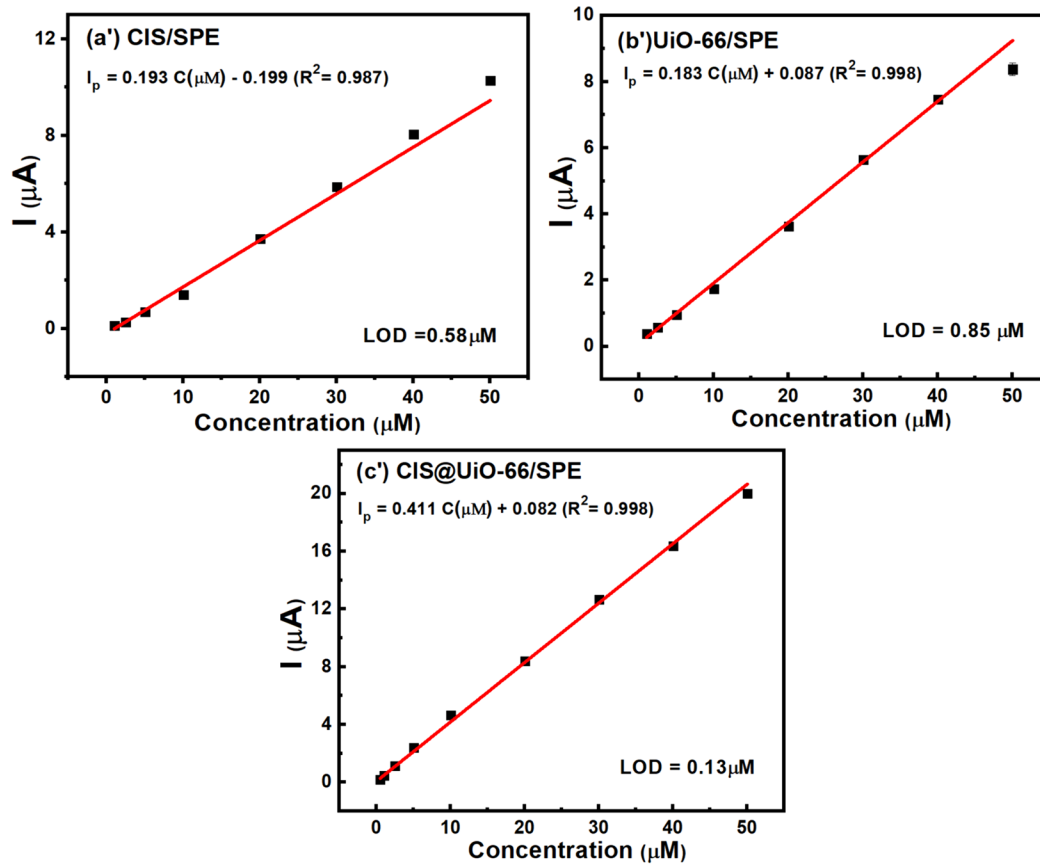
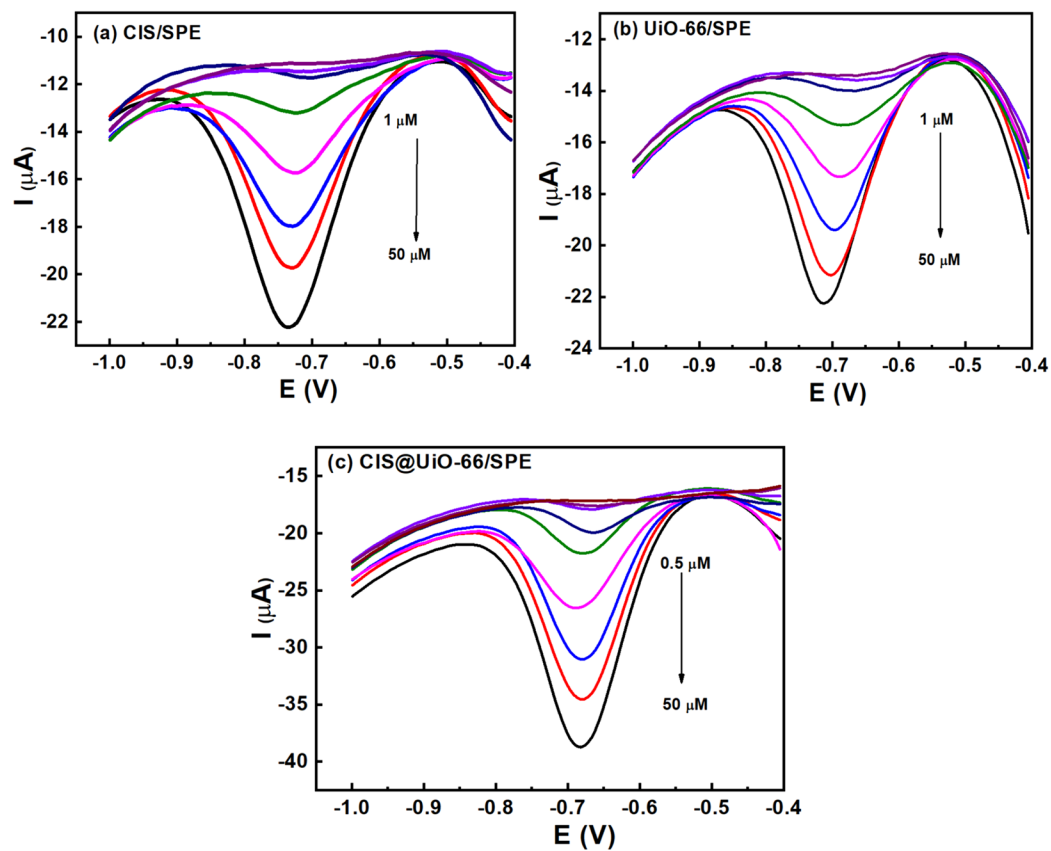


**Fig. 8** a–c DPV curves recorded at CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE with various 4-NP concentrations; a'–c' the calibration plots with error bars. Scan rate of  $6 \text{ mV s}^{-1}$

of the proposed electrodes. As a result, the reduction current response linearly increased with the increase in 4-NP concentration at all electrodes in the range of  $1\text{--}50 \text{ }\mu\text{M}$  for CIS/SPE and UiO-66/SPE, as well as  $0.5\text{--}50 \text{ }\mu\text{M}$  for CIS@UiO-66/SPE. Their curve equations were expressed as follows:  $I_p (\mu\text{A}) = 0.193 C(\mu\text{M}) - 0.199$  ( $R^2 = 0.987$ ) for CIS/SPE,  $I_p (\mu\text{A}) = 0.183 C(\mu\text{M}) + 0.087$  ( $R^2 = 0.998$ ) for UiO-66/SPE, and  $I_p (\mu\text{A}) = 0.411 C(\mu\text{M}) + 0.082$  ( $R^2 = 0.998$ ) for CIS@UiO-66/SPE, respectively. According to that, the limit of detection (LOD) for 4-NP was determined at about 0.58, 0.85, and  $0.13 \text{ }\mu\text{M}$  (using the formula of  $3\text{SD}/\alpha$ ) for CIS/SPE, UiO-66/SPE, and CIS@UiO-66/SPE, respectively. Furthermore, the sensitivity was also found around 3.49, 4.49, and  $0.586 \text{ }\mu\text{M cm}^{-2}$ . As expected, the considerable increase not only in linear concentration range but

also sensitivity at CIS@UiO-66/SPE was observed, further demonstrating the positive impacts of the modification of electrode surface with nanocomposites on the sensing performance of 4-NP, compared with other electrodes. One of the other important characteristics is the reproducibility and repeatability of the proposed electrode. Under the optimal condition, the repeatability was evaluated by recording the response current intensity in the presence of 4-NP for 5 successive times on the CIS@UiO-66/SPE. As expected, the obtained results showed good repeatability with low relative standard deviation (RSD) values of 1.3%. Also, five CIS@UiO-66/SPE electrodes were prepared under the same experimental conditions to check the reproducibility. As a result, the corresponding DPV response signals of 4-NP at  $50 \text{ }\mu\text{M}$  concentration in  $0.1 \text{ M}$  PBS solution were recorded and calculated, corresponding to the relative standard deviation (RSD) being around 2.32% (Fig. S3c), which demonstrates a good reproducibility. In addition, its long-term stability was also determined by evaluating response ability at room temperature. Indeed, the value of current intensity still maintained at a high level of 89% after storage for 10 days, compared with the initial current response (Fig. S3). Furthermore, the structural stability and reusability of CIS@UiO-66 catalyst after 4-NP detection were analyzed by XRD. The results of XRD analysis (Fig. 9) confirm that no obvious structural change occurred in the CIS@UiO-66 catalyst after 5 consecutive cycles of 4-NP detection.

These results demonstrate that CIS@UiO-66/SPE had good repeatability and stability for 4-NP detection. More interestingly, when considering other modified electrodes in previous research, CIS@UiO-66/SPE also exhibited remarkable enhancements in electrochemical performance for 4-NP detection. Hence, the development of CIS@UiO-66/SPE will be a promising path that needs to be more attention and research. Table 1 shows the electrochemical performance for 4-NP detection at various modified electrodes.

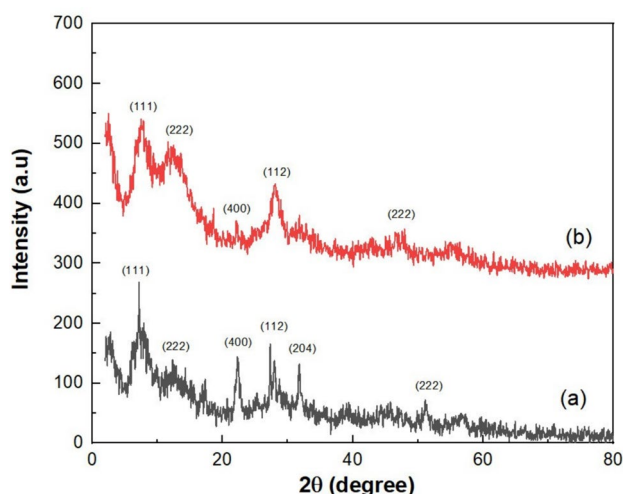


**Fig. 9** XRD pattern of **a** fresh and **b** used CIS@UiO-66 catalyst after reaction

**Table 1** A comparison of electrochemical performance for 4-NP detection at various modified electrodes

| Electrodes                        | Technique | Linear range ( $\mu\text{M}$ ) | LOD ( $\mu\text{M}$ ) | Stability     | Ref.      |
|-----------------------------------|-----------|--------------------------------|-----------------------|---------------|-----------|
| Gr-Ag NI-based PPE                | DPV       | 3.125–100                      | 2.7                   | –             | [40]      |
| TiO <sub>2</sub> -carbon dots/GCE | DPV       | 10–350                         | 0.12                  | –             | [41]      |
| TiO <sub>2</sub> NPs/RGO/GCE      | DPV       | 10–350                         | 0.13                  | 90.2%/2 weeks | [42]      |
| AcSCD-AuNPs-MC/GCE                | SWV       | 5–250                          | 1                     | –             | [43]      |
| BaTiO <sub>3</sub> /rGO/GCE       | DPV       | 5–50                           | 0.44                  | –             | [44]      |
| CIS@UiO-66/SPE                    | DPV       | 0.5–50                         | 0.13                  | 89%/10 days   | This work |

## Conclusions

This paper reports a CIS@UiO-66-based electrode 4-NP sensor. The proposed materials were prepared via a simple method. By electro-modifying of SPE and drop-casting CIS@UiO-66 on the electrode surface, we made modified sensors. As a result, thanks to possessing many advantages and great synergistic effects between CIS and UiO-66, it brought remarkable enhancement in kinetic parameters at electron transfer reactions of both the standard probe and targeted molecules (4-NP). Electrochemical measurements exhibited excellent sensitivity, linear range, detection limit, and selectivity toward the detection of the 4-NP at CIS@UiO-66/SPE compared with CIS/SPE and UiO-66/SPE, demonstrating the high applicability potential of this proposed electrode in the future.

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**Author contribution** Xuan Nui Pham: methodology, conceptualization, data curation, review and editing. Tuyet Nhung Pham: formal analysis, data curation, writing original draft writing. Thi Thanh Pham: investigation, formal analysis. T.-Thanh-Bao Nguyen performed SEM, EDX, and UV-vis-DRS measurements.

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## Declarations

**Competing interests** The authors declare no competing interests.

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