Supporting Information

A fast and highly selective ECL creatinine sensor for diagnosis of chronic kidney disease

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Contents

Reagents and chemicals

Methanol, ethanol, dichloromethane, acetic acid (CH_3COOH), citric acid, ascorbic acid, phosphoric acid (H_3PO4), uric acid, lactic acid, picric acid (PA), urea, glucose, creatinine (Crn), copper sulfate ($CuSO_4$), sodium carbonate (Na_2CO_3) potassium oxalate, ammonium chloride (NH_4Cl), calcium chloride ($CaCl_2$), potassium persulfate ($K_2S_2O_8$), potassium dihydrogen phosphate (KH_2PO_4), dipotassium hydrogen phosphate (K_2HPO_4), potassium acetate (CH_3COOK), potassium chloride (KCl), potassium hydroxide (KOH), potassium citrate, boric acid (H_3BO_3) and nafion were purchased from Merck. These chemicals were of analytical grade and used without any further purifications. Copper (II) carbonate ($CuCO_3$) and Copper (II) picrate ($Cu(pic)_2$) were synthesized as described in following sections. A solution of synthesized and well-characterized N-CQDs from our previous study was used.[1] Deionized water was used for rinsing, synthesis and as solvent for the preparation of all buffer solutions. Human serum was kindly provided by the Iranian Blood Transfusion Organization (IBTO), Ardabil, Iran. Urine and serum samples of four patients diagnosed with kidney disease were obtained from a local hospital in Zanjan, Iran.

Apparatus

Fourier transform infrared (FT-IR) spectroscopy was performed by using a Shimadzu IR Affinity spectrophotometer (Japan). For FT-IR analyses, little amounts of each compound solutions were mixed with KBr powder, dried at 110 °C for 60 min, and used for preparation of pellets. Thermogravimetric (TGA) analysis was performed by using Linseis STA-PT1000 apparatus under N_2 atmosphere and applying heating rate of 10 °C per minute.

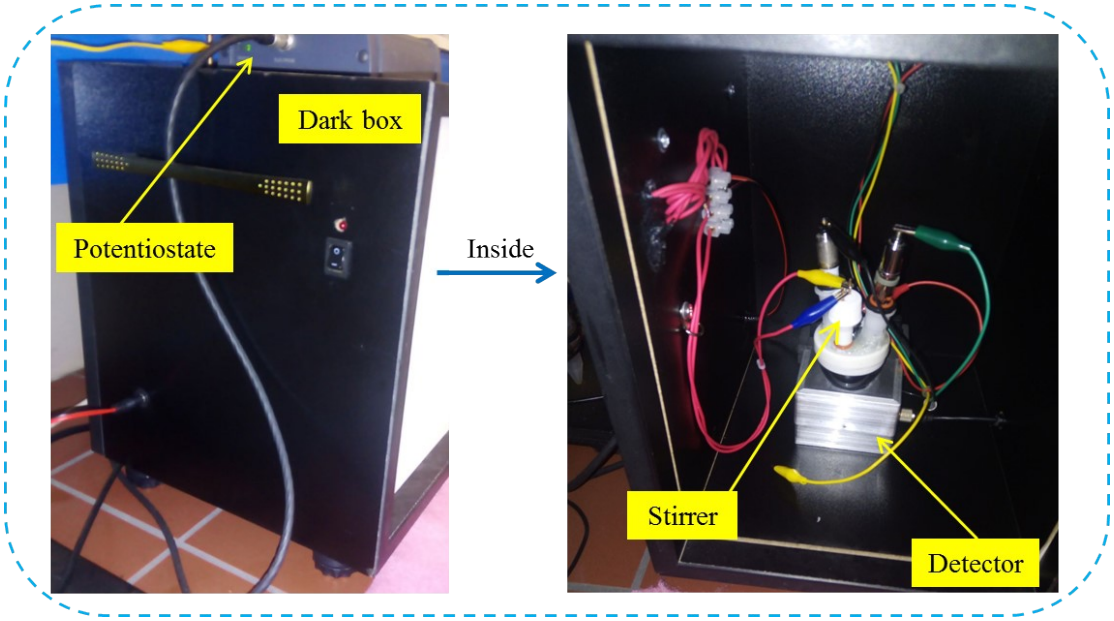


Fig. S1 Photos of lab set up used for ECL experiments.

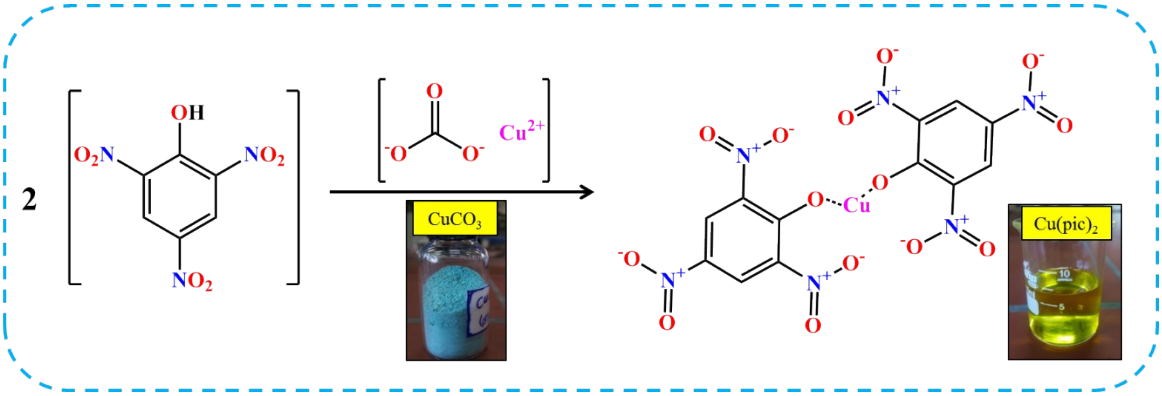
Synthesis of $CuCO_3$

$CuCO_3$ was synthesized by reaction between $CuSO_4$ and Na_2CO_3. At first 0.5 g (2 mmol) of $CuSO_4.5H_2O$ was dissolved in 20 mL water and stirred on a hot plate at 60 °C. Then 20 mL of Na_2CO_3 solution (0.2 M) was added dropwise to this solution. Afterword the cyan blue floated precipitate of the $CuCO_3$ was filtered and washed with water to completely removing the precursors and finally dried in an oven at 60 °C for 2 h.

Synthesis and characterization of $Cu(pic)_2$

Synthesis of $Cu(pic)_2$ from PA and $CuCO_3$ is described in the main paper as reaction is shown in Fig. S2. FT-IR and TGA analyses were used for proving the synthesis of $Cu(pic)_2$ from PA. Results of FT-IR analyses are shown in Fig. S3. FT-IR spectra of PA shows the mean peak of aromatic hydroxyl $(Ar{-}O{-}H)$[2] at 3108 Cm^{-1} due to the stretching vibration that decreased and slightly shifted to 3086 Cm^{-1} in the case of $Cu(pic)_2$ implying to bond formation between Cu and PA and thus successfully synthesis of $Cu(pic)_2$. On the other hand $Ar{-}NO_2$ stretching peaks (at 1531 and 1343 Cm^{-1}) and $N{-}O$ symmetric stretching (at 1270 Cm^{-1}) in both compounds don't show the significance differences from each other due to the presence of nitro groups in same positions in both compounds.[3] TGA analysis was used for comparing the decomposition properties

of PA and $Cu(pic)_2$. As is shown in fig. S4, the fast mass loss is observed in both compounds but $Cu(pic)_2$ decomposition is faster and happens in lower temperature (250 °C) than that of the PA (269 °C). As picrate salts are more unstable than PA,[4] these results show that $Cu(pic)_2$ was synthesized successfully.



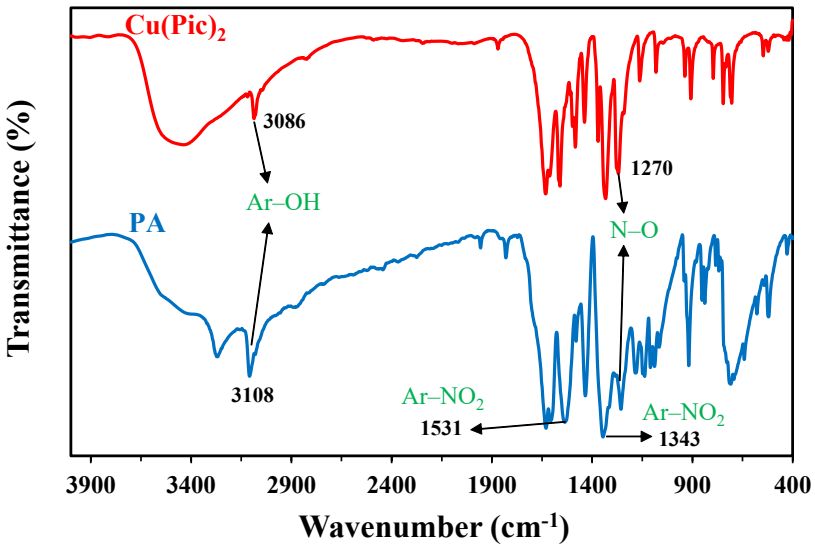


Fig. S2 Preparation of $Cu(pic)_2$

Fig. S3 FT-IR spectra of PA and $Cu(pic)_2$

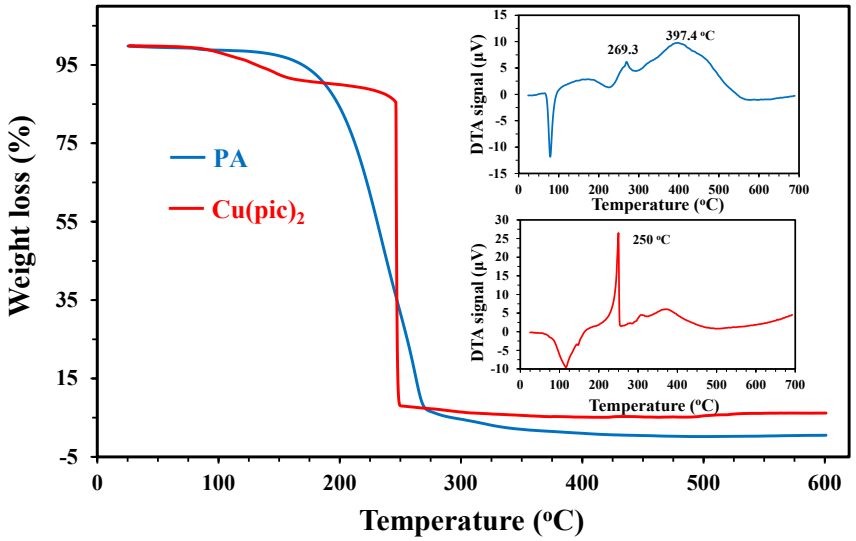


Fig. S4 TGA analysis of PA and $Cu(pic)_2$, inset: differential thermal analyses (DTA)

Effect of electrode modifier on the Crn determination

As described in main paper, formation of Janovsky complex from copper (II) picrate and Crn on the electrode during the determination was considered as the main reason for sensitivity and selectivity of the sensor. As known, PA and Crn react with each other and make orange colored Janovsky complex. Result of the reaction between copper (II) picrate and Crn was compared by Janovsky complex. As shown in fig. S5, FT-IR spectra of the Janovsky complex (c) is similar to that of the complex resulted from copper (II) picrate and Crn. Images of the solutions that are shown in fig. S6 also simply proves the formation of Janovsky complex.[5]

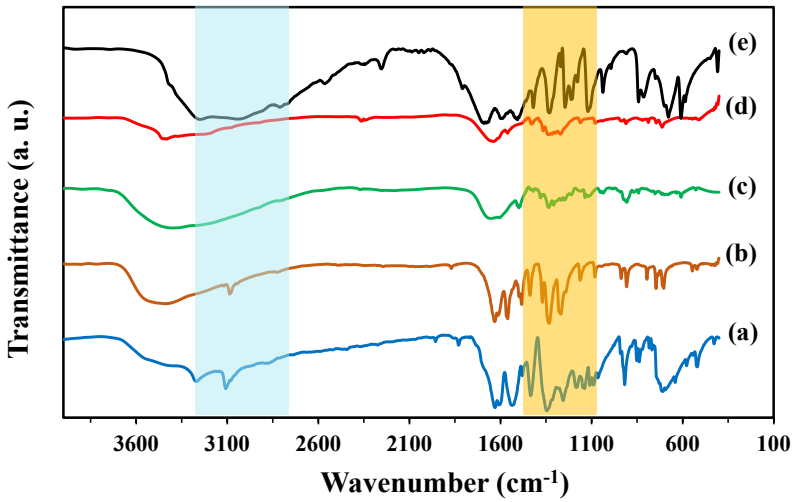


Fig. S5 FT-IR spectra of PA (a), $Cu(pic)_2$ (b), complex resulted from PA and Crn (c) complex resulted from $Cu(pic)_2$ and Crn (d) and Crn (e).

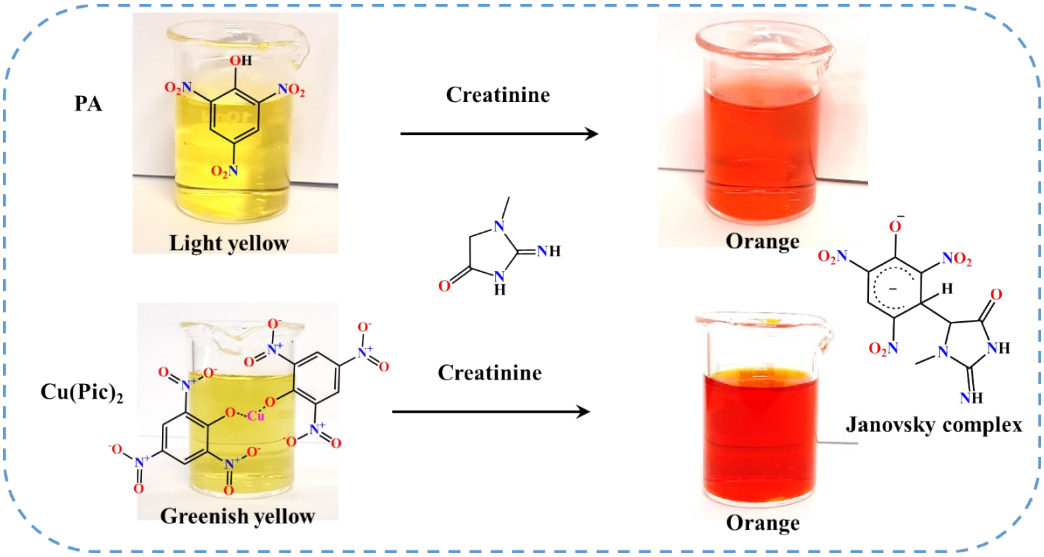


Fig. S6 Comparing results of reaction between PA and Crn with reaction between copper (II) picrate and Crn and real photos of the solutions.

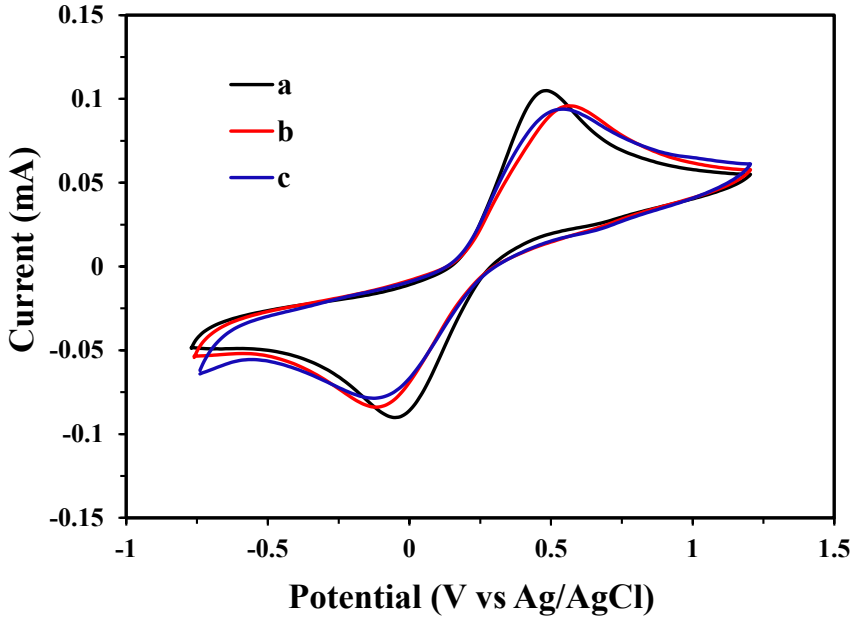


Fig. S7 CV curves of bare GCE (a), prepared sensor (b) and prepared sensor after use (c). Experiment was performed at scan rate of 0.1 Vs^{-1} in solution containing KCl (0.1 M) and $[Fe(CN)_6]^{3-/4-}$ (5 mM).

References

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