Reversible Voltammetric Probe Combined with the Thermally-Gated Method Using Stimuli-Responsive semi-IPN Polypyrrole Nanogels for Selective Chlorambucil (LeukeranTM) Sensing

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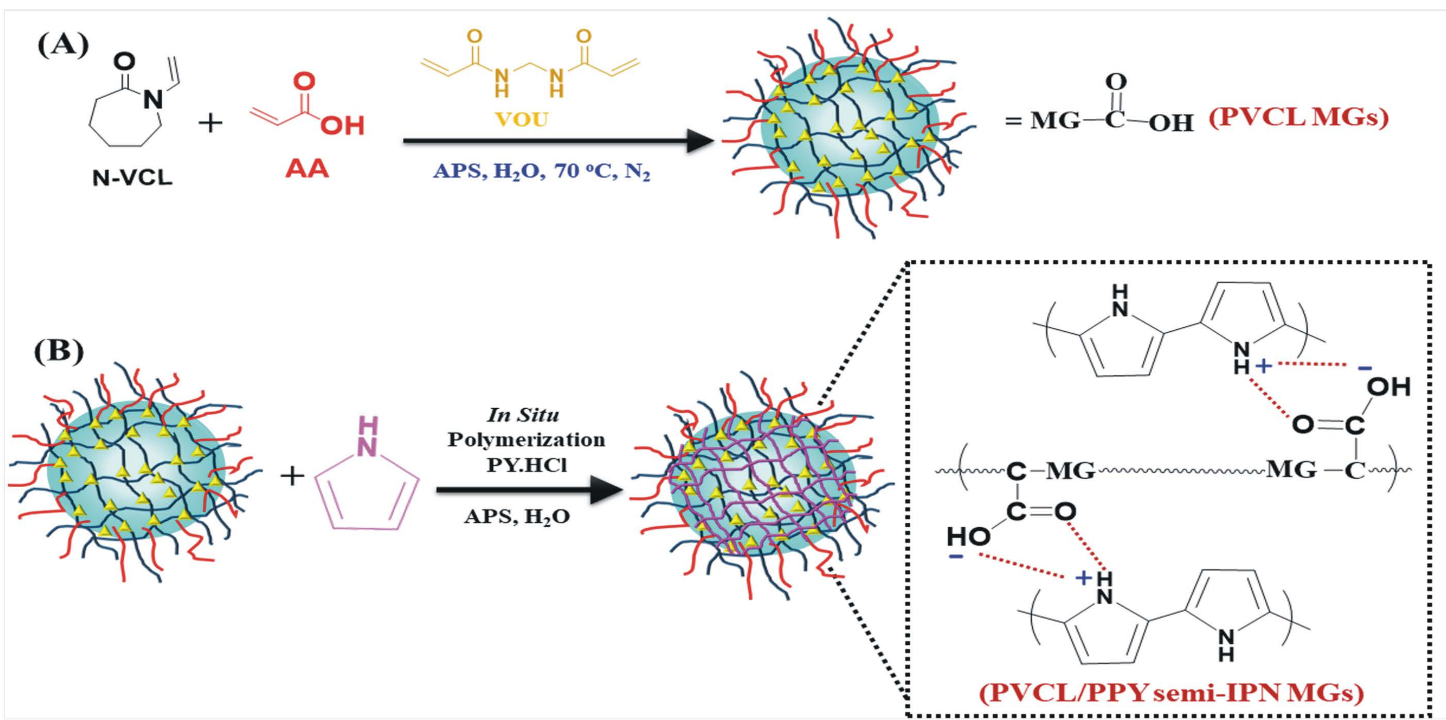
Abstract

- In this study, we report the synthesis of thermosensitive poly(N-vinylcaprolactam) semi-interpenetrated conductive polypyrrole microgels (PVCL/PPY semi-IPN MGs) for "on-off" switchable electrochemical sensing of carcinogenic nitrogen mustard drug chlorambucil (Leukeran[TM], CBL)
- The synthesized PVCL/PPY semi-IPN MGs modified electrode (PVCL/PPY semi-IPN MGs /GCE) acts as a thermo-reversible switch-like sensor for the electrochemical oxidation of CBL due to the temperature stimulus-response of PVCL.
- Cyclic voltammetry (CV) of CBL at the PVCL/PPY semi-IPN MGs /GCE manifest well-defined higher oxidation peak current when the electrolyte temperature is above the T_{LCST} of PVCL, signifying the "on" state. This CBL electro-oxidation peak current clearly reduced below the T_{LCST} of PVCL, signifying the "off" state.
- Repeatable "on-off" switching of the CV responses of CBL at the PVCL/PPY semi-IPN MGs /GCE was attained by controlling the electrolyte temperature. The proposed temperature-responsive switched sensor had a wide dynamic range (0.02 to 420 µM), excellent sensitivity, and a low detection limit of 1.98 nM for CBL at 40 °C compared to 25 °C.
- Interestingly, the proposed sensor proves excellent selectivity for detecting CBL in potential interference compounds. Moreover, the proposed method was successfully used to detect CBL in human blood serum and human urine samples.

Synthesis route of PVCL MGs and PVCL/PPY semi-IPN MGs



Scheme 1. Synthesis route of (A) PVCL MGs and (B) PVCL/PPY semi-IPN MGs.

Results and Discussion

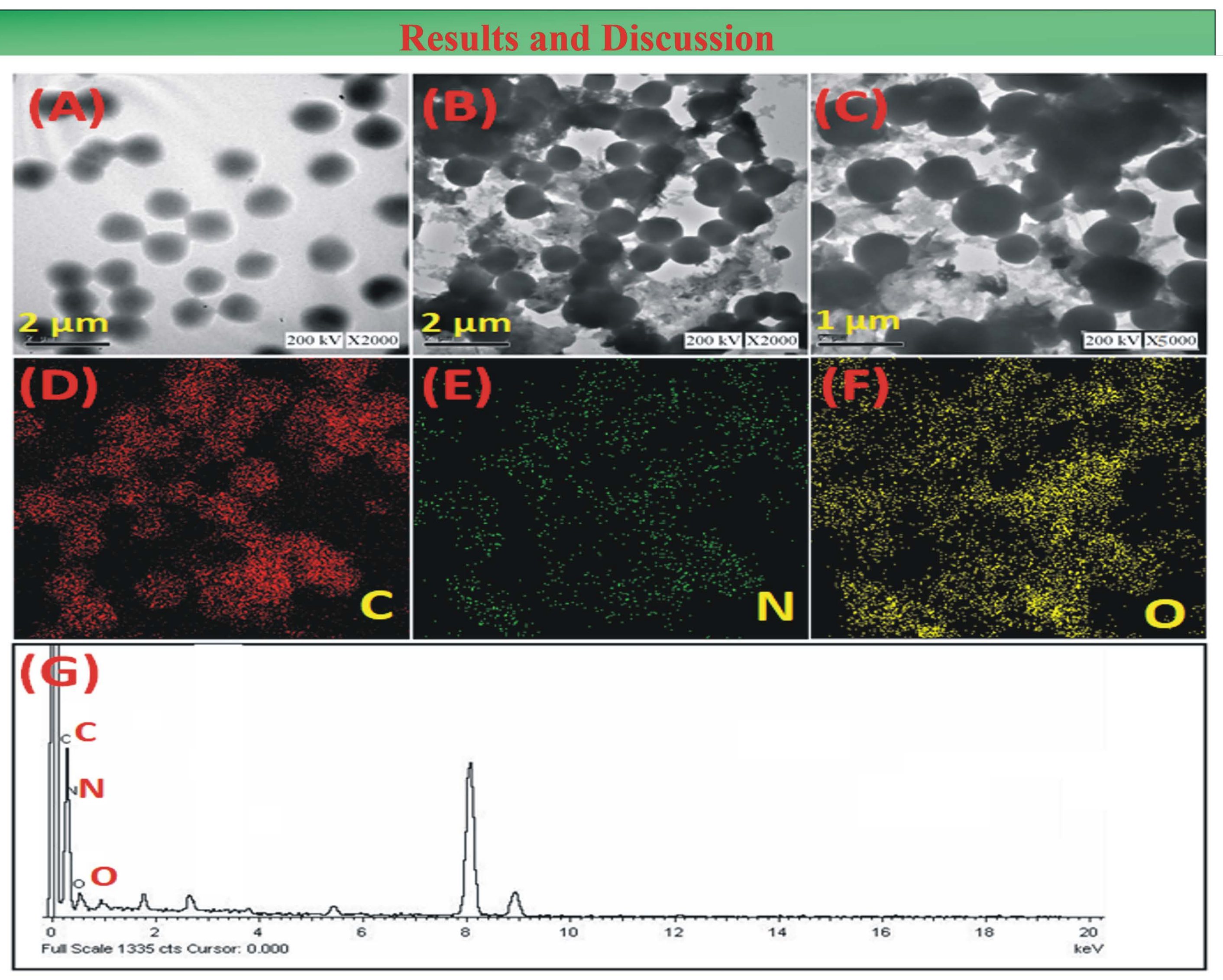


Fig. 1. TEM image of (A)Virgin PVCL MGs, (B-C) PVCL-PPY semi-IPN MGs, (D-F) elemental mapping images of C, N, and O at PVCL-PPY semi-IPN MGs, (G) EDS images of PVCL-PPY semi-IPN MGs.

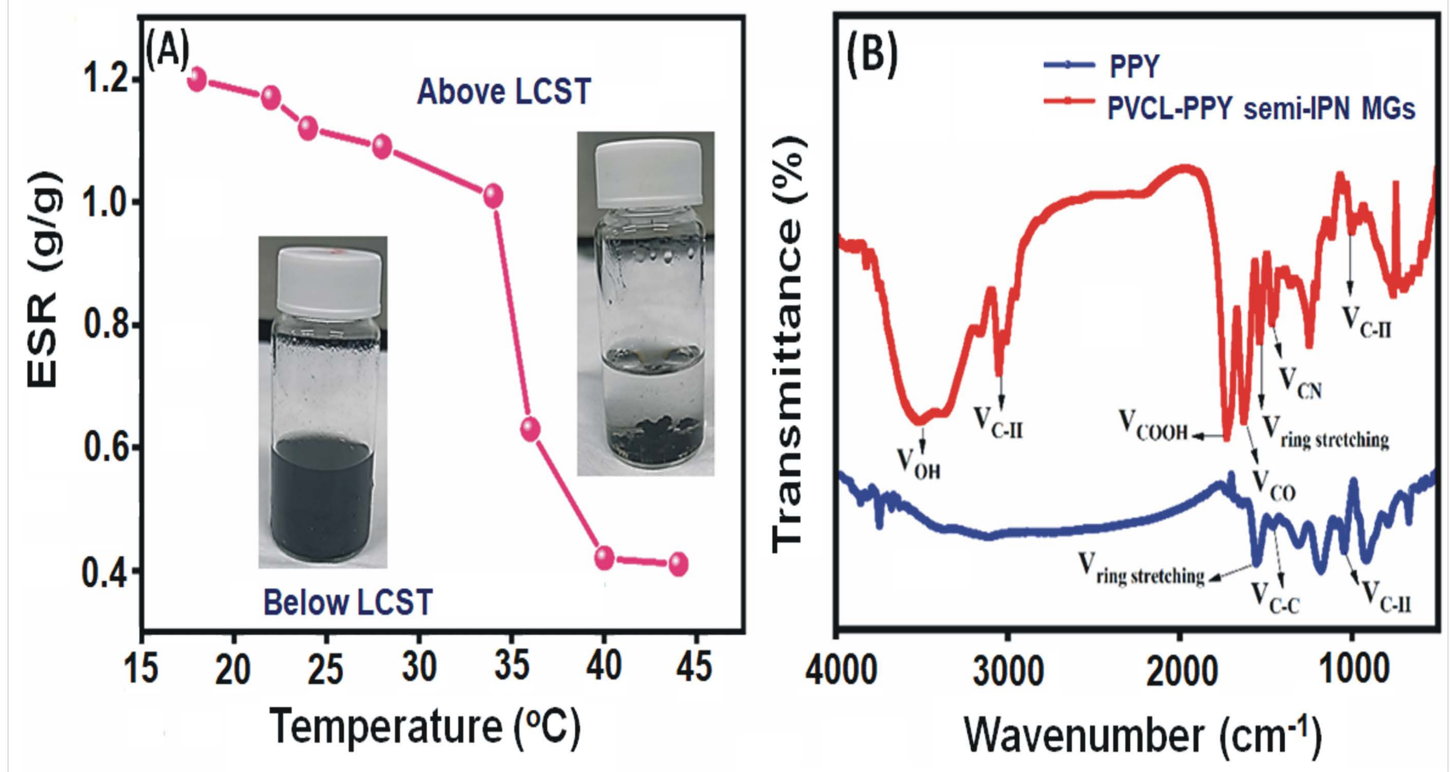


Fig. 2. (A) ESR of the synthesized PVCL-PPY semi-IPN MGs at specific temperatures (18, 22, 24, 28, 32, 36, 40, 44 °C), (B) FTIR images of PPY and PVCL-PPY semi-IPN MGs.

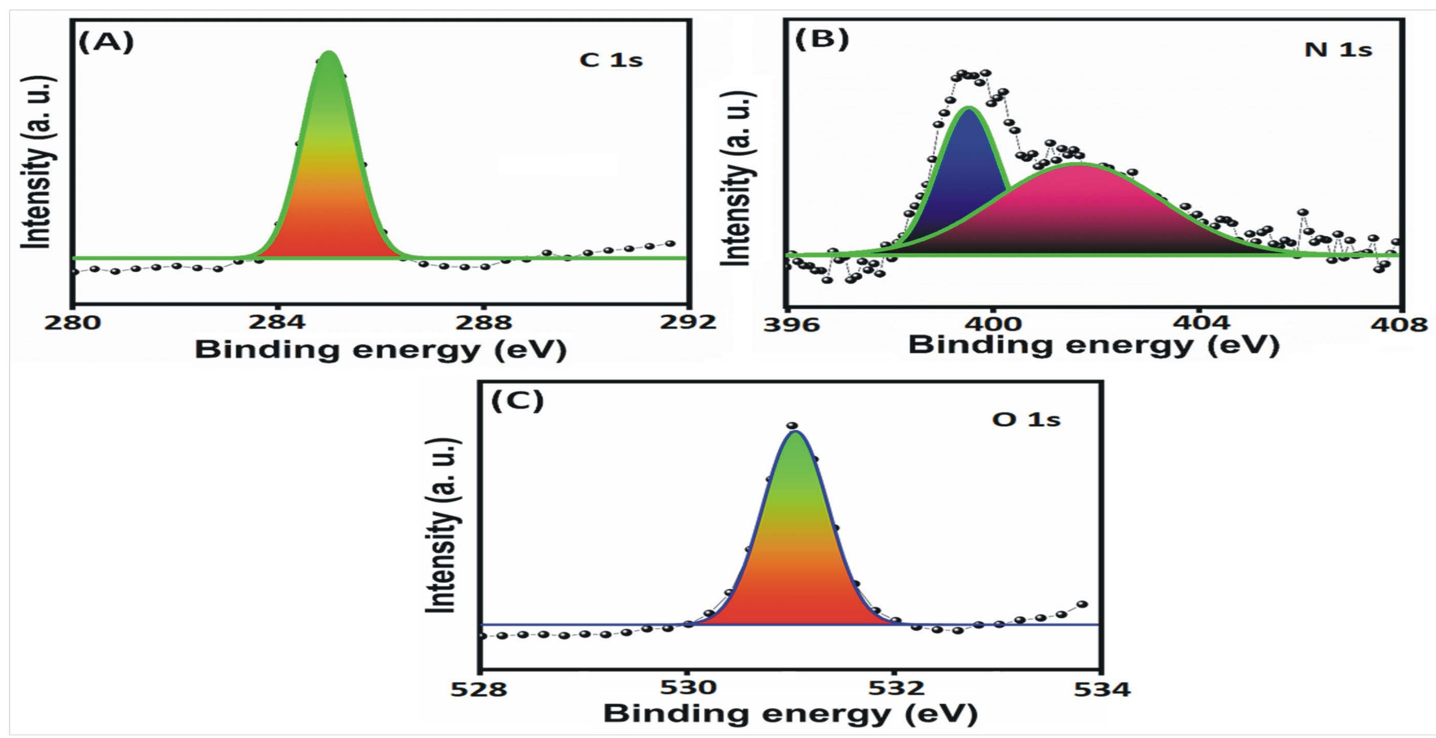


Fig. 3. Core-level XPS spectrum of C 1s, N 1s, and O 1s.

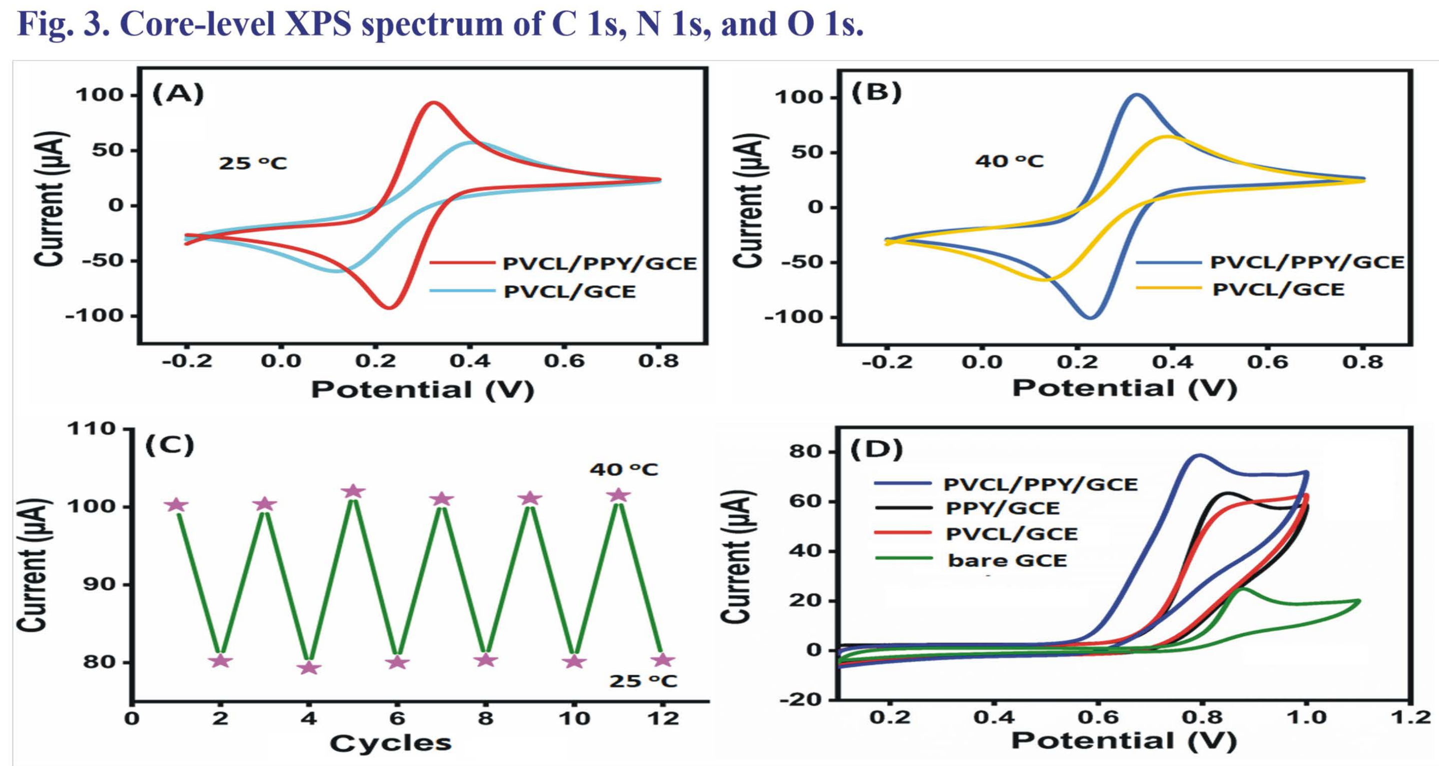
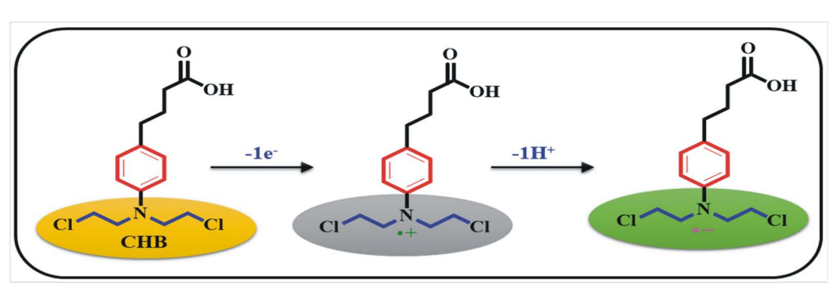


Fig. 4. (A and B) Cyclic voltammograms of PVCL/GCE and PVCL/PPY semi-IPN MGs/GCE in ferricyanide redox probe at 40 and 25 °C (scan rate; 50 mV/s). (C) Reversible changes of the oxidation peak current of the ferricyanide redox probe at the temperatures between 25 and 40 °C. (D) Cyclic voltammograms of CBL (150 µM) at the bare GCE, PVCL/GCE, PPY/GCE, and PVCL/PPY semi-IPN MGs/GCE in 0.1 M PBS at a scan rate of 50 mV/s (at 40 °C).



Scheme 2. The feasible electrochemical oxidation mechanism of CBL at PVCL/PPY semi-IPN MGs/GCE.

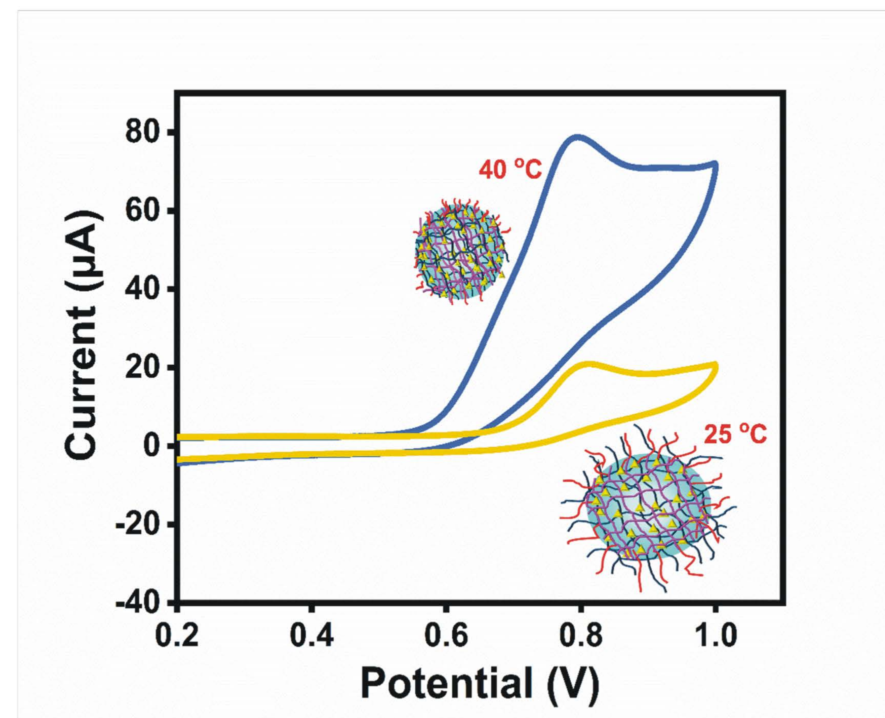


Fig. 5. Temperature-reversible Cyclic voltammograms of PVCL/PPY semi-IPN MGs/GCE in 0.1 M PBS with 150 µM CBL at 25 and 40 °C (scan rate; 50 mV/s).

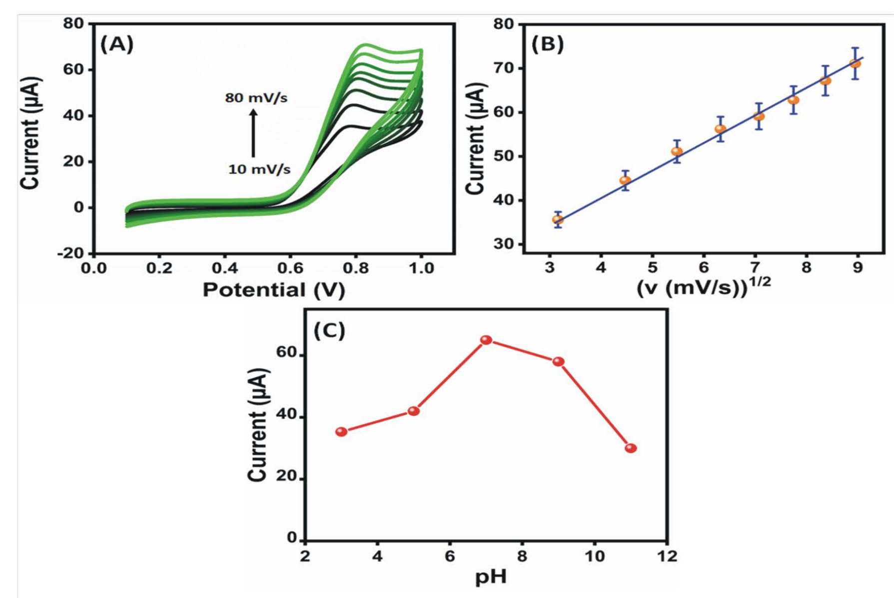


Fig. 6. (A) Cyclic voltammograms of CBL at the PVCL/PPY semi-IPN MGs/GCE in 0.1 M PBS over a scan rate ranges of 10 to 80 mV/s (Testing temperature: 40 °C). (B) The plot of peak current vs. square root of the scan rate. (C) The plot of anodic peak current vs. different pH values (Testing temperature: 40 °C).

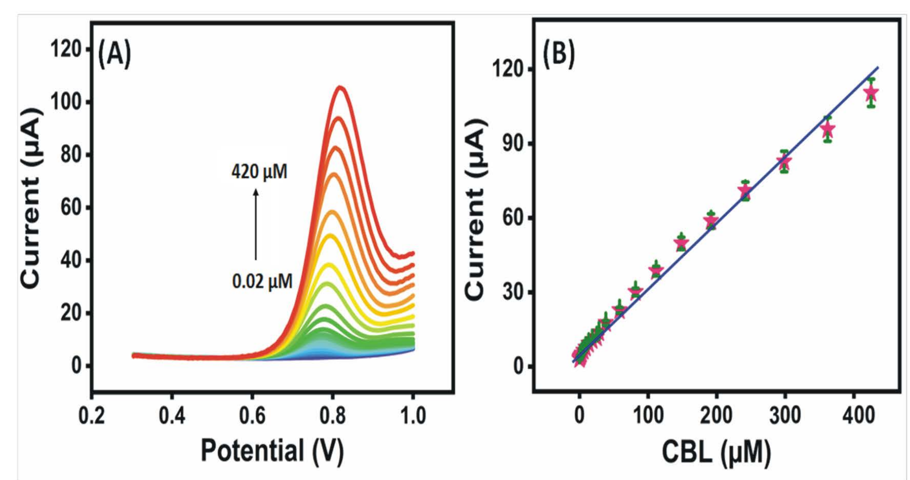


Fig. 7. (A) Differential pulse voltammograms of the PVCL/PPY semi-IPN MGs/GCE in 0.1 M PBS at various concentrations of CBL from 0.02 to 420 µM at 50 mV/s (Testing temperature: 40 °C). (B) The linear plot of anodic peak current vs. concentrations of CBL.

Conclusions

- We controlled the electrochemical process of the CBL sensor by changing the electrolyte temperature. Thermo-controlled deactivation-activation behavior of CBL electrocatalytic oxidation was witnessed at 25 °C ("off" state) and 40 °C ("on" state), and the mechanism of switch-like electrocatalytic action of PVCL/PPY semi-IPN MGs was also examined.
- The thermo-controlled electrocatalytic CV behavior of the PVCL/PPY semi-IPN MGs are attributed to the shrinking-swelling phase transition of PVCL MGs. The PVCL/PPY semi-IPN MGs/GCE showed a great CBL electrochemical response at above LCST (40 °C) than below LCST (25 °C)

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