

Hybrid nanostructures of urchin-like $\text{MnCo}_2\text{O}_{4.5}$ micro flowers on N, B co-doped rGO for electrochemical determination of paracetamol

N. Yavai¹, Kh. Ghanbari^{*1}

*¹Department of Analytical Chemistry, Faculty of Chemistry, Alzahra University, P. O. Box 1993893973,
Tehran, Iran*

*Corresponding author. Tel.: +98 21 88044040; fax: +98 21 88035187.
E-mail address: kh.ghanbari@alzahra.ac.ir (kh_ghanb@yahoo.com).

Chemicals and Instruments

All materials used in this study were analytical reagent grade. Graphite powder, paraffin, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaNO_3 , Paracetamol (PAR), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), ethanol, boric acid (H_3BO_3), hydrazine, Urea, phosphoric acid (H_3PO_4), Na_2HPO_4 , and KH_2PO_4 from Sigma-Aldrich or Merck were obtained. Phosphate buffer solution (PBS, 0.1 M, pH 7.2) was used as a supporting electrolyte. All solutions were prepared with double-distilled water. All experiments were done at room temperature (22-25 °C). A Tensor 27 (Bruker) instrument was used for ATR-FTIR analysis. The surface properties and morphologies and energy dispersive X-ray analysis (EDS) were examined by field emission scanning electron microscopy with an accelerating voltage of 20 kV (FE-SEM) (MIRA 3, TESCAN, Czech Republic). A Metrohm Autolab B. V.® Autolab PGSTAT 204 potentiostat/galvanostat (Utrecht, UT, the Netherlands) was used to carry out all electrochemical experiments. As a working electrode, a bare or modified carbon paste electrode (CPE, diameter=3.5 mm), as a counter electrode, a platinum wire, and as a reference electrode an Ag/AgCl/saturated KCl was used as a three-electrode cell system.

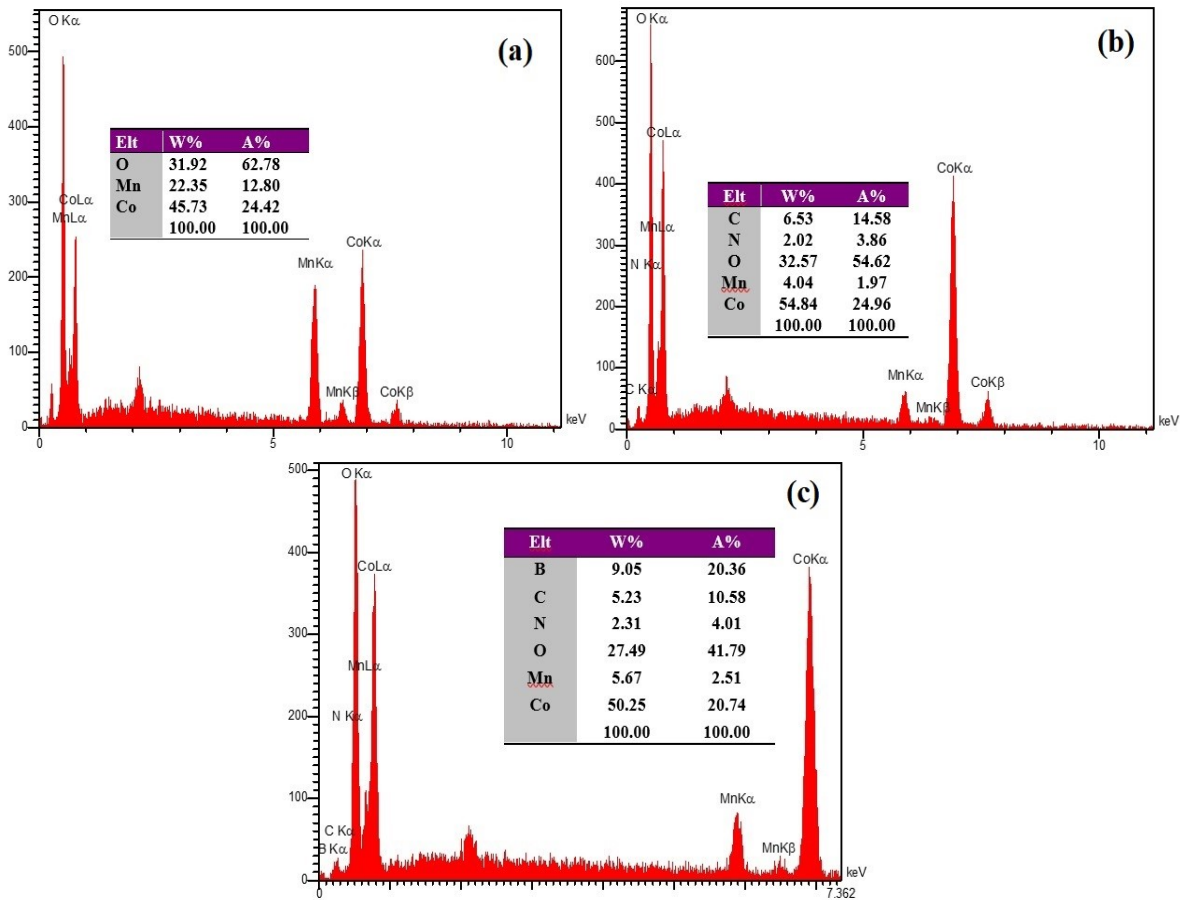


Fig. S1. EDX patterns of (a) $\text{MnCo}_2\text{O}_{4.5}$, (b) $\text{MnCo}_2\text{O}_{4.5}/\text{N-rGO}$, and (c) $\text{MnCo}_2\text{O}_{4.5}/\text{BN-rGO}$.

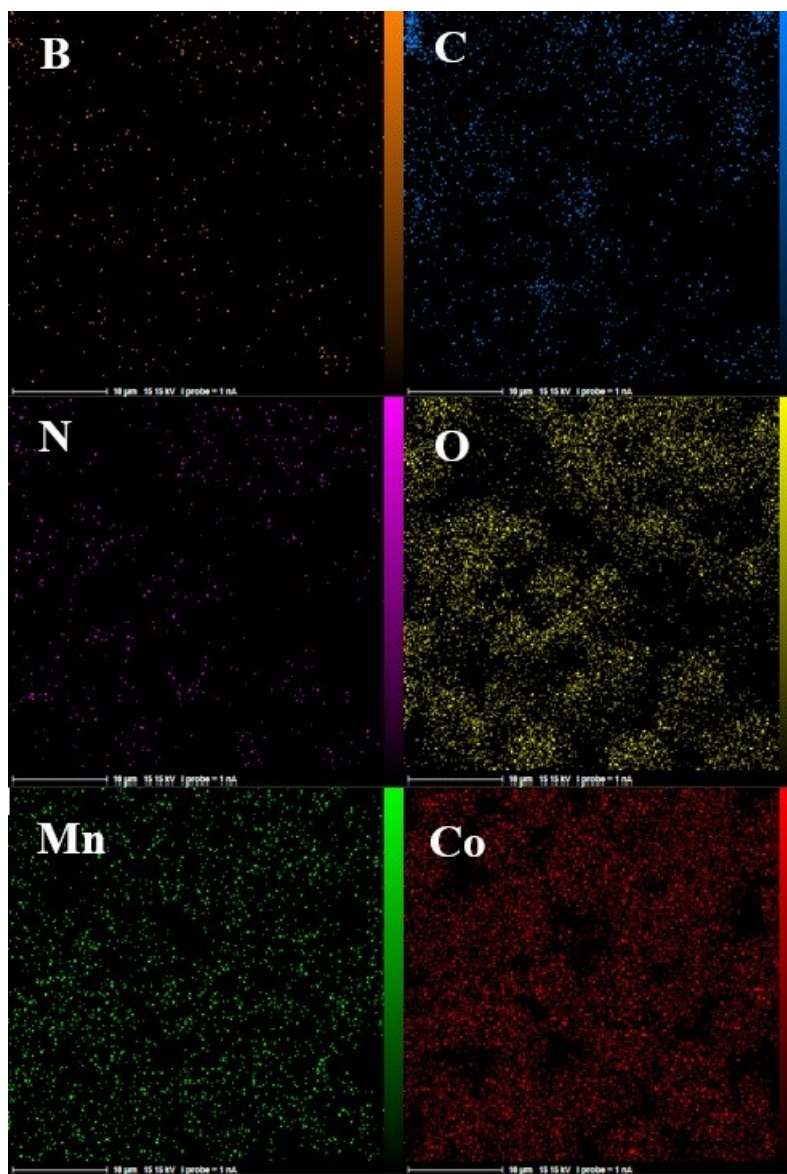


Fig. S2. Elemental mapping of MnCo₂O_{4.5}/BN-RGO nanocomposite.

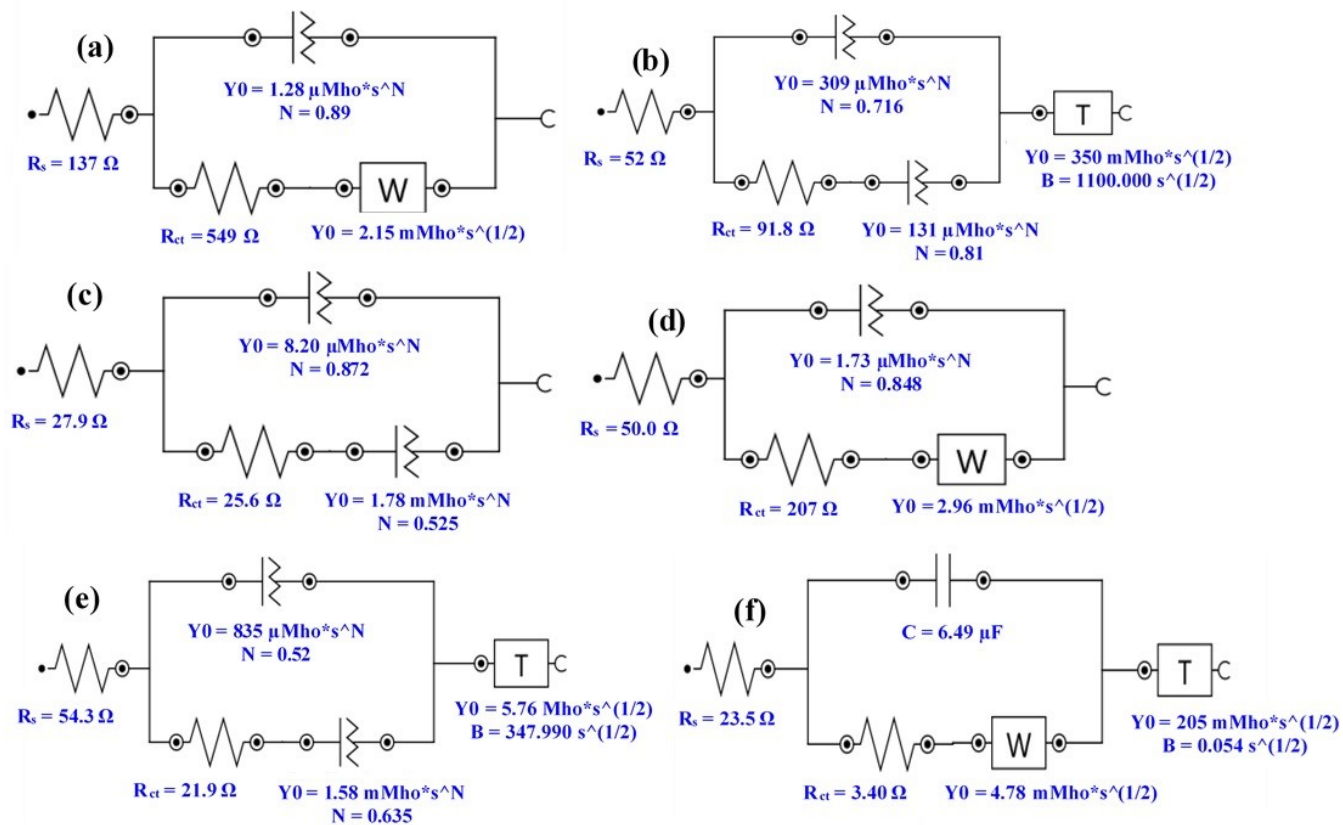


Fig. S3. Equivalent circuits for bare (a) bare CPE, (b) rGO/CPE, (c) BN-rGO/CPE, (d) MnCo₂O_{4.5}/CPE, (e) MnCo₂O_{4.5}/rGO/CPE, and (f) MnCo₂O_{4.5}/BN-rGO/CPE

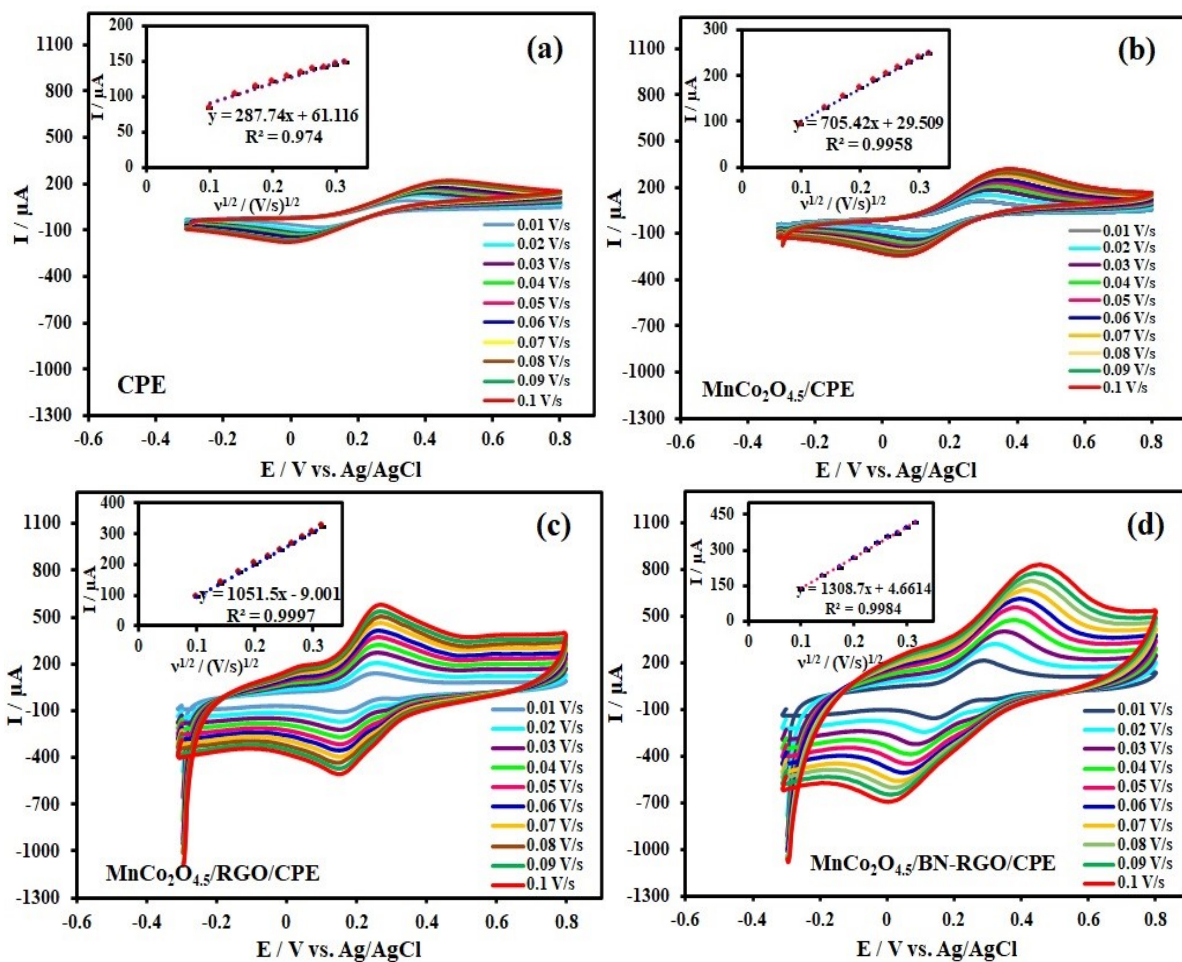


Fig. S4. Cyclic voltammograms of 0.1 M KCl solution containing 5.0 mM $\text{Fe}(\text{CN})_6^{3-/4-}$, at different scan rates (10 to 100 mV s^{-1}) at the surface of (a) bare CPE, (b) $\text{MnCo}_2\text{O}_{4.5}/\text{CPE}$, (c) $\text{MnCo}_2\text{O}_{4.5}/\text{RGO}/\text{CPE}$, and (d) $\text{MnCo}_2\text{O}_{4.5}/\text{BN-RGO}/\text{CPE}$. Insets: a plot of I_p vs. $v^{1/2}$ obtained from cyclic voltammograms.

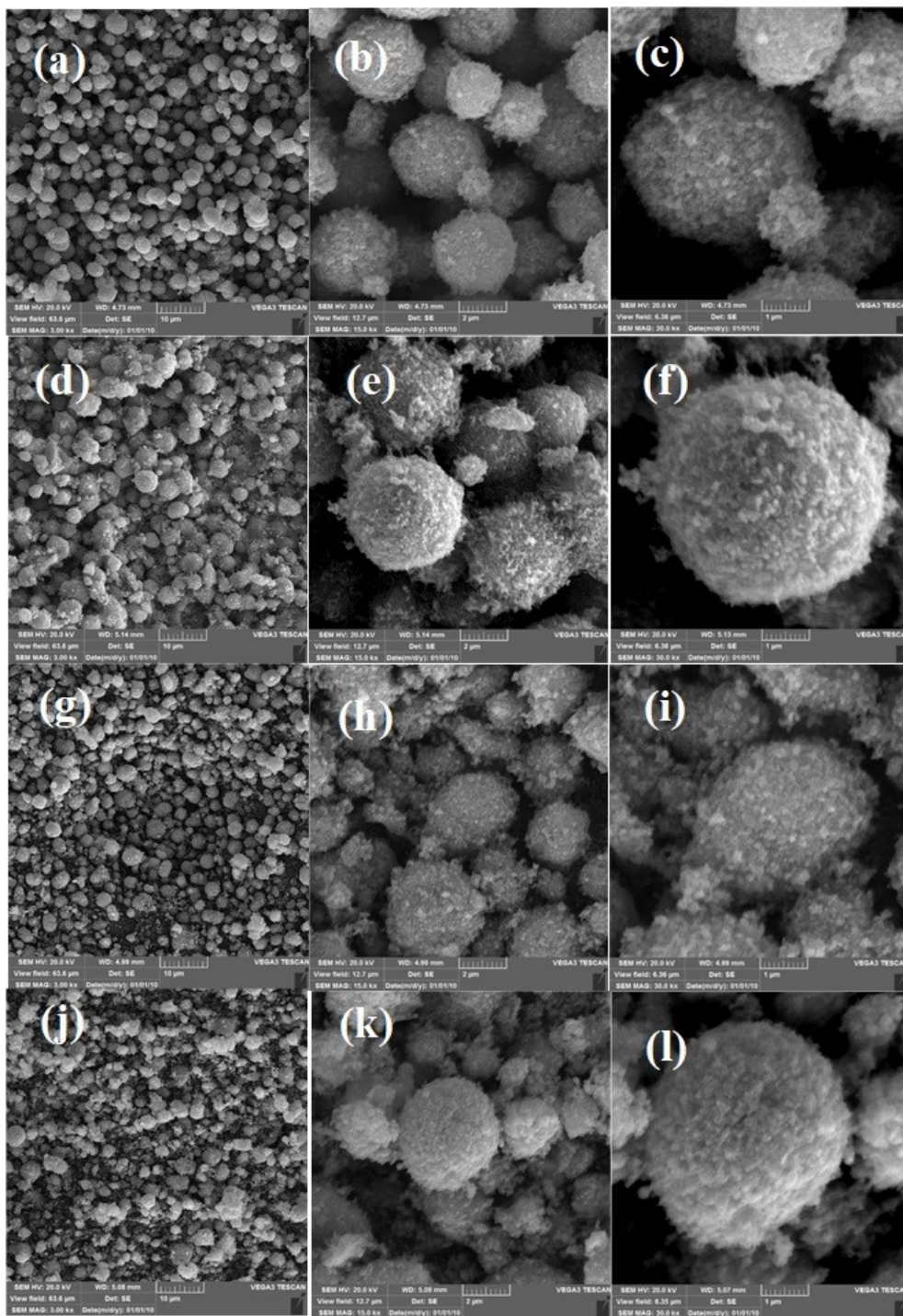


Fig. S5. Optimization of the amount of urea (a-c) 10 mmol; (d-f) 23 mmol; (g-i) 46 mmol; and (j-l) 69 mmol for synthesis $\text{MnCo}_2\text{O}_{4.5}$.

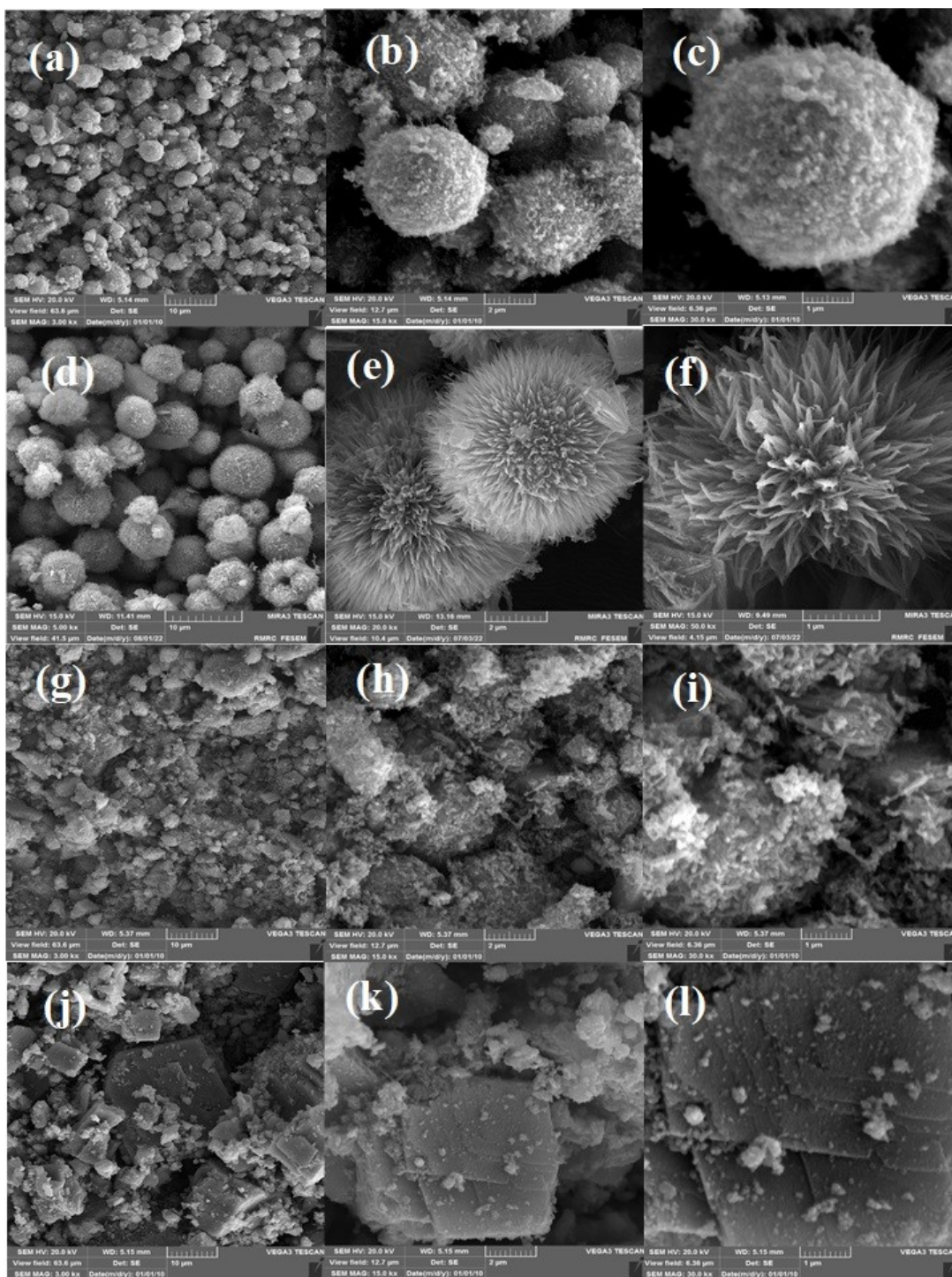


Fig. S6. Optimization of the oven temperature (a-c) 90 °C; (d-f) 120 °C; (g-i) 150 °C; and (j-l) 180 °C for synthesis $\text{MnCo}_2\text{O}_{4.5}$

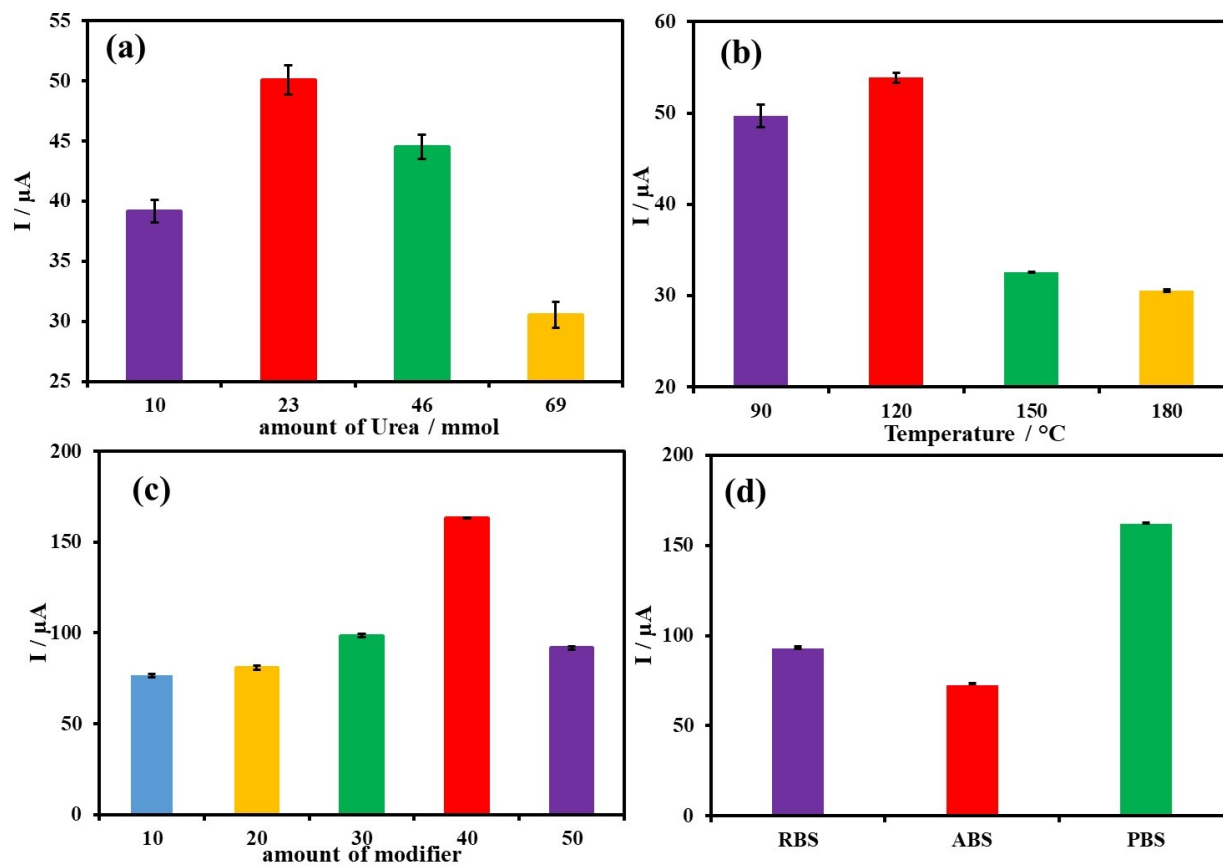


Fig. S7. Optimization of different conditions affecting the determination of PAR. Variation of electrode response for 1.0 mM PAR with changes of (a) the amount of urea; (b) the oven temperature for synthesis $\text{MnCo}_2\text{O}_{4.5}$; (c) the amount of modifier, and (d) the buffer type.

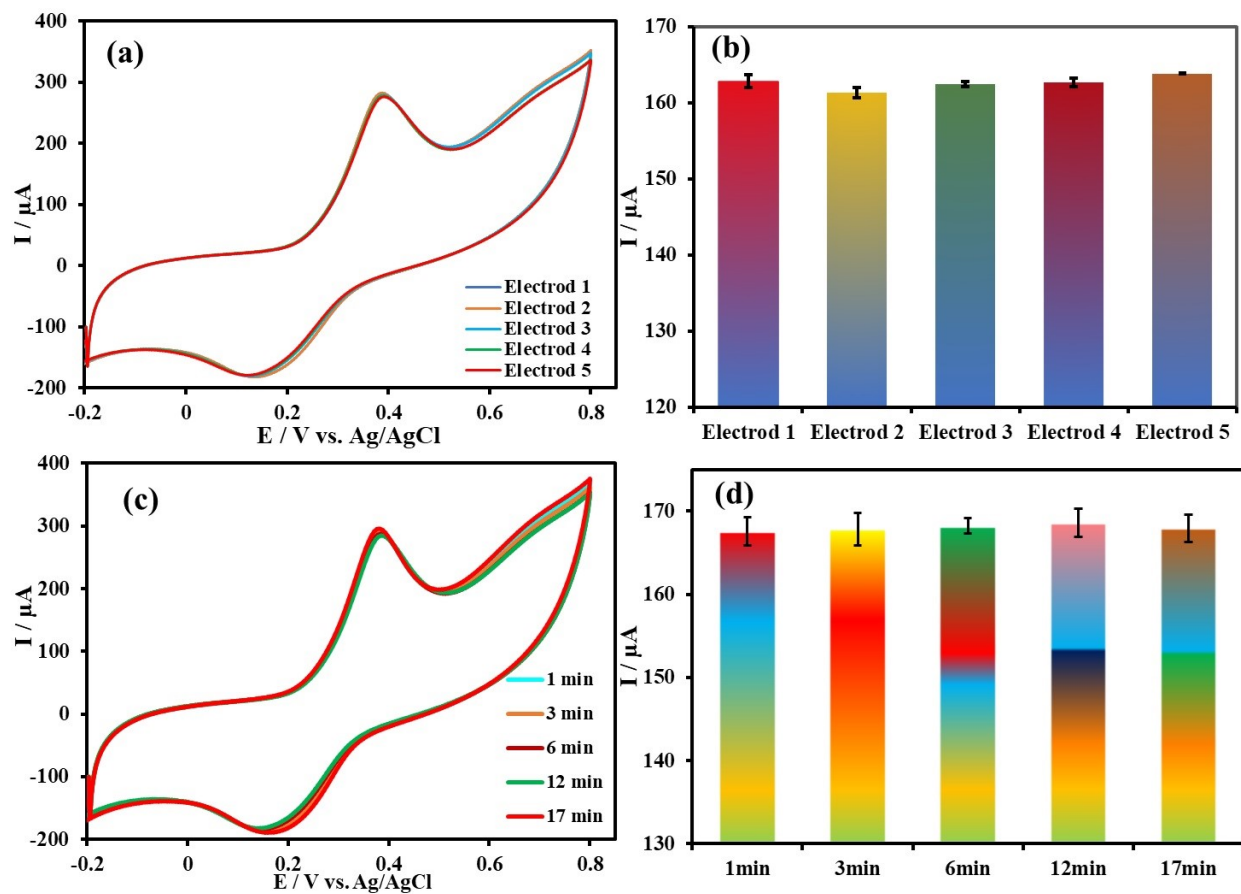
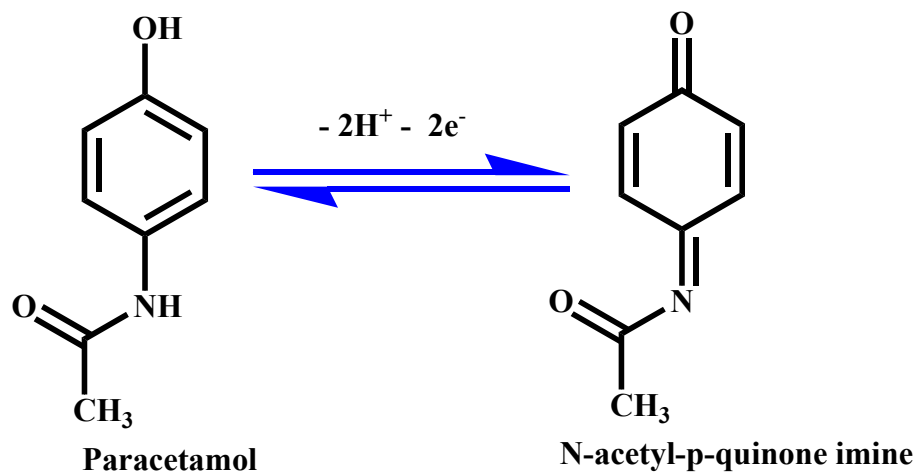


Fig S8. CVs of MnCo₂O_{4.5}/BN-rGO/CPE in 50 μM PAR and 0.1 M PBS solution (pH = 7.2) to investigate: (a) reproducibility; (b) corresponding bar diagram of current vs. number of the electrode; (c) repeatability; (d) corresponding bar diagram of current to times;



Scheme S1. Mechanism of the electrochemical oxidation of paracetamol.