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Facile synthesis of nanostructured $CuCo_2O_4$ as a novel electrode material for high-rate supercapacitors

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Electronic Supplementary Information (ESI†)

Synthesis of $CuCo_2O_4$ nanoparticles. All of the employed chemicals were purchased from Merck and used without any purification. Stoichiometric amounts of $Cu(NO_3)_2.3H_2O$ (0.032 mol) and $Co(NO_3)_2.3H_2O$ (0.064 mol) were dissolved in 50 ml doubly distilled water and mixed together. The obtained solution was sonicated in 50 °C for 1 h in an ultrasonic bath. Then, urea (0.192 mol) was added to the solution and temperature was raised to 80 °C and maintained at this temperature for 12 h to gradually evaporate the water. The obtained powder was ground and then calcined at 400 °C for 6 h in an electrical furnace.

Synthesis of $CuCo_2O_4$ microparticles. Stoichiometric amounts of copper and cobalt nitrates were dissolved in 50 ml doubly distilled water and mixed together. Then, 20 mL of 2 M NaOH solution was gradually added and stirred at 60 °C for 1 h. The obtained precipitation was filtered, washed and dried at 60 °C. The powder was ground and then calcined at 400 °C for 3 h.[S1]

Characterization of the sample. The prepared samples were structurally characterized using powder X-ray diffraction (XRD, Philips X´pert diffractometer with CuKα radiation (λ = 0.154 nm) generated at 40 kV and 30 mA with a step size of 0.04 $°s^{-1}$). The crystalline size of the particles was calculated by Debye-Scherer equation:

$$d = K\lambda/(\beta cos\theta) \quad (1)$$

where *d* is the particle dimension, *K* is the spherical shape factor (0.89), and *β* is the full width at half-maximum height (*fwhm*) of the respective peaks. The average crystallite size was obtained from (311), (511), and (440) peaks.

The structure of the prepared $CuCo_2O_4$ nanoparticles was also characterized with energy dispersive X-ray (EDX) analysis (Fig. S2).

The morphology of the samples were investigated by a Zeiss field-emission scanning electron microscope (FESEM). The FESEM images were further analyzed by Measurements software and size distribution of $CuCo_2O_4$ nanoparticles is shown in Fig. S1.

Nitrogen adsorption and desorption experiments were carried out by employing a Belsorp analyzer (Japan). The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and the porosity distribution was obtained from the desorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) analysis.

Electrochemical measurements. The electrochemical measurements of the prepared samples were performed in a three-electrode configuration in 3 M KOH electrolyte. The working electrodes were prepared by mixing active material, carbon black, and polyvinylidene fluoride (PVDF) (10% solution in N-methyl-2-pyrollidone) with a mass ratio of 75:20:5. A 5% solution of the mixture in isopropanol was sprayed on Ni foam as the current collector. The prepared electrodes were dried in 60 °C overnight. A Pt plate was used as the auxiliary electrode and Hg/HgO as the reference electrode. An Autolab PGSTAT30 was employed to measure electrochemical properties of the samples through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. A Solartron battery test unit equipped with Cell Test software (v. 3.5.0) was used for galvanostatic charge-discharge measurements.

Specific Capacitance, Specific Energy and Specific Power calculations. Specific capacitance of the electrode can be calculated through galvanostatic charge-discharge measurements using the following equation:

$$C_{sp} = \frac{I\,\Delta t}{m\,\Delta V} \qquad (2)$$

where C_{sp} is the specific capacitance, I is the discharge current density in A, Δt is the discharge duration in s, m is the loaded mass of the active material in g, and ΔV is the potential range in V.

Specific energy can be derived from the galvanostatic discharge curves using the following equation:

$$SE = \frac{C_{sp}\,\Delta V^2}{2} \qquad (3)$$

where C_{sp} is specific capacitance (F) and ΔV is the potential window (V). The specific power of the electrode can also be calculated from the following equation:

$$SP = \frac{I\Delta V}{m} \qquad (4)$$

where SP is the specific energy, and Δt is the discharge time (s).

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Table S1 Electrical parameters for $CuCo_2O_4$ nanostructures obtained from EIS measurements.

Circuit elements	**Before Cycling**	**After 2000 Cycles**
ESR (Ω)	0.970	1.263
R_{ct} (Ω)	6.575	23.12
n_1	0.816	0.846
n_2	0.829	0.998

Table S2 Comparison of specific power of some previously reported works on Co_3O_4 and CuO materials in supercapacitor applications with here presented $CuCo_2O_4$ nanoparticles.

Sample	**Synthesis method**	**Electrolyte**	**Specific power (kW kg^{-1})**	**Ref (year)**
Ultra-layered Co_3O_4	Hydrothermal (template assisted)	1 M KOH	32	9 (2011)
Mesoporous Co_3O_4 nanocubes	Hydrothermal (template assisted)	6 M KOH	2	S2 (2013)
mesoporous Co_3O_4 nanosheet arrays	Electrodeposition of hydroxides followed by a calcination process	2 M KOH	3.2	S3 (2012)
Hierarchical Co_3O_4 nanosheet@nanowire arrays	Urea precipitation followed with annealing	1 M KOH	1.74	S4 (2012)
Co_3O_4 nanowire	Hydrothermal	2 M KOH	11	S5 (2012)
CuO nanosheet	Chemical growth	6 M KOH	1.7	S6 (2011)
Nanostructured $CuCo_2O_4$ cauliflower-like particles	Facile urea combustion	3 M KOH	22.11	current study

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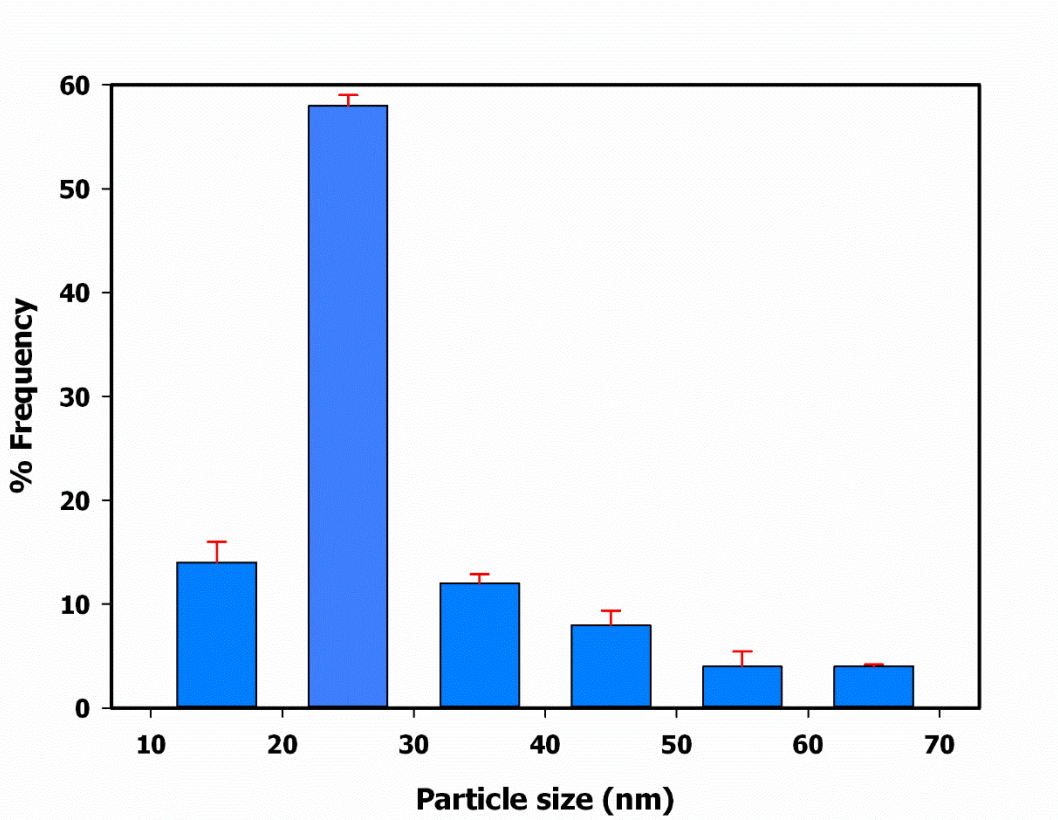

Fig. S1 Size distribution of $CuCo_2O_4$ nanoparticles, based on FESEM image (Fig. 1c).

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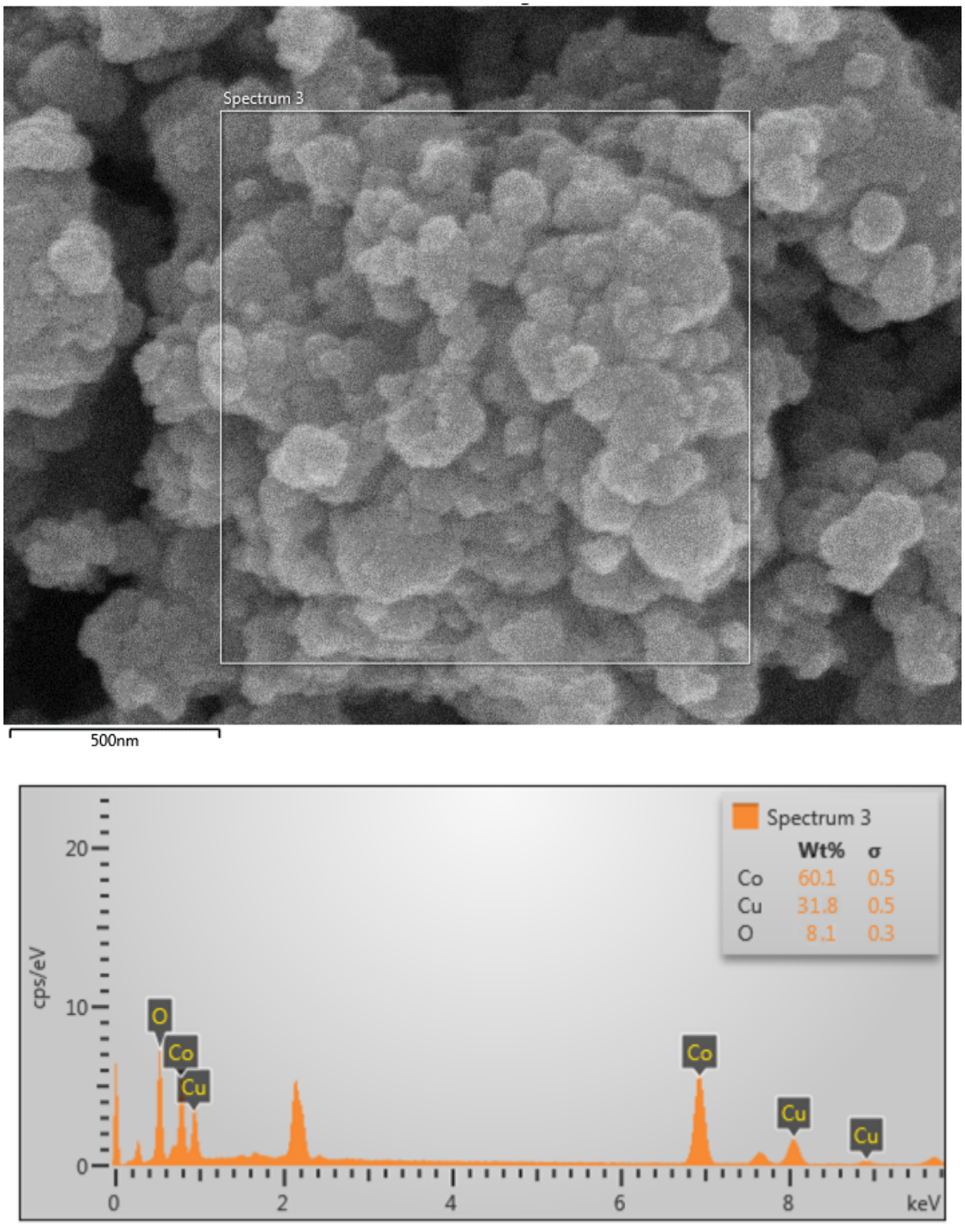

Fig. S2 EDX spectrum of $CuCo_2O_4$ nanostructures along with the corresponding SEM image.

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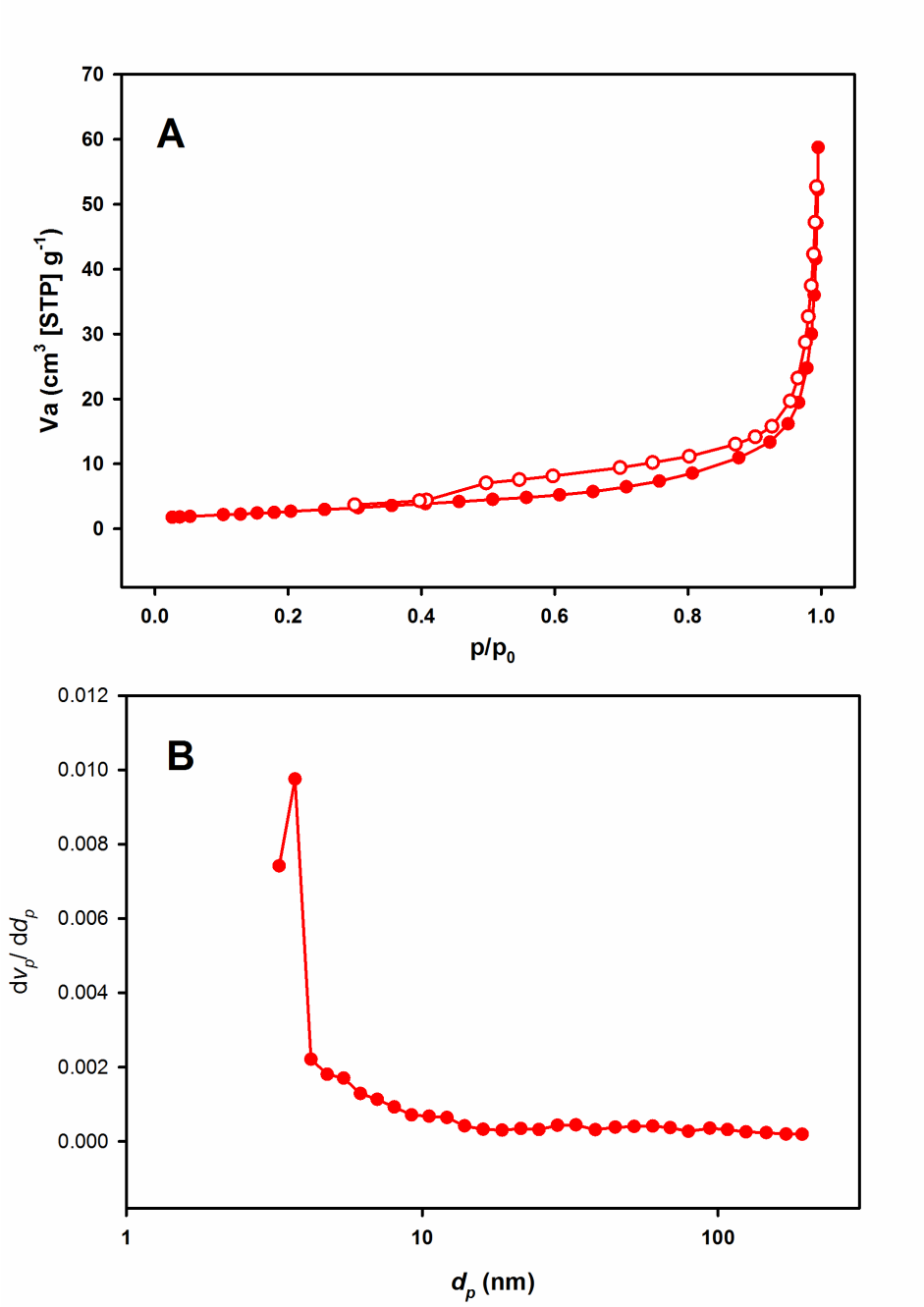

Fig. S3 N_2 adsorption desorption isotherm of $CuCo_2O_4$ nanostructures (A), and BJH pore size distribution based on desorption branch (B).

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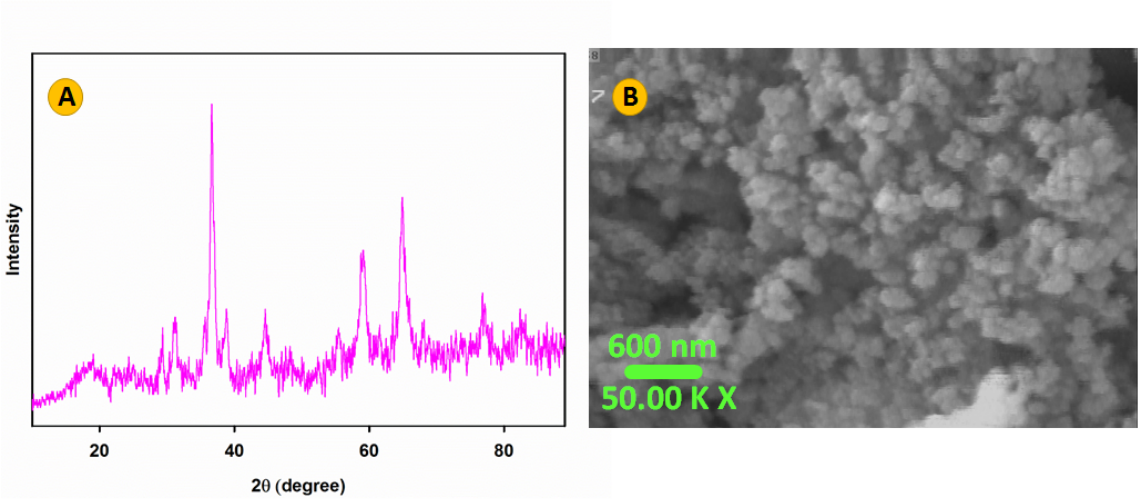

Fig. S4 XRD pattern (A) and FESEM of $CuCo_2O_4$ microparticles.

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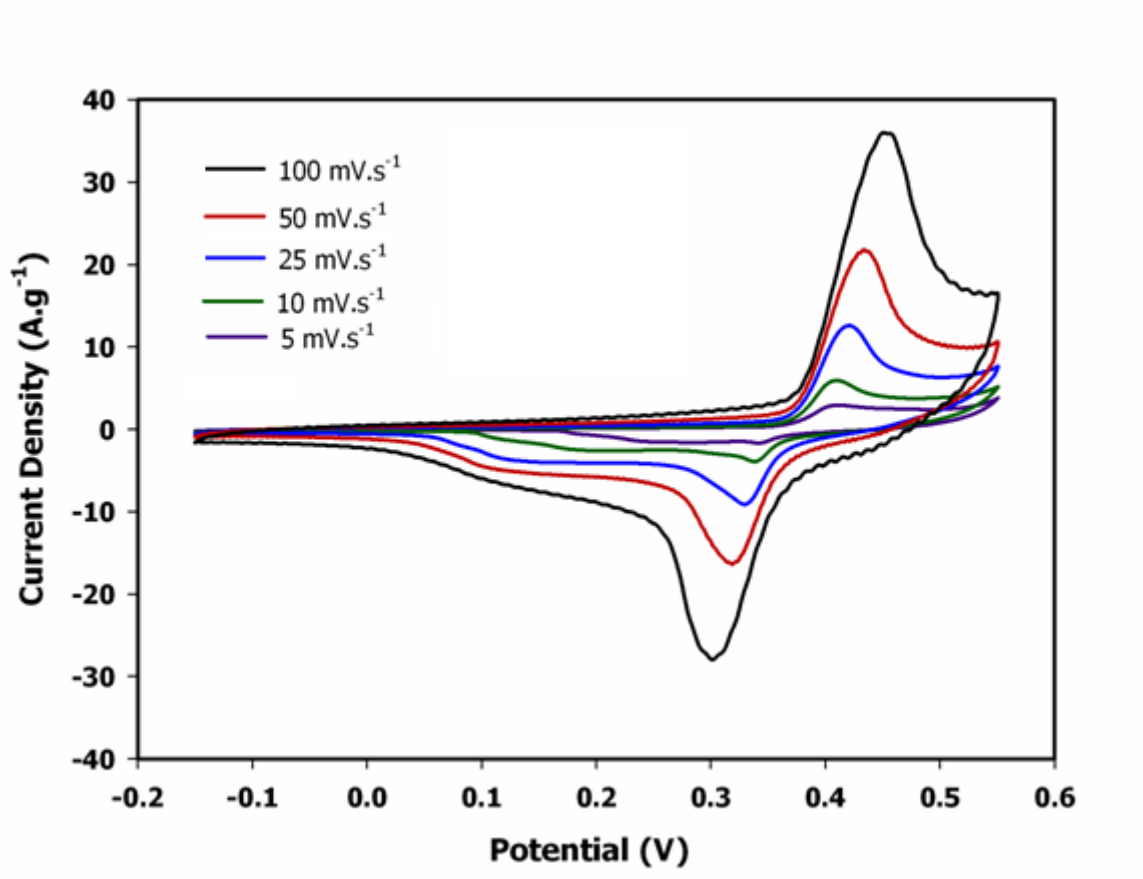

Fig. S5 CV curves for $CuCo_2O_4$ nanostructures at various scan rates ranged in 5-100 mV s^{-1} in 3 M KOH.

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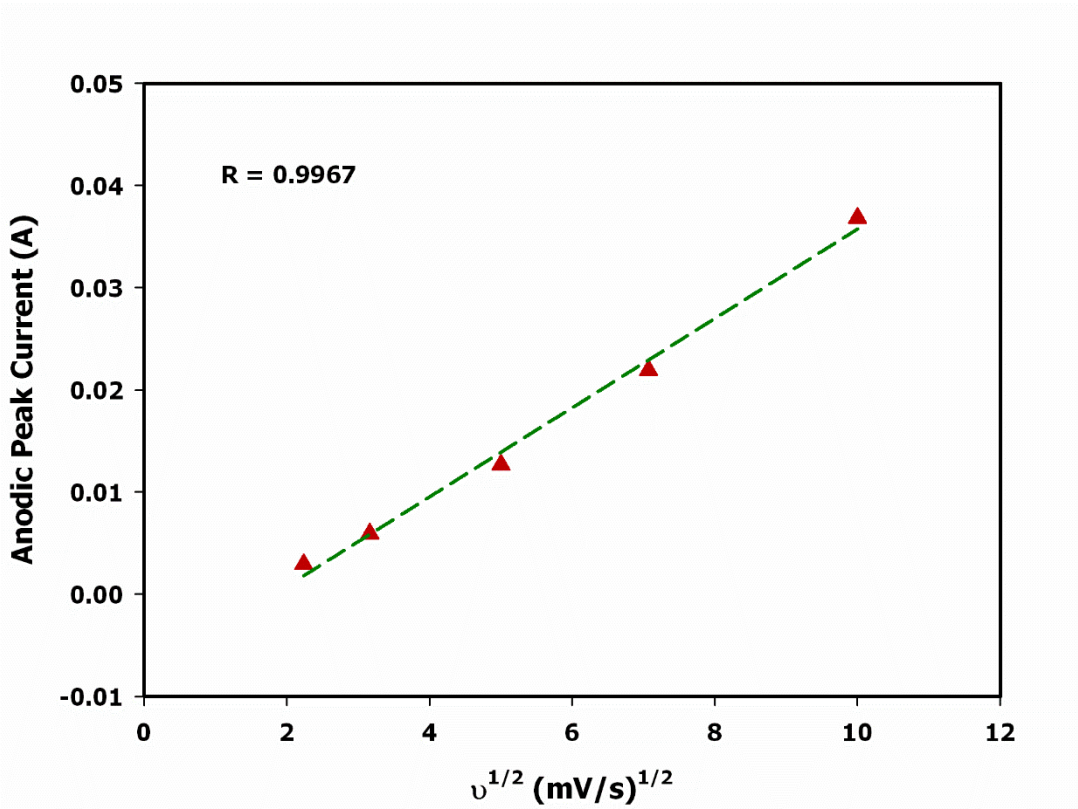

Fig. S6 Relation between the anodic peak currents and square root of scan rate.

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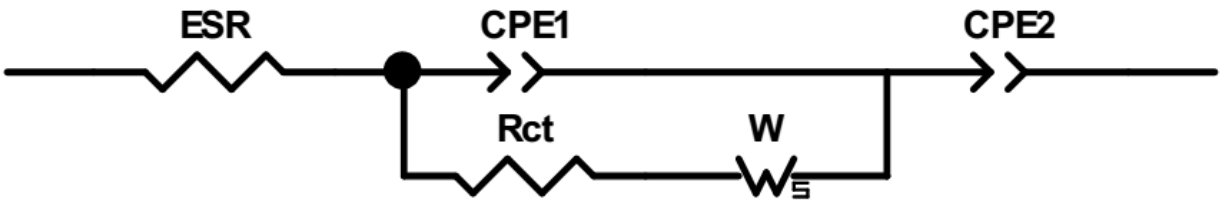

Fig. S7 The equivalent circuit employed for fitting of the experimental results.

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