

Versatile Double Hydrophilic Block Copolymers: Dual Role as Synthetic Nanoreactor and Ionic and Electronic Conducting Layer for Ruthenium Oxide Nanoparticle Supercapacitors

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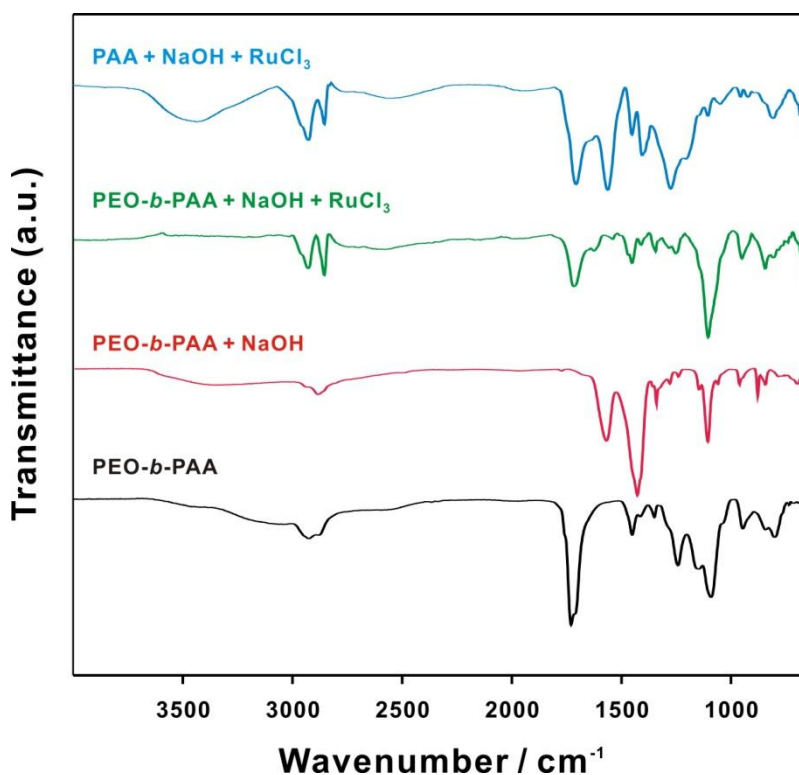


Figure S1. FT-IR spectra of (a) PEO-*b*-PAA, (b) PEO-*b*-PAA with NaOH, (c) PEO-*b*-PAA with NaOH and RuCl₃·*x*H₂O, and (d) PAA with NaOH and RuCl₃·*x*H₂O. Note that the PEO-*b*-PAA shows the C=O stretching vibration of the carboxylic group at 1729 cm⁻¹ and the C-O stretching vibration of PEO block and PAA block at 1241 and 1091 cm⁻¹, respectively. Upon complexation with Ru³⁺ through electrostatic interaction to form micellar structure, the carboxylic acid groups of PAA block are dissociated into COO⁻ groups, which correspond to the absorption peaks at 1625 and 1410 cm⁻¹ assigned to asymmetric and symmetric stretching vibrations of COO⁻, while a peak of C-O observed in PEO block still remains at 1104 cm⁻¹. This implies that the carboxylate groups of PAA block are easily involved in the reaction by combining with Ru³⁺. In a control experiment using only PAA polymer, the absorption peaks at 1561 and 1404 cm⁻¹ could be assigned to asymmetric and symmetric stretching vibrations of COO⁻, supporting carboxylate groups in PAA complex with Ru³⁺.

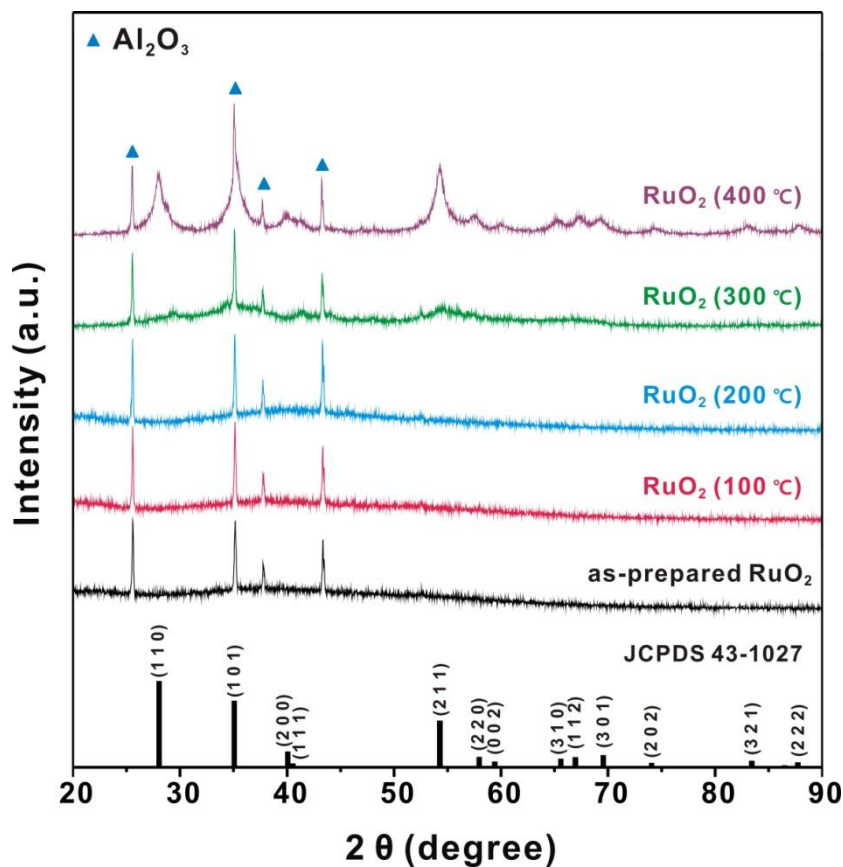


Figure S2. *In situ* XRD patterns of hydrous RuO₂·xH₂O nanoparticles with increasing temperature under ambient condition. It indicates that the crystalline RuO₂ structure is evolved from amorphous structure of as-prepared hydrous RuO₂·xH₂O near at 300 °C. Note that the peaks marked with blue triangle are assigned to the Al₂O₃ substrate, where the sample was loaded.

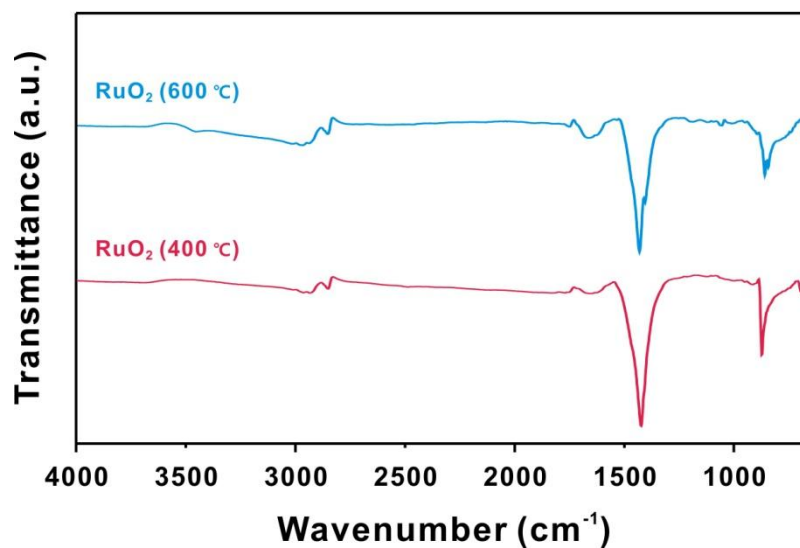


Figure S3. FT-IR spectra of RuO₂ nanoparticles annealed at 400 °C and 600 °C. Both spectra reveals the presence of residual polymeric layer, including symmetric stretching of carboxylate peaks at 1435 cm⁻¹, which corresponds to the surface-bound strong coordinating carboxylate groups, and the other strong peak observed at 863 cm⁻¹ due to the strong rocking of methylene (-CH₂-) backbone of the polymer.

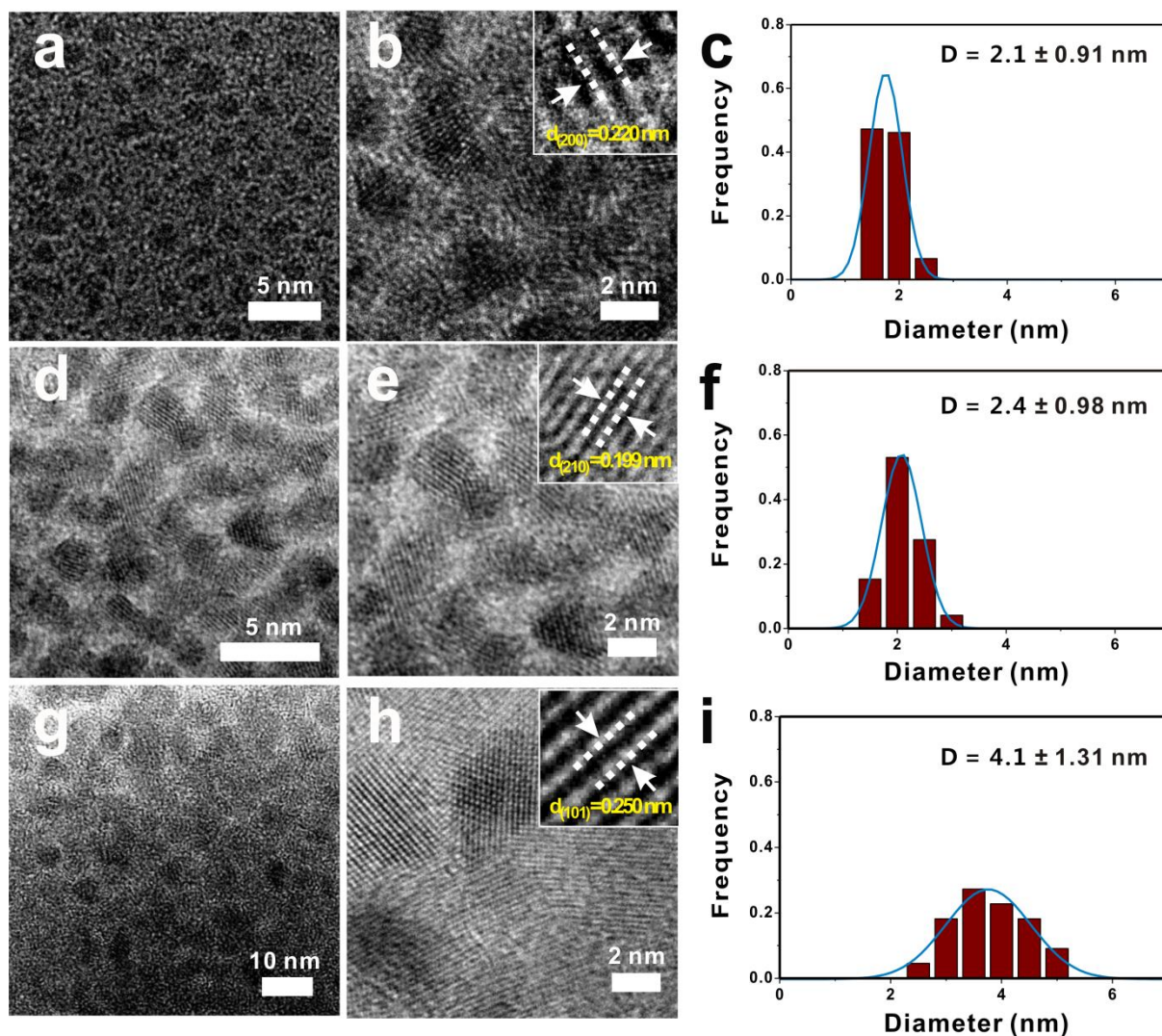


Figure S4. Representative TEM images of RuO₂ nanoparticles annealed at various temperatures. (a, b) 200 °C, (d, e) 400 °C and (g, h) 600 °C. The inset images show the crystalline plane of RuO₂ nanoparticles. (c, f, i) The corresponding size distribution histograms of RuO₂ nanoparticles averaged over 50 samples.

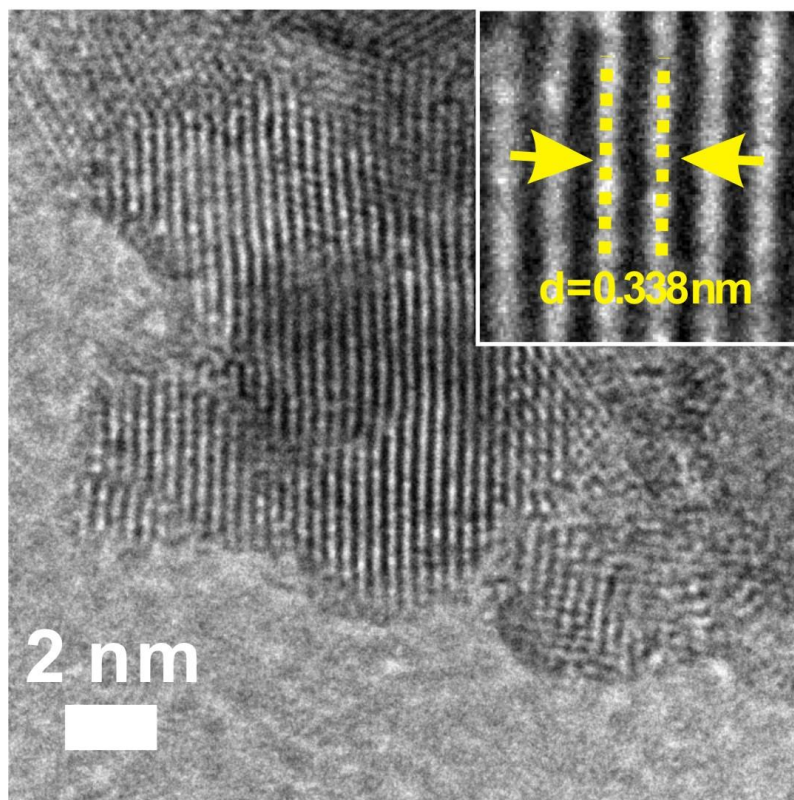


Figure S5. Representative HR-TEM image of RuO₂ nanoparticles annealed at 600 °C. Highly crystalline carbon layer is formed on the surface of RuO₂ nanoparticles.

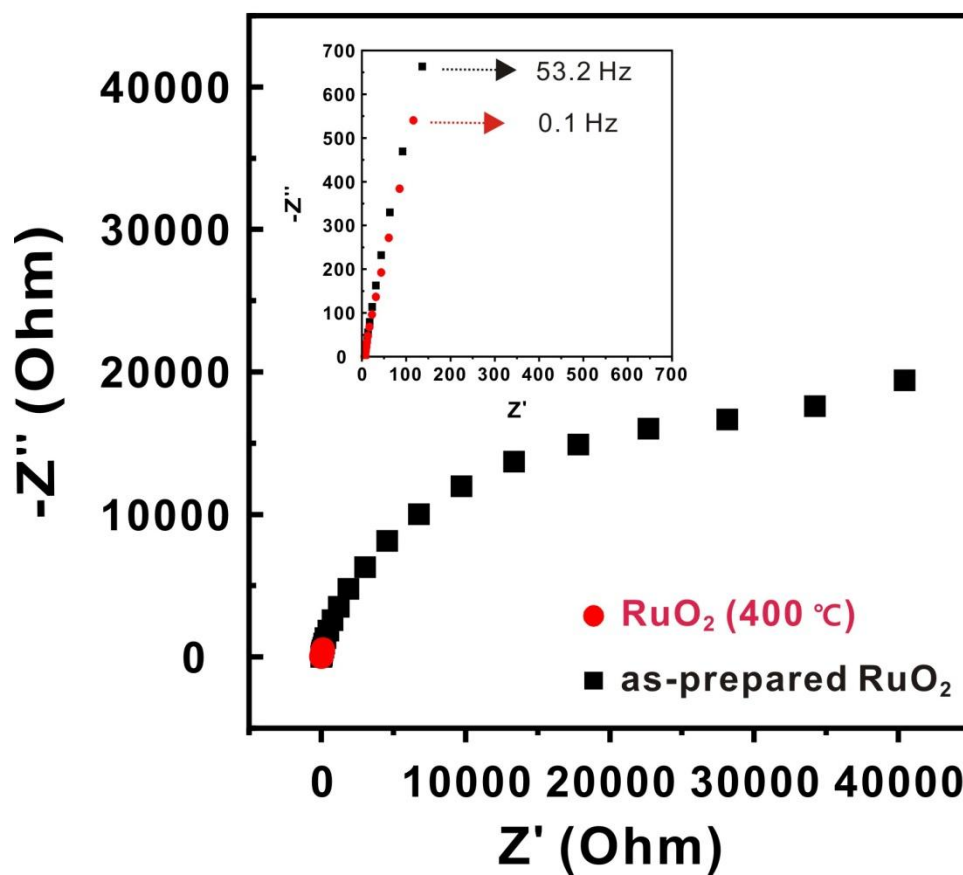


Figure S6. Nyquist plots for an electrode of (black square) as-prepared RuO₂ and (red circle) RuO₂ annealed at 400 °C, measured over a frequency range from 100 mHz to 200 kHz at 0.6 V.

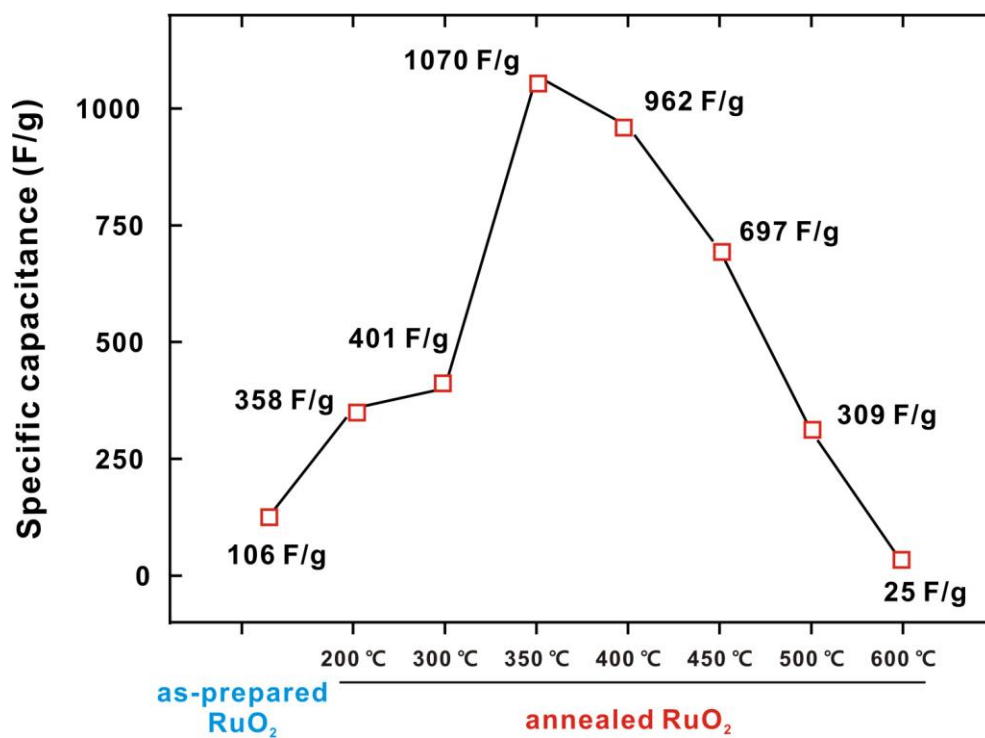


Figure S7. Comparison of capacitance values of all RuO₂ nanoparticles samples annealed at different temperature ranges. Capacitance values were obtained with a cyclic voltammetry measurement at a scan rate of 10 mV/s.

Table 1. Comparison of capacitance values of all RuO₂ nanoparticles samples annealed at different temperature ranges measured at various scan rates.

| Scan rate (mV/s) | as-prepared hydrous RuO ₂ | annealed RuO ₂ nanoparticles | | | | | | |
|---------------------|---|---|-------|-------|-------|-------|-------|-------|
| | | 200°C | 300°C | 350°C | 400°C | 450°C | 500°C | 600°C |
| 10 | 106 | 358 | 401 | 1070 | 962 | 697 | 309 | 25 |
| 20 | 59 | 306 | 314 | 953 | 637 | 464 | 293 | 35 |
| 50 | 29 | 254 | 260 | 858 | 553 | 426 | 284 | 32 |
| 100 | 17 | 223 | 231 | 819 | 472 | 396 | 276 | 30 |
| 200 | 11 | 166 | 209 | 751 | 430 | 362 | 266 | 28 |