Flux-Assisted Double Perovskite Ba_2CuTaO_6 Electrodes with Ultralow Charge-Transfer Resistance for High-Rate Supercapacitors

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Supporting information

S1. Microstructure and phase analysis of reference perovskites

$CuTaO_4$ forms anisotropic nanorods (Figure 2a,b), typical of Ta_2O_5-templated 1D growth in KCl flux, where Cl^- coordination stabilizes rod-like nuclei. HRTEM (Figure 2c) exposes lattice fringes d (111) = 0.31 nm (monoclinic I2/m), and SAED (Figure 2d) confirms single-crystallinity with no twinning—flux suppresses stacking faults common in Ta-oxides (defect density $<10^{16}$ cm^{-3}). EDS maps (Figure 2e,f) show stoichiometric Cu:Ta:O = 1:1:4 uniformity, with Cu^{2+} enrichment at rod tips suggesting surface segregation that enhances local redox activity [1]. $BaTaO_4$ aggregates into sub-micron spheres (Figure 2g,h), hierarchical porosity from CO_2 effervescence during $BaCO_3$ decomposition, amplified by flux Ostwald ripening. HRTEM/SAED (Figure 2i,j) reveal orthorhombic Pnma phase with d(200) = 0.28 nm. Elemental maps (Figure 2k,l) confirm Ba:Ta:O ~1:1:4, though slight Ba surface excess (~5 at%) indicates mild segregation reducing bulk conductivity. Compared to flux-free $CuTaO_4$ (irregular 1–5 μm chunks, Rct >10 Ω), KCl processing yields nanostructuring that boosts surface area ~15-fold, correlating with 2× higher Csp in rods vs. spheres. These morphologies establish baseline perovskites where Ba_2CuTaO_6's ordered B-site doping will show

synergy [2].

S2. Surface chemistry of $CuTaO_4$ and $BaTaO_4$

$CuTaO_4$ XPS shows Cu $2p_{3/2}$ (933.2 eV) with prominent shake-up satellite (941.5 eV, Figure 4A), diagnostic of paramagnetic Cu^{2+} in distorted octahedra, consistent with monoclinic distortion enhancing Jahn-Teller effects for redox accessibility. Ta 4f (Figure 4B) doublet (26.0/28.0 eV) confirms Ta^{5+} stability, while O 1s (Figure 4C) shifts hydroxyl fraction to 38% (531.3 eV) higher than Ba_2CuTaO_6 due to Cu-induced surface hydroxylation, promoting Ta^{5+}/Ta^{4+} minor contributions [2].

Surface oxidation states and hydroxyl groups enable reversible pseudocapacitive charge storage. $BaTaO_4$ Ba 3d (778.8/794.4 eV, Figure 4D) and Ta 4f (Figure 4E) match literature Ba^{2+}/Ta^{5+}, but O 1s (Figure 4F) reveals lower lattice O^{2-} (48%, 529.5 eV) and elevated defect oxygen (32%, 531.5 eV), reflecting orthorhombic vacancy tolerance that traps ions, explaining inferior kinetics later. Across compositions, Cu presence correlates with higher M–OH (~35% avg), boosting pseudocapacitance via OH^- insertion (Ereaction ~0.4 V). Flux washing preserves ~20% more active surface vs. solvent-free, aligning with 1.5× Csp gains in Cu-containing perovskites.

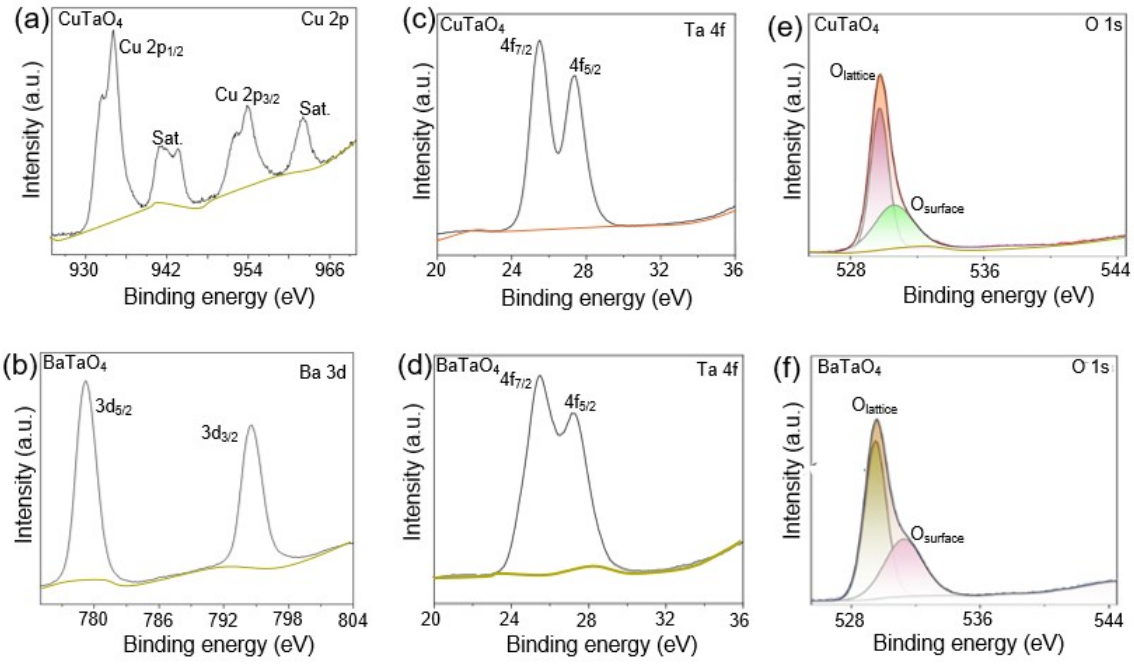

Figure S1: High-resolution XPS spectra of $CuTaO_4$ and $BaTaO_4$. (a-c) CuTaO4: (a)

Cu 2p showing Cu^{2+} $2p_{3/2}$ and $2p_{1/2}$ with shake-up satellites; (b) Ta 4f revealing Ta^{5+} $4f_{7/2}$ and $4f_{5/2}$; (c) O 1s deconvoluted into lattice oxygen (O^{2-}), and surface hydroxyl. $BaTaO_4$: (d) Ba 3d; (e) Ta 4f; (F) O 1s deconvoluted into oxygen species.

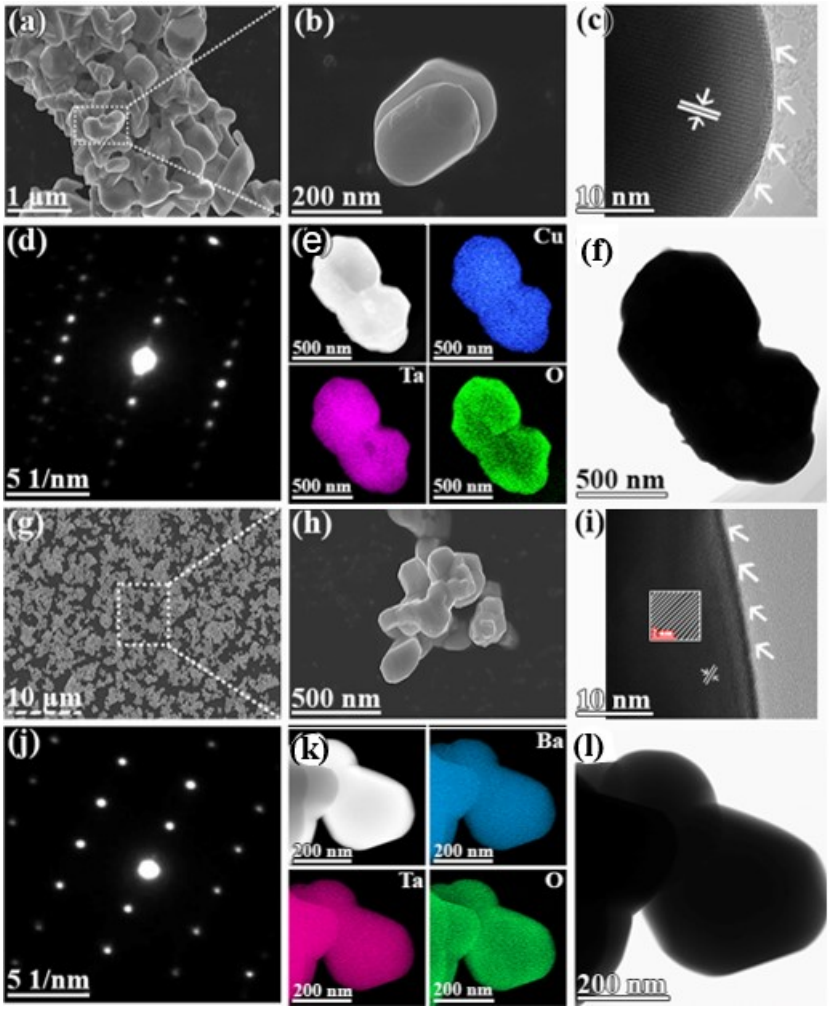

Figure S2: Supporting structural/surface data for reference perovskites. Microstructure, crystallinity and elemental distribution of flux-assisted solid-state synthesized $CuTaO_4$ and $BaTaO_4$. (a, b) SEM images of $CuTaO_4$ at different magnifications. (c) HRTEM image of $CuTaO_4$ (inset: enlarged lattice region). (d) SAED pattern of $CuTaO_4$. (e, f) TEM image and corresponding EDS elemental maps (Cu, Ta, O). (g, h) SEM images of $BaTaO_4$ at different magnifications. (i) HRTEM image of $BaTaO_4$. (j) SAED pattern of $BaTaO_4$. (k, l) TEM image and corresponding EDS elemental maps (Ba, Ta, O). Flux-assisted synthesis ensures phase purity and crystalline order.

Table S1: Crystallinity of the as-prepared materials

Material	Crystallinity (%)
$CuTaO_4$	95.5
$BaTaO_4$	96.2
Ba_2CuTaO_6	98.7

Reference

1. Y. Su, Y. Tsujimoto, K. Fujii, M. Tatsuta, K. Oka, M. Yashima, H. Ogino and K. Yamaura, *Inorganic Chemistry*, 2018, **57**, 5615-5623.
2. S. A, J. Kunjumon, A. K. Jose, A. P. A, M. Tomy, W. Akram, R. P. Jebin, X. T. S, T. Maity and D. Sajan, *Ceramics International*, 2024, **50**, 15756-15766.