Supplementary Information (SI) for Nanoscale.

Supplementary information

Atmospheric Pressure Plasma Synthesis of Faceted Monophase Bismuth Nanocrystals

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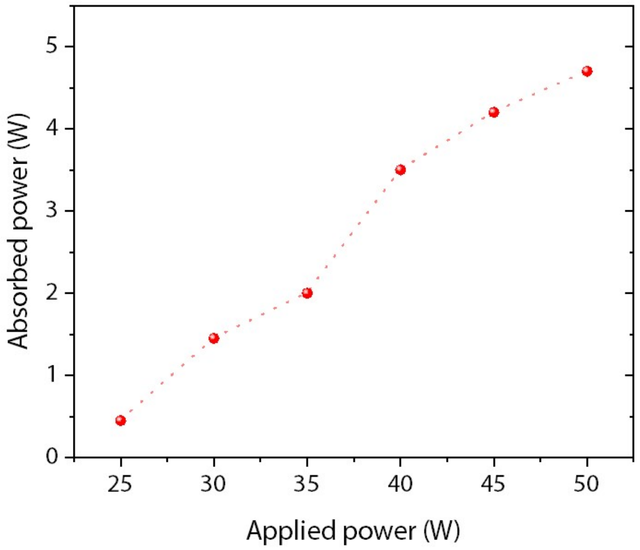

Figure S1: Experimental relationship between applied power and absorbed power.

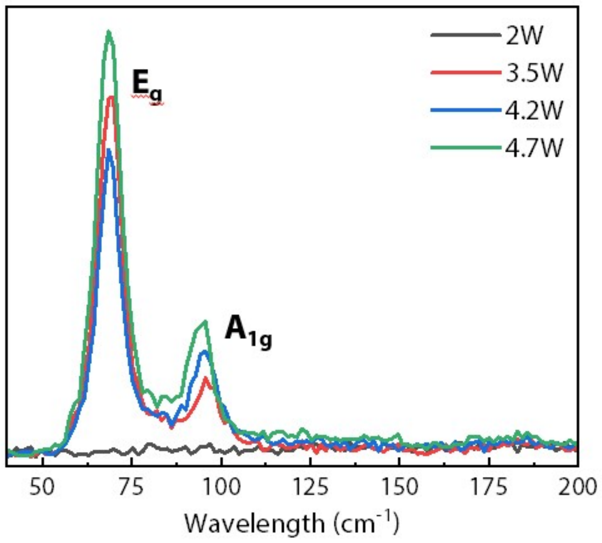

Figure S2. Raman spectra of BiNCs synthesized at different discharge power from 2W to 4.7W.

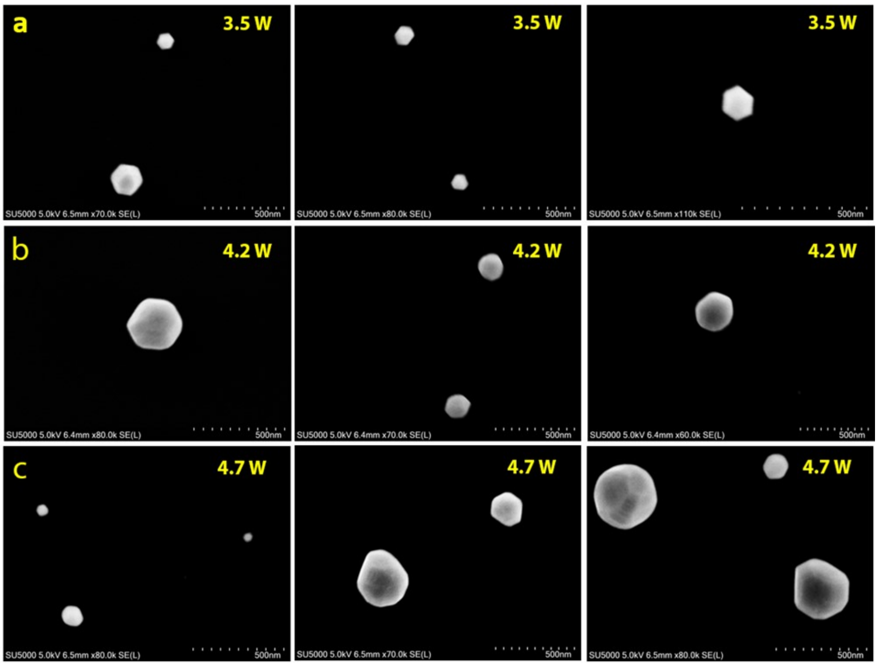

Figure S3. Additional secondary electron SEM

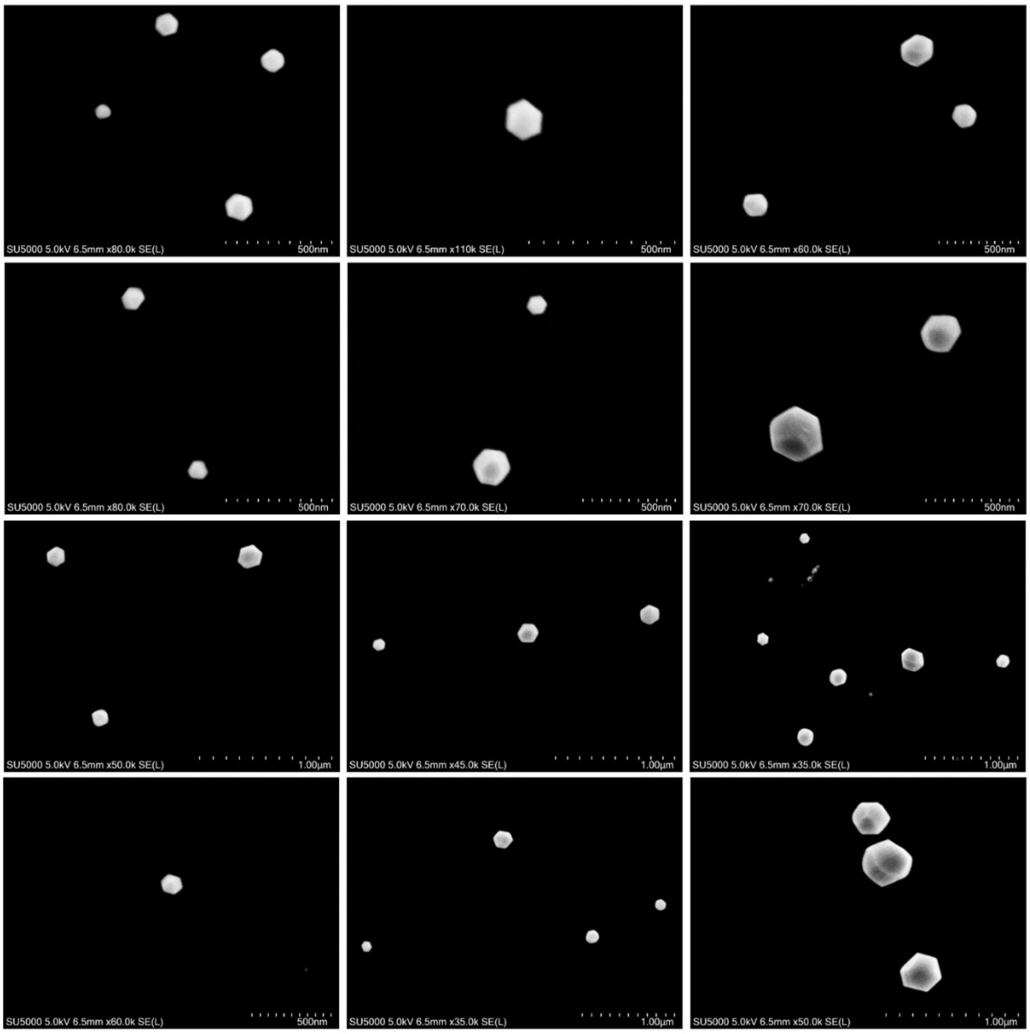

Figure S4. Additional secondary electron SEM of BiNCs synthesized at 3.5W

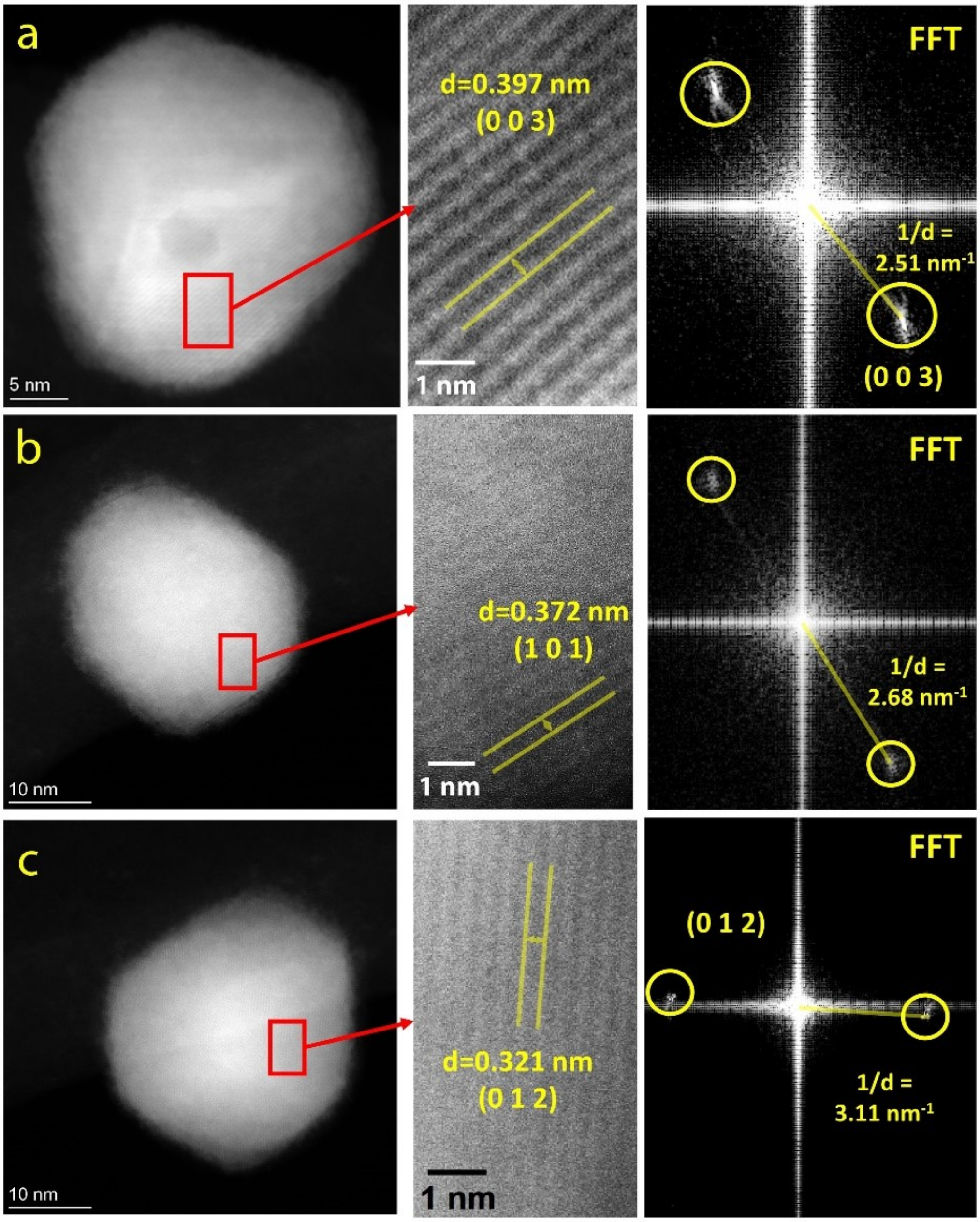

Figure S5. HAADF-STEM images and FFTs of BiNCs synthesized at 3.5W, confirming their Rhombohedral phase and corresponding to figure 3e-g to allow for comparison

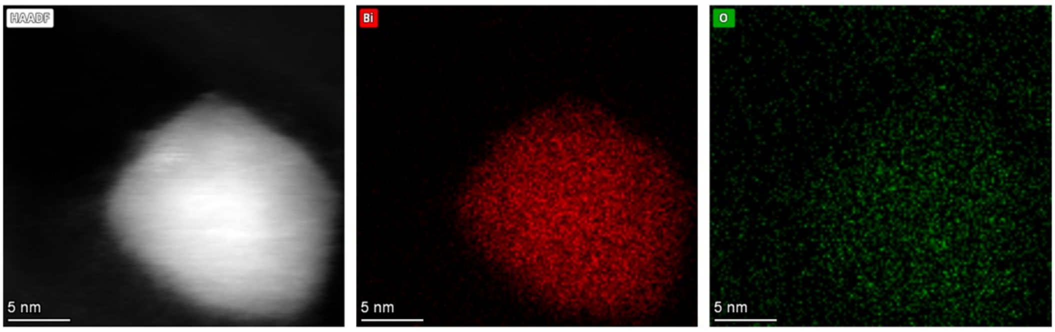

Figure S6. STEM-EDX elemental mapping of faceted BiNCs synthesized at 3.5W.

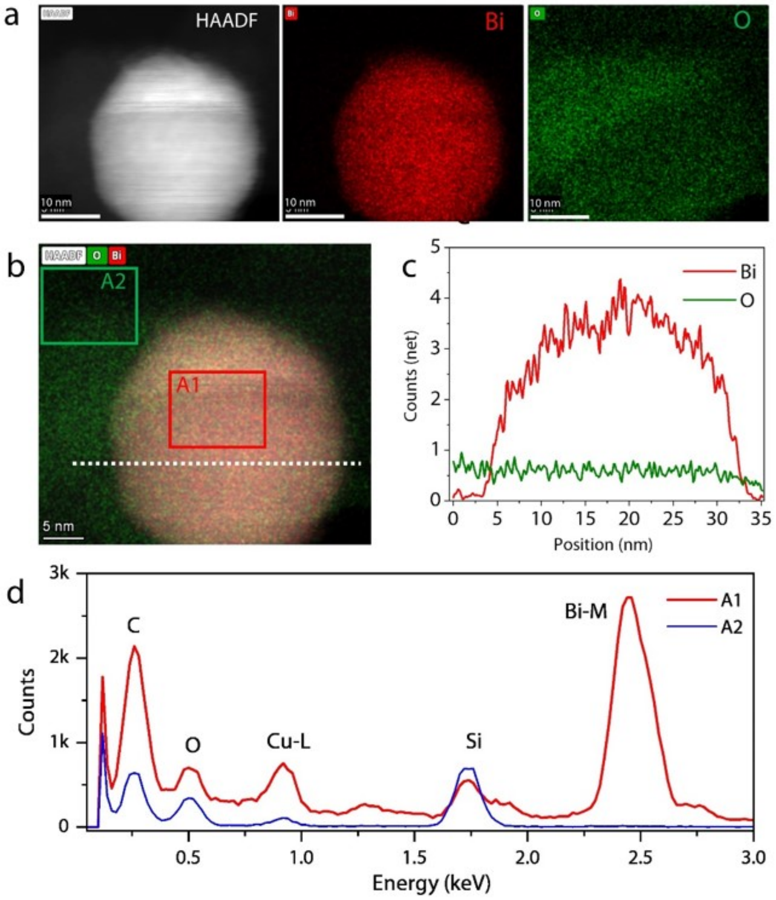

Figure S7. a) Elemental mapping of BiNCs (3.5 W) confirms the forming of a high-purity mono-elemental Bi (red) with a low contribution of oxygen (green). b) overlay of dark field image of BiNCs together with elemental maps for Bi (M line) and O (K line). c) STEM-EDX line profiles revealing a higher signal for Bi (M line). d) EDX spectra correspond to the hole (A1), carbon film (A2), and area inside BiNCs (A3).

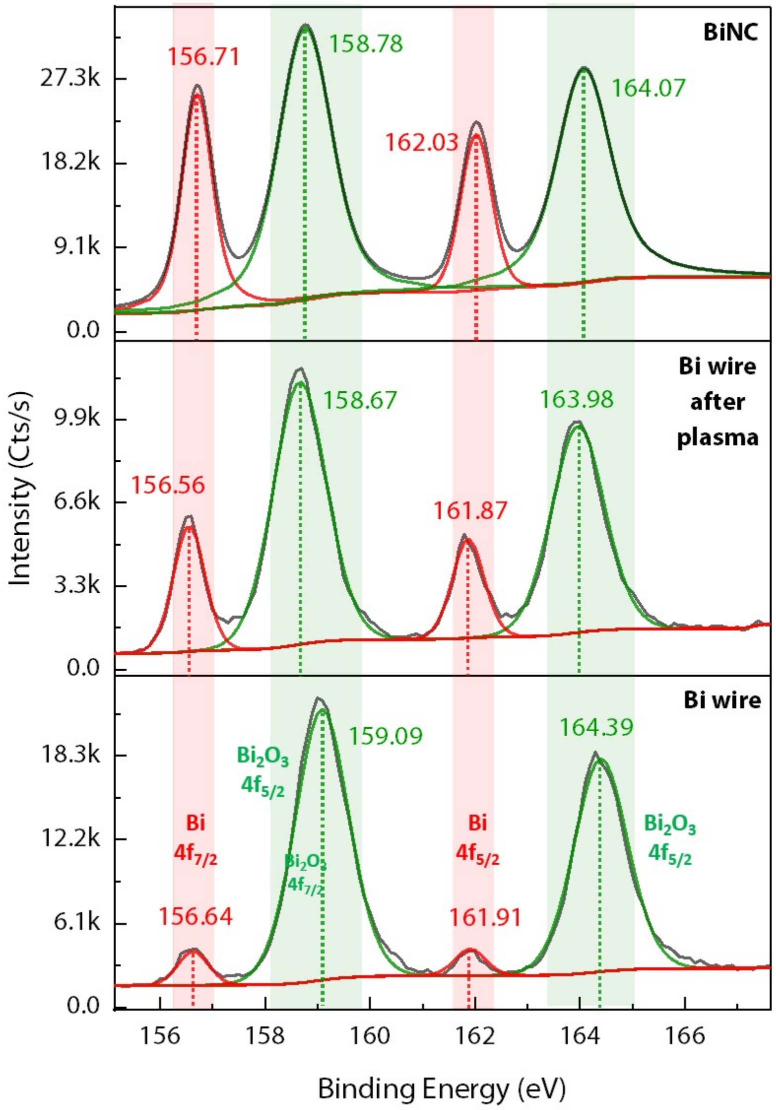

Figure S8. High-resolution XPS spectra of the Bi 4f region for (top) BiNC, (middle) Bi wire after plasma exposure, and (bottom) pristine Bi wire.

In the pristine Bi wire, two chemically distinct Bi species are resolved. The lower-binding-energy doublet at 156.64 eV and 161.91 eV corresponds to metallic Bi^0, while the higher-binding-energy component at 159.09 eV and 164.39 eV is characteristic of oxidised bismuth (Bi^{3+}), consistent with reported Bi_2O_3 values. After plasma treatment, the oxide component shifts slightly to 158.67 eV and 163.98 eV, giving a small negative shift (~0.4 eV). This change is consistent with the formation of a more sub-stoichiometric or partially reduced Bi–O environment. The Bi^0 component remains present and its position is largely unchanged. In the BiNC sample, two components are also present. The doublet at 156.71 eV and 162.03 eV corresponds to metallic Bi^0, while the higher-binding-energy pair at 158.78 eV and 164.07 eV arises from oxidised Bi species, attributable to the thin native oxide layer formed upon air exposure after synthesis. The relative intensity and peak sharpness indicate that the BiNCs contain a metallic bismuth core with a thin oxidised shell. The spin–orbit splitting remains approximately 5.3 eV across all spectra, consistent with the expected Bi 4f separation and not indicative of any new bonding environment. No additional low-binding-energy shoulder or systematic negative shift is observed that would support the presence of Bi–H (bismuth hydride) bonds. Although hydrogen adsorption can in some cases produce a small negative binding-energy shift, such an effect is not resolvable here.

References

Kerber, S. J. et al. “The nature of hydrogen in X-ray photoelectron spectroscopy: general patterns from hydroxides to hydrogen bonding.” J. Vac. Sci. Technol. A **14** (3), 1314-1320 (1996).

Kalha, C. et al. “Revealing the bonding nature and electronic structure of metal hydrides via hard-X-ray photoelectron spectroscopy.” PRX Energy **3**, 013003 (2024).