Electronic supplementary information

Surface oxygen vacancy engineering in weak Bi–O bonded ferroelectric bismuth sodium titanate for boosting the photocatalytic CO_2 reduction reaction

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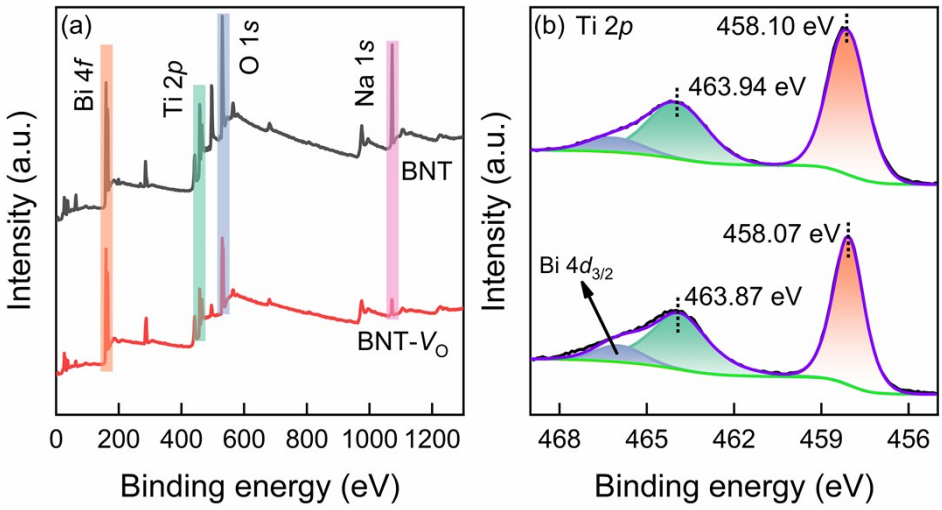

Fig. S1 (a) XPS spectra containing the four constituent elements survey scan. (b) Ti 2*p* XPS spectra.

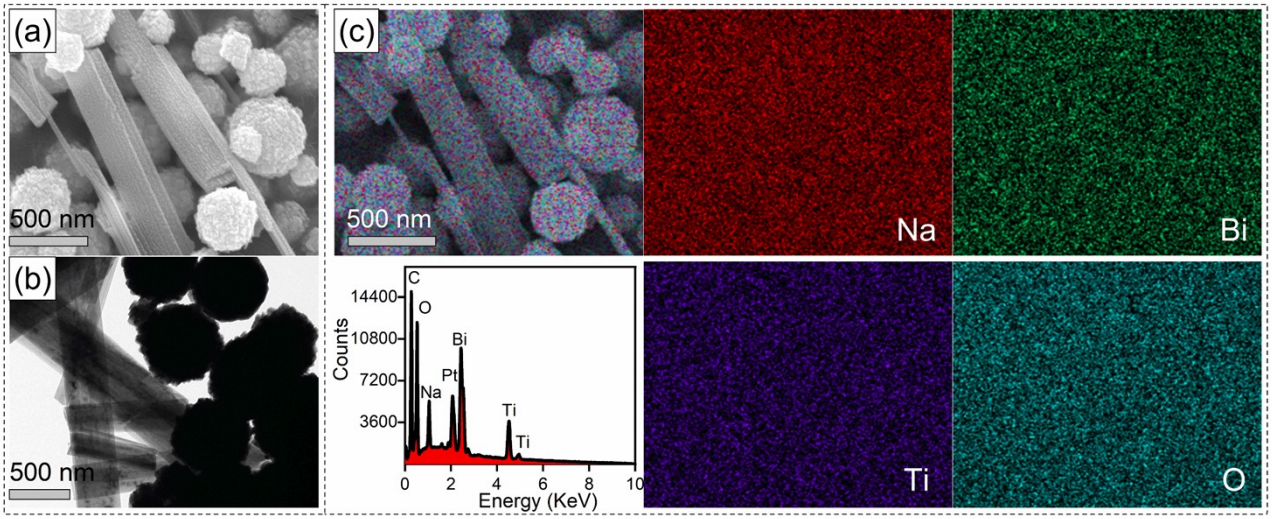

Fig. S2 (a) FE-SEM, (b) TEM and (c) EDS mapping of BNT.

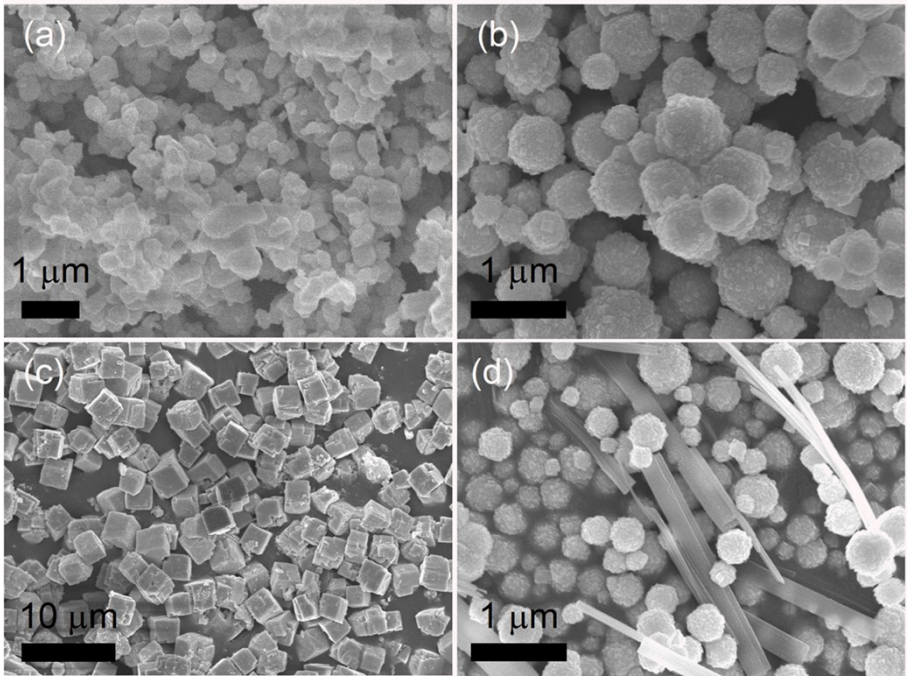

Fig. S3 SEM of different morphologies of BNTs: (a) Bulk, (b) Sphere, (c) Cube and (d) BNT.

The formation mechanism of BNT-based nanostructures with different morphologies, is influenced by the concentration of the mineralizer. $C_{16}H_{36}O_4Ti$ and $Bi(NO_3)_3{\cdot}5H_2O$ undergo hydrolyzed to form $TiO_2{\cdot}nH_2O$ and $Bi_2O_3{\cdot}nH_2O$, which are further dissolved into Ti^{4+} and Bi^{3+}. NaOH was directly dissolved into Na^+ and OH^-. The solubility of $TiO_2{\cdot}nH_2O$ is lower than that of $Bi_2O_3{\cdot}nH_2O$, resulting in slow dissolution crystallization. When the NaOH concentration is low, the pre-dissolved Ti^{4+}, Bi^{3+}, Na^+ and OH^- ions are adsorbed onto the $TiO_2{\cdot}nH_2O$ particles, forming nucleated clusters to reduce the surface energy and eventually grow into nanospheres with a stepped

surface. At relatively high concentrations of mineralizer, some hydrolyzed $TiO_2 \cdot nH_2O$ nanoparticles underwent Ostwald ripening, transforming into small TiO_2 nano-cubes. Subsequently, adjacent small cubes self-assembled along the same crystal orientation to form TiO_2 nanowires. Meanwhile, Bi^{3+} ions and Bi_2O_3 molecules were adsorbed on the surface, reducing their surface energy. The TiO_2 nanowires served as a template for in-situ conversion into nanobelts. However, higher NaOH concentration and processing temperatures favored the formation of homogeneous cubes in the hydrothermal reaction.

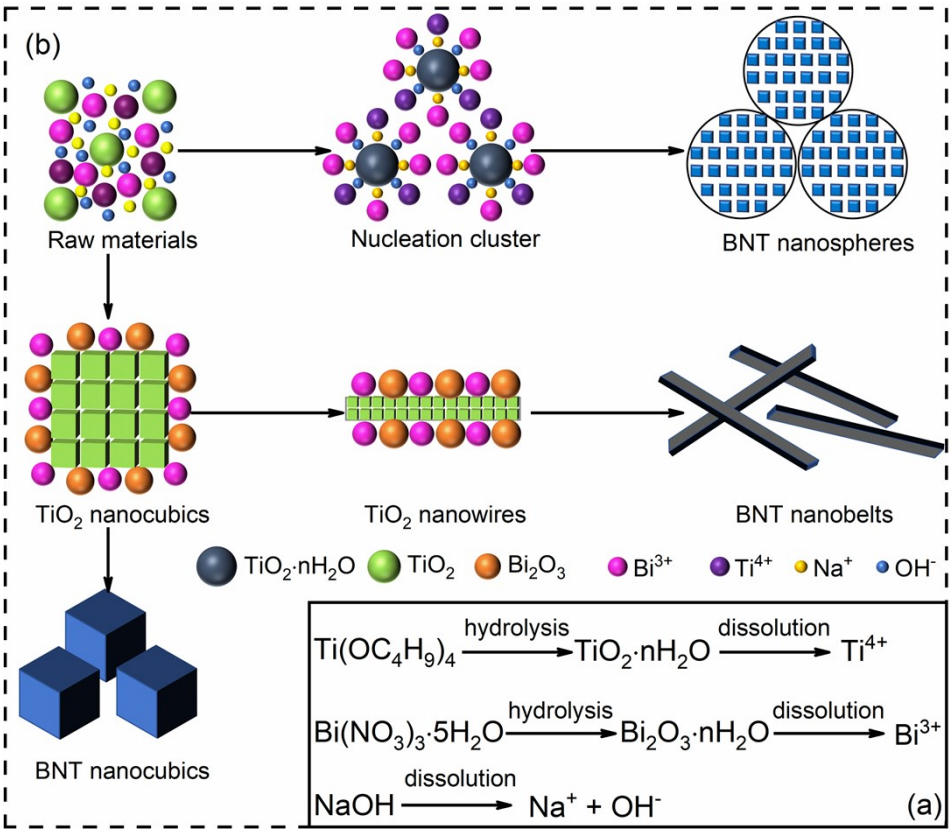

Fig. S4 Schematic of the formation mechanisms for BNT-based nanoparticles and nanobelts.

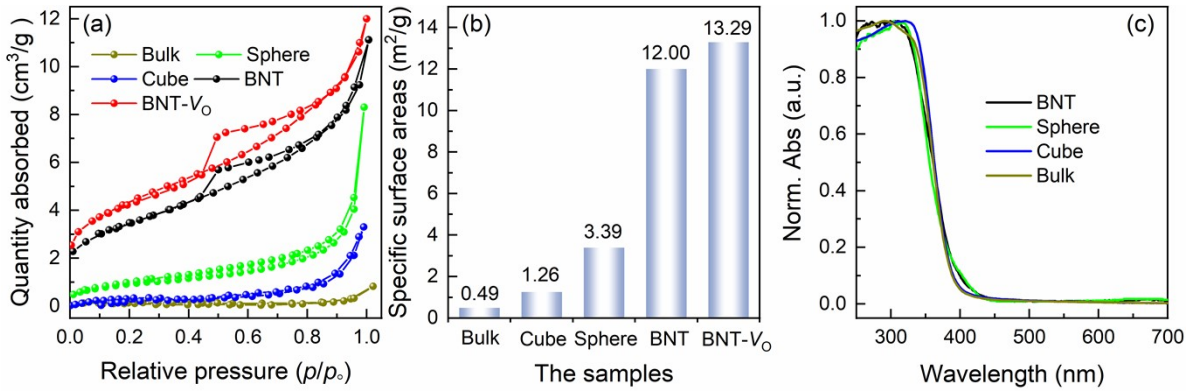

Fig. S5 (a) N_2 adsorption isotherm and (b) corresponding specific surface area of Bulk, Sphere, Cube, BNT and BNT-V_O. (c) UV-vis spectra of Bulk, Sphere, Cube and BNT.

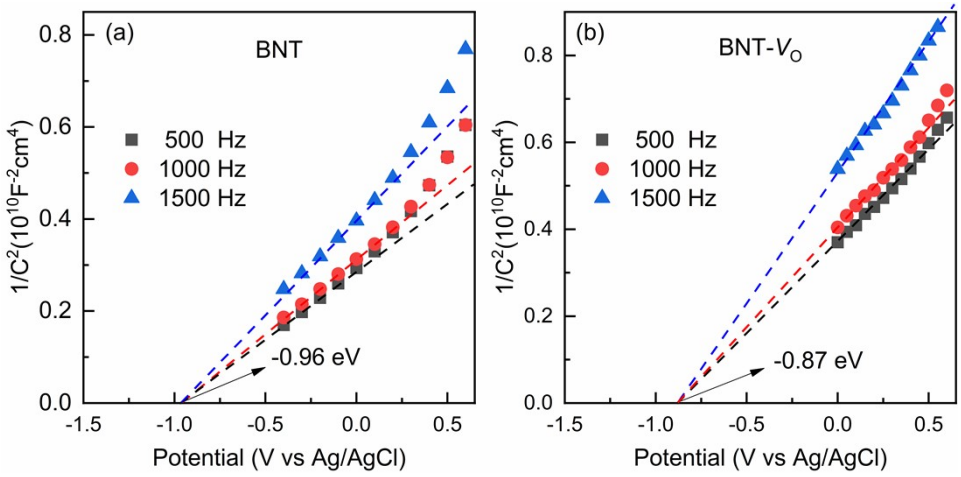

Fig. S6 Mott–Schottky plots of (a) BNT and (b) BNT-V_O at frequencies of 500 Hz, 1000 Hz and 1500 Hz.