

## Electronic Supplementary Information. Water-dispersible and ferroelectric PEGylated barium titanate nanoparticles

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# S1 SUPPLEMENTARY METHODS

## S1.1 Materials

High-purity barium(II) acetylacetonate hydrate ( $\text{Ba}(\text{acac})_2 \cdot x\text{H}_2\text{O}$ ) and titanium diisopropoxide bis(acetylacetonate) ( $(\text{O-}i\text{-Pr})_2\text{Ti}(\text{acac})_2$ , 75 wt.% in isopropanol), poly(ethylene glycol) ( $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ); PEG<sub>400</sub>:  $M_w = 400$ ) and potassium hydroxide (KOH, 85%) were purchased from Sigma Aldrich. Ethanol, glacial acetic acid (99.7%) and formic acid (98%) were used for nanoparticles' washing procedure. All chemicals and solvents were used as-received without any further purification. High-purity water (resistivity of 18 M $\Omega$ -cm) was used in all experiments.

## S1.2 Nanoparticle Synthesis

**Synthesis of BT-0.** We mixed powdered  $\text{Ba}(\text{acac})_2 \cdot x\text{H}_2\text{O}$  (355 mg, 1 mmol) and  $(\text{O-}i\text{-Pr})_2\text{Ti}(\text{acac})_2$  solution (273 mg, 1 mmol) in a round-bottom flask under nitrogen atmosphere, and let the solution stir for 30 min. We then added aqueous KOH (6 mL, 1.5 M) to the mixture. Immediately after, we increased the reaction temperature to reflux (*ca.* 100  $\pm$  5  $^\circ\text{C}$ ), and allowed the reaction to reflux for 2 hrs.

**Synthesis of BT-2.** We mixed powdered  $\text{Ba}(\text{acac})_2 \cdot x\text{H}_2\text{O}$  (710 mg, 2 mmol) and  $(\text{O-}i\text{-Pr})_2\text{Ti}(\text{acac})_2$  solution (273 mg, 1 mmol) in 3 mL of PEG<sub>400</sub> in a round-bottom flask under nitrogen atmosphere, and let the solution stir for 30 min. We then added aqueous KOH (6 mL, 1.5 M) to the mixture. Immediately after, we increased the reaction temperature to reflux (*ca.* 100  $\pm$  5  $^\circ\text{C}$ ), and allowed the reaction to reflux for 2 hrs.

**Synthesis of BT-3.** We mixed powdered  $\text{Ba}(\text{acac})_2 \cdot x\text{H}_2\text{O}$  (355 mg, 1 mmol) and  $(\text{O-}i\text{-Pr})_2\text{Ti}(\text{acac})_2$  solution (273 mg, 1 mmol) in 6 mL of PEG<sub>400</sub> in a round-bottom flask under nitrogen atmosphere, and let the solution stir for 30 min. We then added aqueous KOH (6 mL, 1.5 M) to the mixture. Immediately after, we increased the reaction temperature to reflux (*ca.* 100  $\pm$  5  $^\circ\text{C}$ ), and allowed the reaction to reflux for 2 hrs.

**Synthesis of BT-4.** We mixed powdered  $\text{Ba}(\text{acac})_2 \cdot x\text{H}_2\text{O}$  (355 mg, 1 mmol) and  $(\text{O-}i\text{-Pr})_2\text{Ti}(\text{acac})_2$  solution (273 mg, 1 mmol) in 3 mL of PEG<sub>400</sub> in a round-bottom flask under nitrogen atmosphere, and let the solution stir for 30 min. We then added aqueous KOH (6 mL, 1.6 M) to the mixture. Immediately after, we increased the reaction temperature to reflux (*ca.* 100  $\pm$  5  $^\circ\text{C}$ ), and allowed the reaction to reflux for 2 hrs.

**Synthesis of BT-5.** We mixed powdered  $\text{Ba}(\text{acac})_2 \cdot x\text{H}_2\text{O}$  (355 mg, 1 mmol) and  $(\text{O-}i\text{-Pr})_2\text{Ti}(\text{acac})_2$  solution (273 mg, 1 mmol) in 3 mL of PEG<sub>400</sub> in a round-bottom flask under nitrogen atmosphere, and let the solution stir for 30 min. We then added aqueous KOH (6 mL, 1.7 M) to the mixture. Immediately after, we increased the reaction temperature to reflux (*ca.* 100  $\pm$  5  $^\circ\text{C}$ ), and allowed the reaction to reflux for 2 hrs.

For all syntheses, the color of solution gradually changed from orange/brown to white. After 2 hrs of reflux, we added 6 mL of distilled water to the mixture and maintained it at 100  $\pm$  5  $^\circ\text{C}$  for an additional 2 hrs. We then opened the system to air and let the reaction cool down to room temperature. white precipitates were collected by washing and centrifugation (6000 rpm for 10 min) two times with ethanol, followed by formic acid (1 M). Carbonate impurities were removed by washing the product with diluted (0.5 w/w %) acetic acid. Finally, the nanoparticles were dried at 60  $^\circ\text{C}$  in a vacuum oven overnight.

## S1.3 Determination of crystallite size via the Scherrer equation

To determine crystallite size of particles, the (110) Bragg peak at was fit as a Lorentzian peak, and crystallite size ( $D_{\text{XRD}}$ ) was calculated using the Scherrer equation:<sup>31</sup>

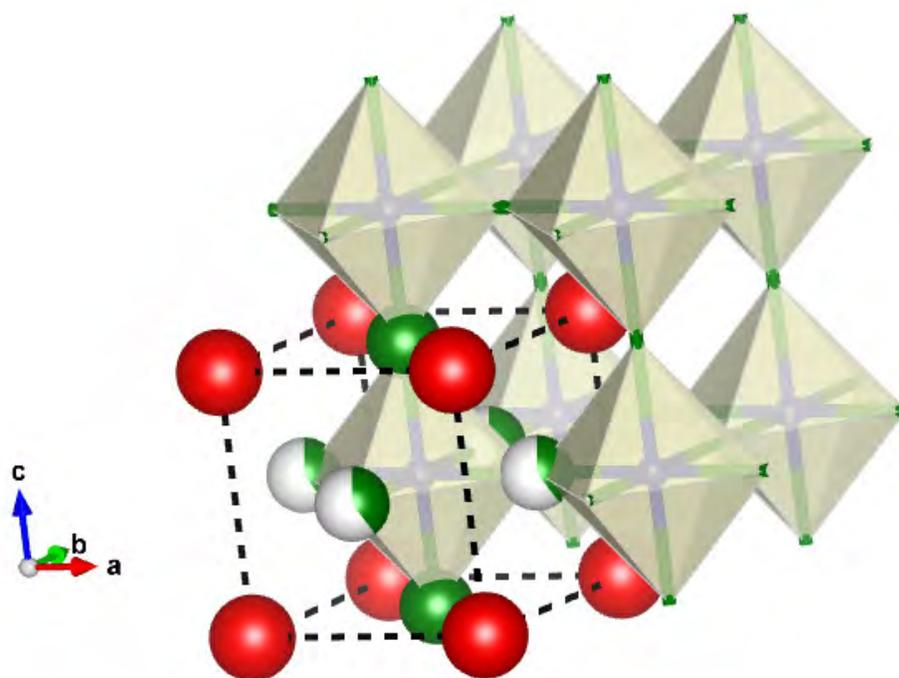
$$D_{\text{XRD}} = \frac{K\lambda}{\beta \cos\theta} \quad (\text{S1})$$

where  $\lambda$  is the incident wavelength,  $K$  is the shape factor (= 0.94 for spherical crystallites),  $\beta$  is the instrument-corrected line broadening of the sample at half the maximum intensity (FWHM), in radians, which is estimated through equation:

$$\beta = \beta_{\text{observed}} - \beta_{\text{ref}}. \quad (\text{S2})$$

Here,  $\beta_{\text{observed}}$  is the measured line broadening at half the maximum intensity for the nanoparticle sample (see Fig. S3), while  $\beta_{\text{ref}}$  and is the measured line broadening at half the maximum intensity for microcrystalline  $\text{BaTiO}_3$ , taken to be representative of instrumental broadening. Errors in the crystallite size  $D_{\text{XRD}}$  were estimated as  $D_{\text{XRD}} \cdot (\Delta\beta/\beta)$ , where  $\Delta\beta$  is uncertainty from peak fitting.

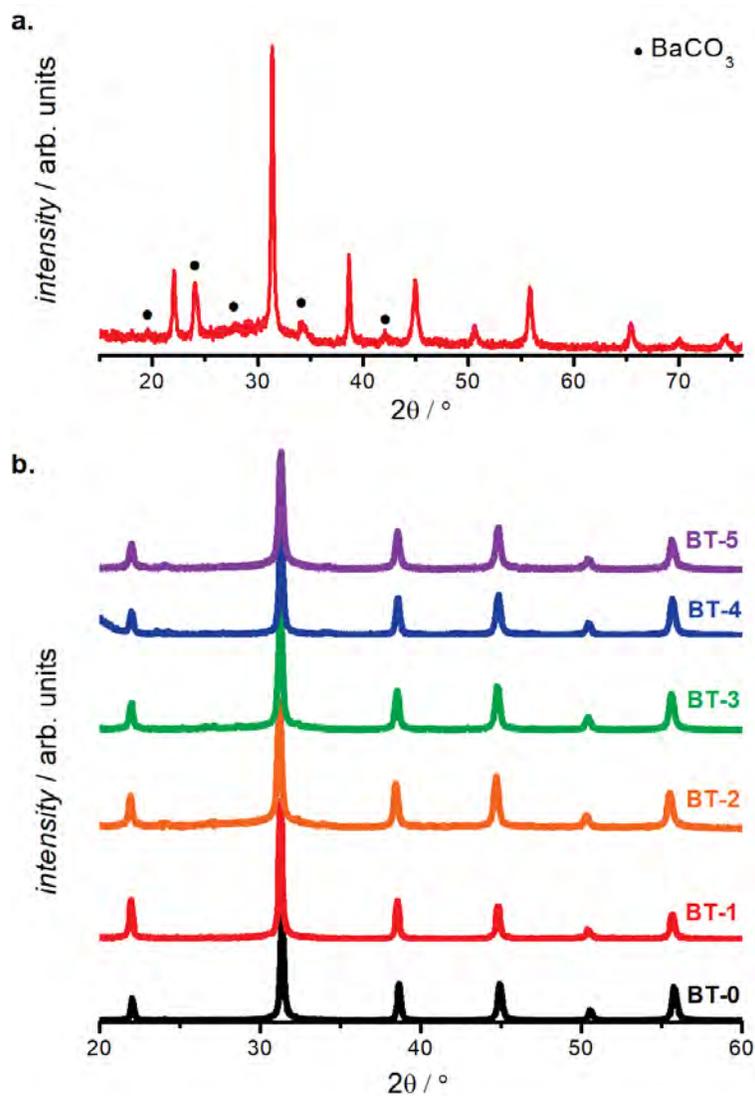
## S2 SUPPLEMENTARY DATA



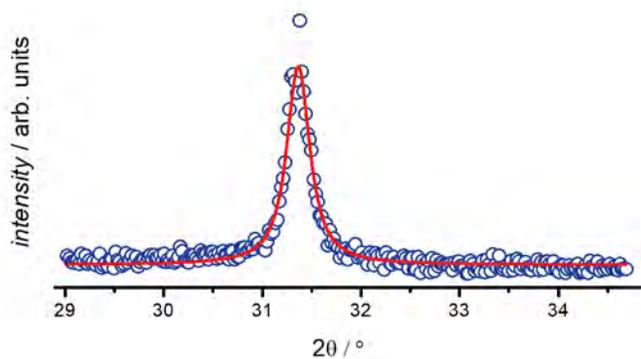
**Fig. S1** The tetragonal crystal structure of BaTiO<sub>3</sub> nanopowders. Ti<sup>4+</sup> ions (blue atoms) with ionic radius of 0.605 Å are surrounded by six oxygen ions (green atoms) and create the TiO<sub>6</sub> octahedral, while Ba<sup>2+</sup> ions with ionic radius of 1.61 Å and coordination number of 12 are located at the corner of unit cell cube (shown with dashed line). Solid green balls are O<sub>1</sub> and green/white balls are labeled as O<sub>2</sub> atoms.

**Table S1** Multiplicity, Wyckoff positions and an atomic positions in BaTiO<sub>3</sub> structure with tetragonal structure (space group of *P4/mmm*).

Atom	Multiplicity	Wyckoff	Coordinates
Ba	1	1a	(0, 0, 0)
Ti	1	1b	(0.5, 0.5, 0.5)
O1	1	1b	(0.5, 0.5, 0)
O2	2	2c	(0.5, 0, 0.5)



**Fig. S2** a. PXRD pattern of **BT-1** before washing with dilute acetic acid. Circles correspond to Bragg peaks arising from BaCO<sub>3</sub> impurity. These impurities were removed after washing the powders with diluted acetic acid (0.5 wt%). b. PXRD patterns of all BaTiO<sub>3</sub> samples after washing with dilute acetic acid. All peaks are assigned to the pure BaTiO<sub>3</sub> phase.



**Fig. S3** Lorentzian fit of the (110) Bragg reflection for sample **BT-1**.

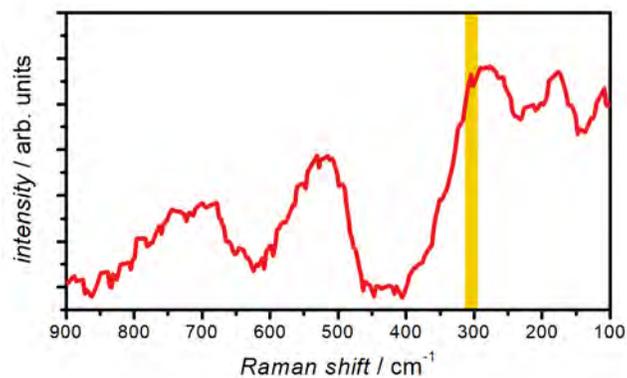


Fig. S4 Raman spectrum of sample **BT-1**, highlighting the B1 band at  $\sim 305 \text{ cm}^{-1}$  characteristic of the tetragonal phase.

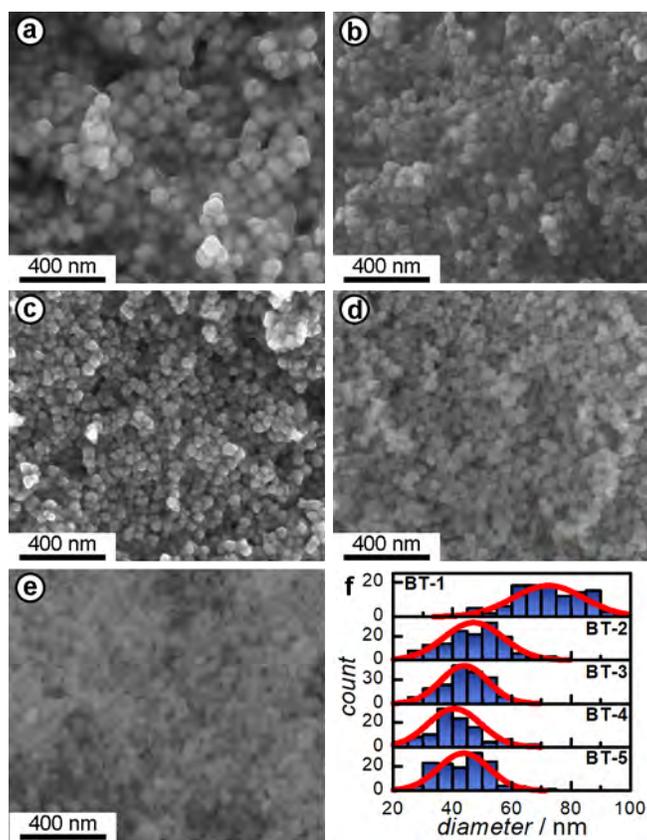


Fig. S5 SEM micrographs of PEGylated- $\text{BaTiO}_3$  nanopowders for samples a) **BT-1** ( $N = 146$ ), b) **BT-2** ( $N = 113$ ), c) **BT-3** ( $N = 185$ ), d) **BT-4** ( $N = 104$ ), and e) **BT-5** ( $N = 131$ ) and f) corresponding histograms (number of particles  $N$  measured is indicated for each sample).

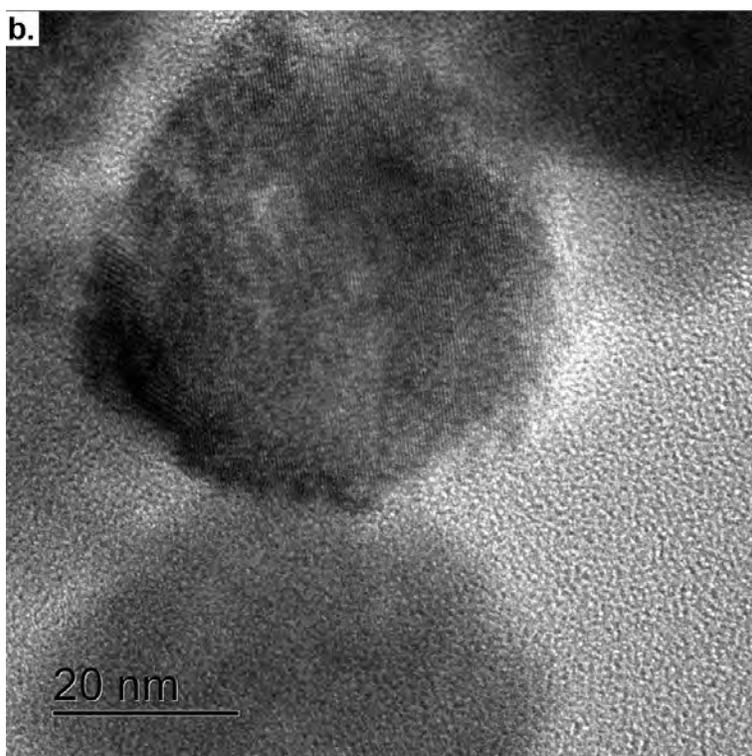
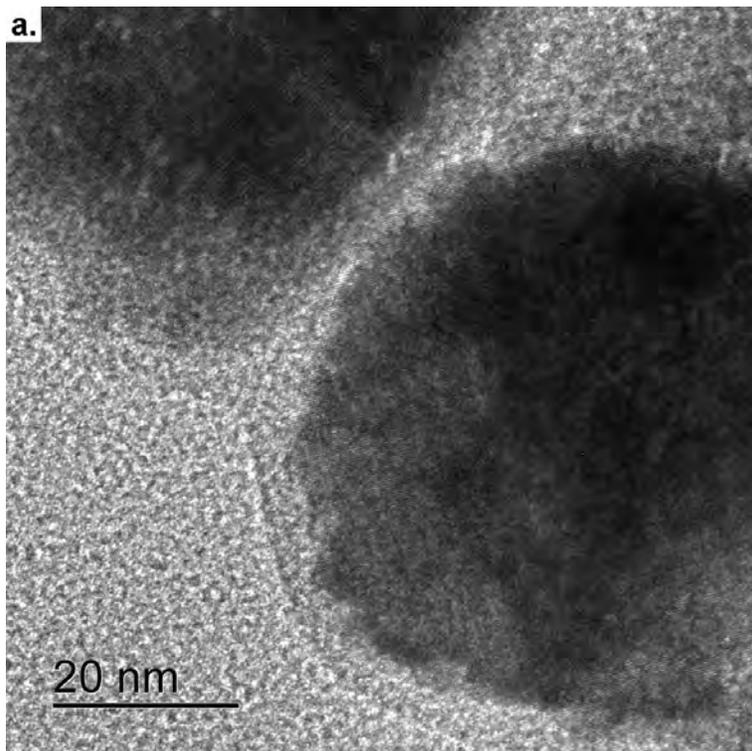


Fig. S6 HRTEM of BT-1, showing lattice fringes across the NPs. a) Fig. 2b, expanded.

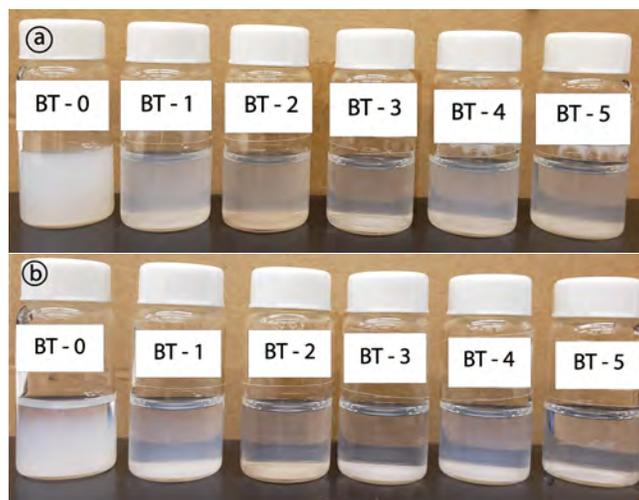


Fig. S7 Stability test of 100 ppm nanoparticles in DI water ( $\text{pH} \approx 7$ ) at room temperature: a) Fresh solutions, b) after 24 hrs.

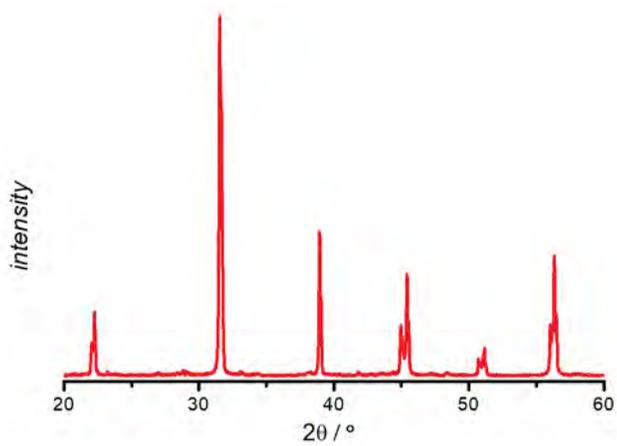


Fig. S8 X-ray diffractogram of the BT-1 pellet used for characterization of ferroelectric properties.