# Supporting information

# One-pot synthesis of silica-titania binary nanoparticles with acid-base pairs via biomimetic mineralization to fabricate highly proton-conducting membranes

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Table S1. Summary of the commonly used precursors and inducers in the synthesis of silica and titania.

| Inorganic particle | Precursor | Inducer [a] | Ref. |
|---|---|---|---|
| $SiO_2$ | Tetraethoxysilane (TEOS) | $NH_3 \cdot H_2O$ | 1-3 |
| | Tetramethoxysilane (TMOS) | NaOH, $H_2O$ | 4 |
| | | HCl, $H_2O$ | 5 |
| | Sodium silicate ($Na_2SiO_3$) | HCl, $H_2O$ | 6, 7 |
| $TiO_2$ | Tetrabutyl titanate (TBT) | $H_2O$ | 8, 9 |
| | Titanium tetrachloride ($TiCl_4$) | $H_2O$ (70 °C) | 10 |
| | | HCl, $H_2O$ (100 °C) | 11 |
| | | Benzyl Alcohol (70 °C) | 12 |
| | Dihydroxybis (ammonium lactato) titanium (TiBALDH) | Methanol | 13 |
| | | $NH_3 \cdot H_2O$ (150 °C) | 14 |
| | | Spermidine | 15 |

[a] The synthesis processes are conducted under room temperature except labeled ones.

Table S2. Measured mole ratio of silicon to titanium in the binary nanoparticles prepared with various mole ratio of TMOS to TiBALDH.

| Mole Number of TiBALDH \ Mole Number of TMOS | 1 | 2 | 4 |
|---|---|---|---|
| 1 | Si:Ti=1:2 [a] | Si:Ti=1:1 | Si:Ti=2:1 |
| 2 | Si:Ti=1:4 | Si:Ti=1:2 | Si:Ti=1:1 |
| 4 | Si:Ti=1:8 | Si:Ti=1:4 | Si:Ti=1:2 |

[a] The data are detected by EDX elemental analysis.

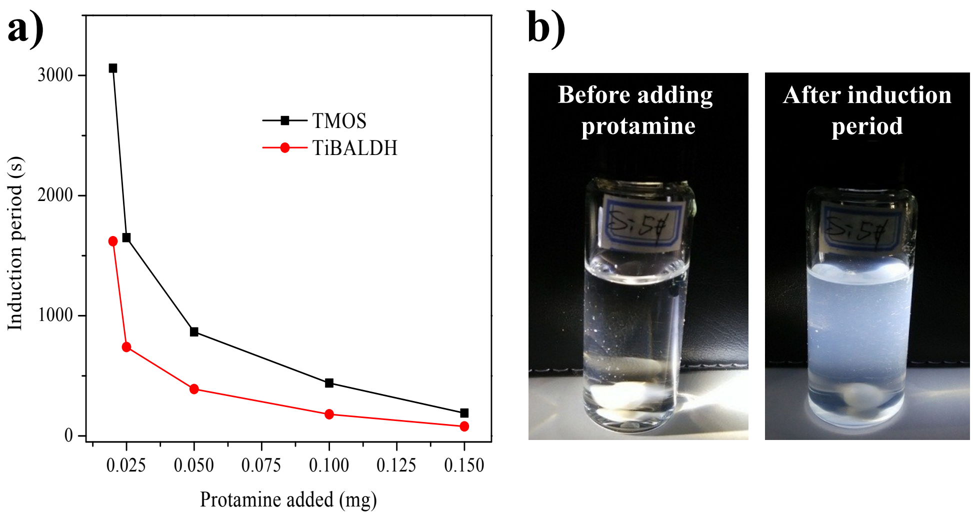


Fig. S1 (a) The induction periods of TMOS (15 mM) and TiBALDH (15 mM) in mixing solvent of water and ethanol (v:v=1:1) over a range of protamine adding quantity at room temperature. (b) Photos of TMOS solution before adding protamine and after induction period.

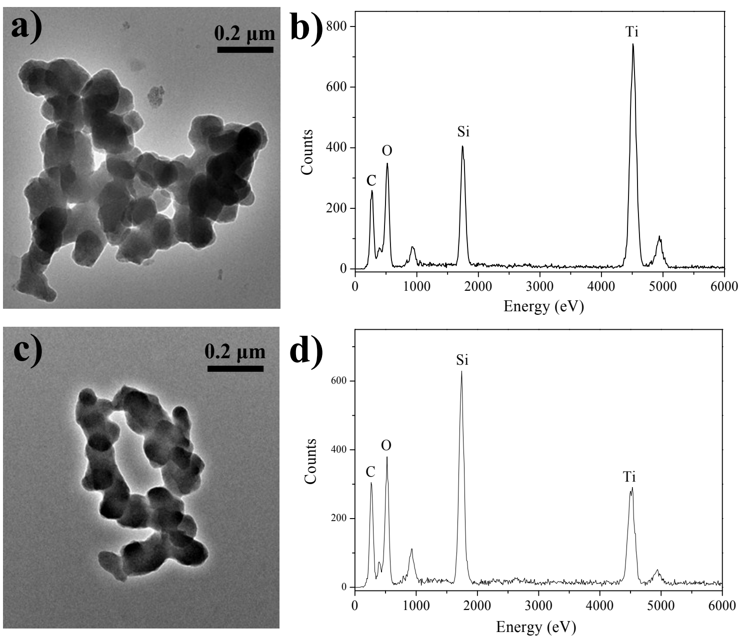


Fig. S2 (a) TEM micrographs, (b) EDX elemental analysis of Si1-Ti2 and (c) TEM micrographs, (d) EDX elemental analysis of Si2-Ti1.

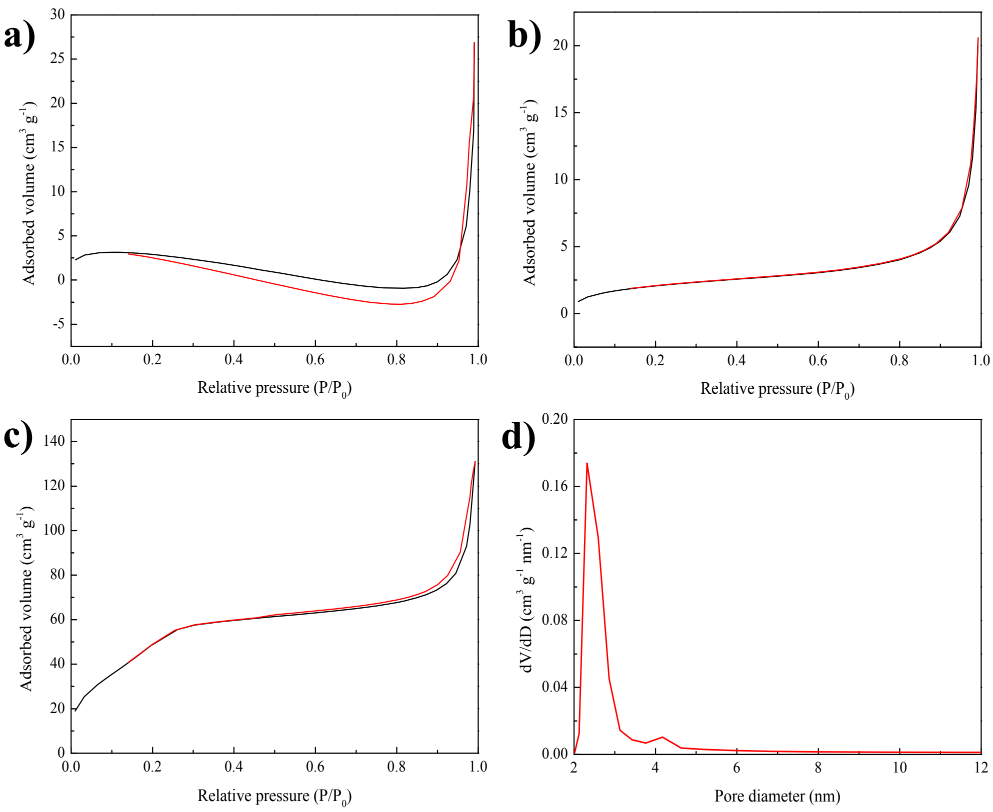


Fig. S3 $N_2$ adsorption-desorption isotherms of (a) alkali-catalyzed $SiO_2$, (b) alkali-catalyzed $TiO_2$ and (c) protamine-induced Si1-Ti1 binary nanoparticles. (d) Pore size distributions of protamine-induced Si1-Ti1 binary nanoparticles.

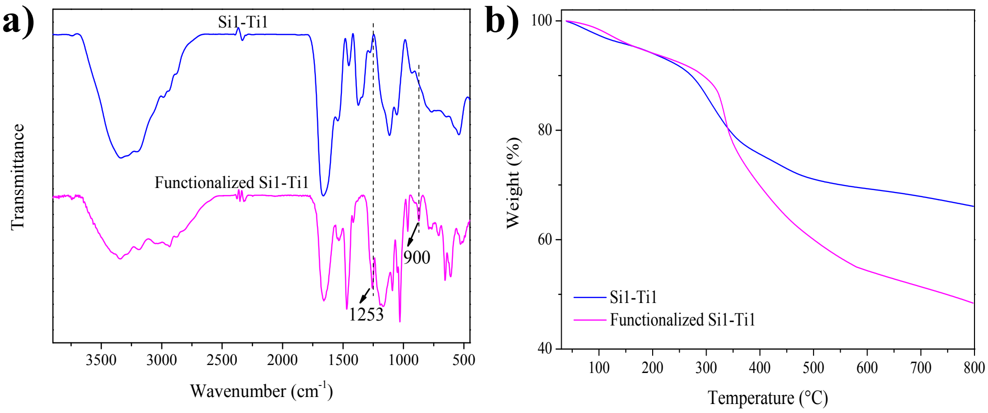


Fig. S4 (a) FTIR spectra and (b) TG curves of protamine-induced Si1-Ti1 binary nanoparticles and functionalized Si1-Ti1 particles.

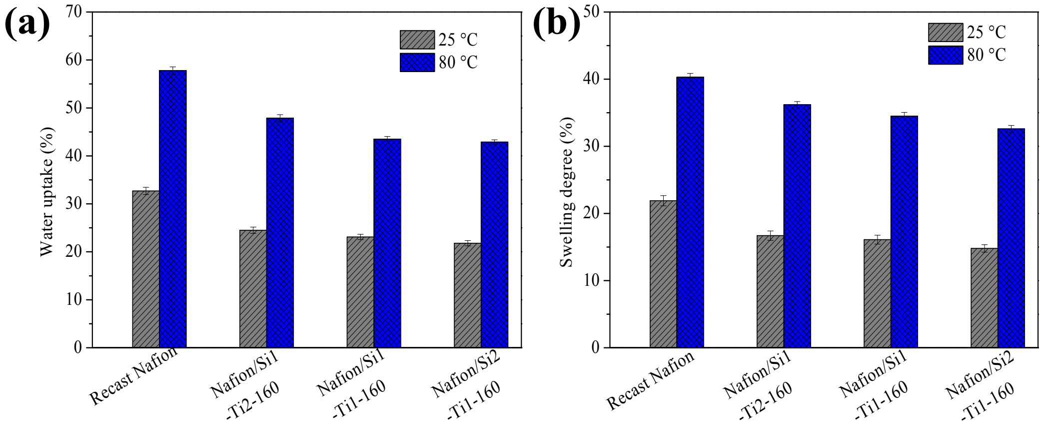


Fig. S5 (a) Water uptake, (b) swelling degree of Nafion/Si1-Ti2-160, Nafion/Si1-Ti1-160, Nafion/Si2-Ti1-160 hybrid membranes and recast Nafion at 25 and 80 °C.

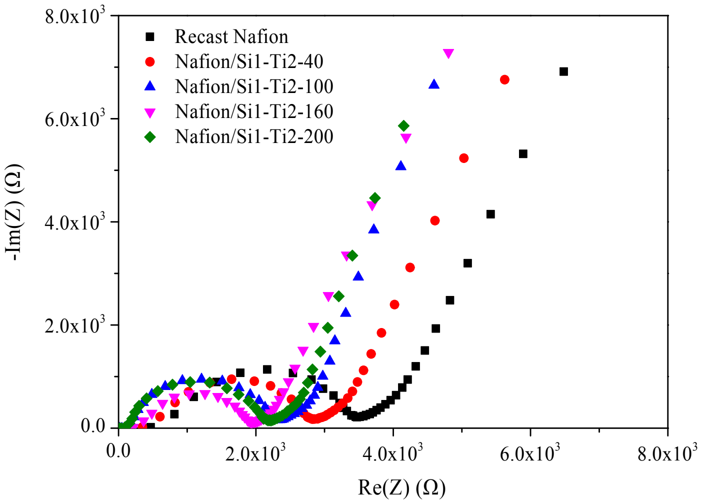


Fig. S6 Nyquist plots of Nafion/Si1-Ti2 hybrid membranes and recast Nafion at 30 °C.

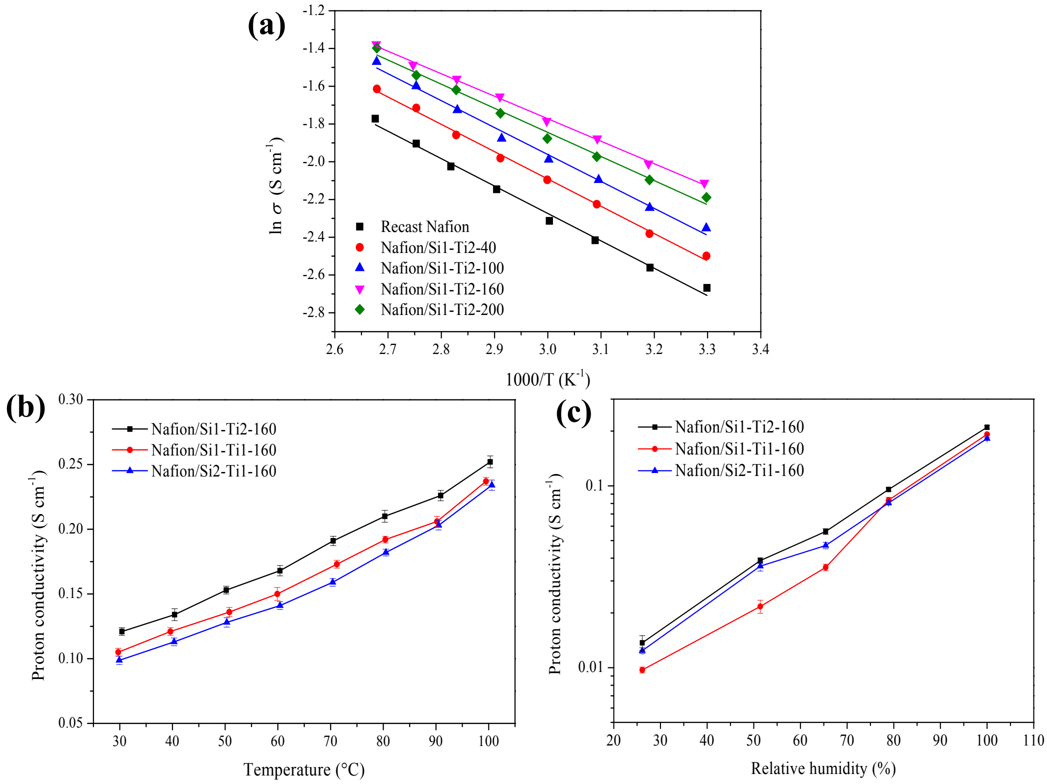


Fig. S7 (a) Arrhenius plots of the proton conductivity for Nafion/Si1-Ti2 hybrid membranes and recast Nafion. Proton conductivity of Nafion/Si1-Ti2-160, Nafion/Si1-Ti1-160, Nafion/Si2-Ti1-160 hybrid membranes (b) under 100% RH, variable temperature conditions and (c) under 80 °C, variable RH conditions.

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