Supporting Information

Novel Ultralight Three-Dimensional House-of-Cards Titania Monolith of Extraordinary Heavy-Metal Adsorption

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Table S1. Preparation and properties of titania foams.

Samples	concentration of TNS (mg/L)	Additive	Wall thickness (nm)	Density (mg/cm^3)	SSA (m^2/g)	Theoretical porosity
1	8	None	~5	5	185	99.88%
2	10	None	~10	6	135	99.86%
3	12	None	~20	8	121	99.81%
4	8	Agar (1%)	~50	10	110	99.76%
5	8	Agar (5%)	~80	12	88.5	99.72%

Table S2. Langmuir parameters of adsorption isotherm of M^{n+} on 3D titania foam.

Parameters	Pb^{2+}	Cu^{2+}	Cr^{3+}	Fe^{3+}
Q_{max} (mmol g^{-1})	4.54	6.23	3.65	11.75
b (L $mmol^{-1}$)	31.15	107.53	11.47	126.74
R^2	0.9994	0.99937	0.9979	0.999

Table S3. Adsorption capacities of titania foam and other well-known adsorbents for heavy metals ions. The literature data obtained at various pH can be compared with our data at pH 3.5 because as pH increases, the titania foam becomes more negatively charged, thus higher adsorption results. (See **Figure S3b**.)

Adsorbate	Adsorbent	Max adsorption capacity (mmol/g)	pH	Reference
Pb^{2+}	Titania foam	4.54	3.5	This work
	Activated carbon-zeolite composite	2.65	7	ref. 37
	Montmorillonite	0.131	5.1	ref. 40
	EDTA-graphene oxide	2.194	3	ref. 41
	Activated carbon	1.998	–	ref. 42
Cu^{2+}	Titania foam	6.23	3.5	This work
	Activated carbon-zeolite composite	1.72	7	ref. 37
	Montmorillonite	0.223	5.1	ref. 40
	Multiwalled carbon nanotubes	0.448	5	ref. 43
	EDTA- Graphene oxide	1.71	5	ref. 41
Cr^{3+}	Titania foam	3.65	3.5	This work
	Modified zeolite	1.6	–	ref. 38
	Activated carbon	0.658	7.53	ref. 42
Fe^{3+}	Titania foam	11.75	3.5	This work
	Montmorillonite-polyacrylate composite	2.94	–	ref. 39
	Natural zeolite	0.118	4.0	ref. 44
	Tannic acid immobilized activated carbon	0.031	4.0	ref. 45
	Carboxymethylated chitosan hydrogels	0.331	4.7	ref. 46

Table S4. Ionic radius, Pauling electronegativity, and field strength of Pb^{2+}, Cu^{2+}, Cr^{3+} and Fe^{3+}.

Cation	Ionic radius (Å)	Pauling electronegativity	Field strength (valence/radius (Å))
Pb^{2+}	1.19	2.33	1.68
Cu^{2+}	0.73	1.90	2.73
Cr^{3+}	0.65	1.66	4.61
Fe^{3+}	0.64	1.83	4.68

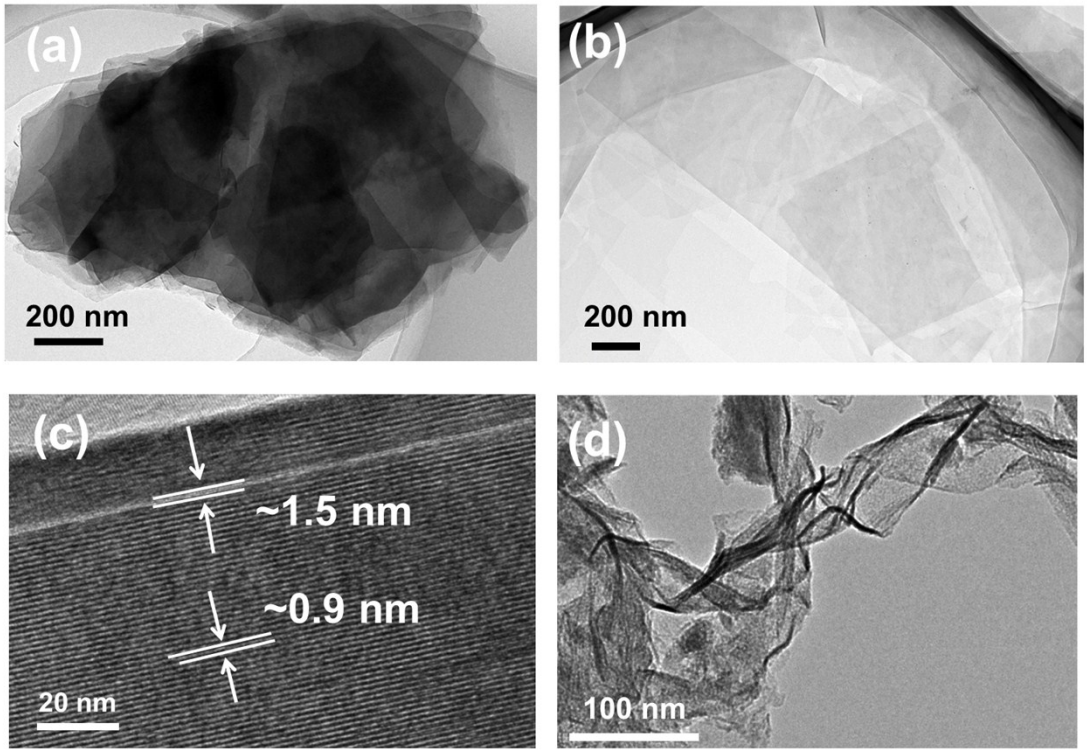

Figure S1. (a) TEM image of $H_xTi_{2-x/4}O_{x/4}O_4 \cdot H_2O$. (b) TEM image of exfoliated titanate nanosheets. (c) An exfoliated layer forms with ~1.5 nm layer spacing among many layers of ~1 nm spacing. (d) TEM image of 3D titania foam consisting of restacking titanate nanosheets.

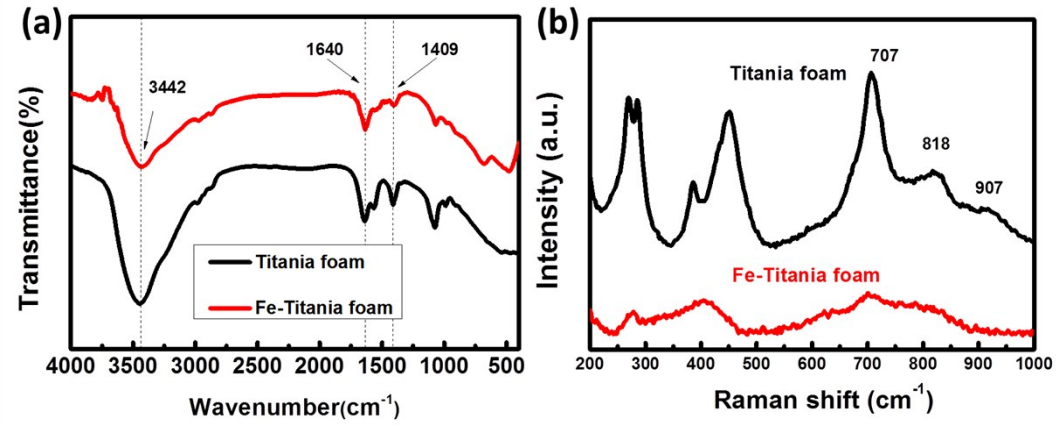

Figure S2. (a) FTIR and (b) Raman spectra of 3D titania foam before (Titania foam) and after (Fe-Titania foam) Fe^{3+} adsorption.

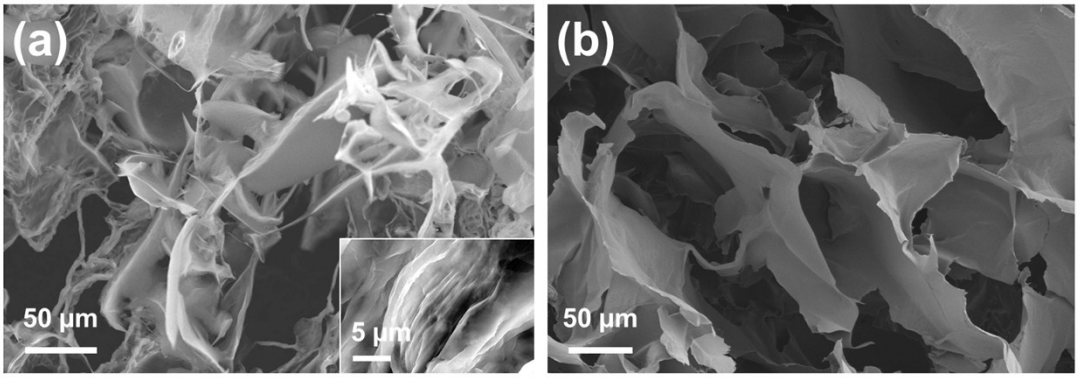

Figure S3. (a-b) SEM images of foams with densities of 5 and 10 mg cm^{-3} (1% agar), respectively.

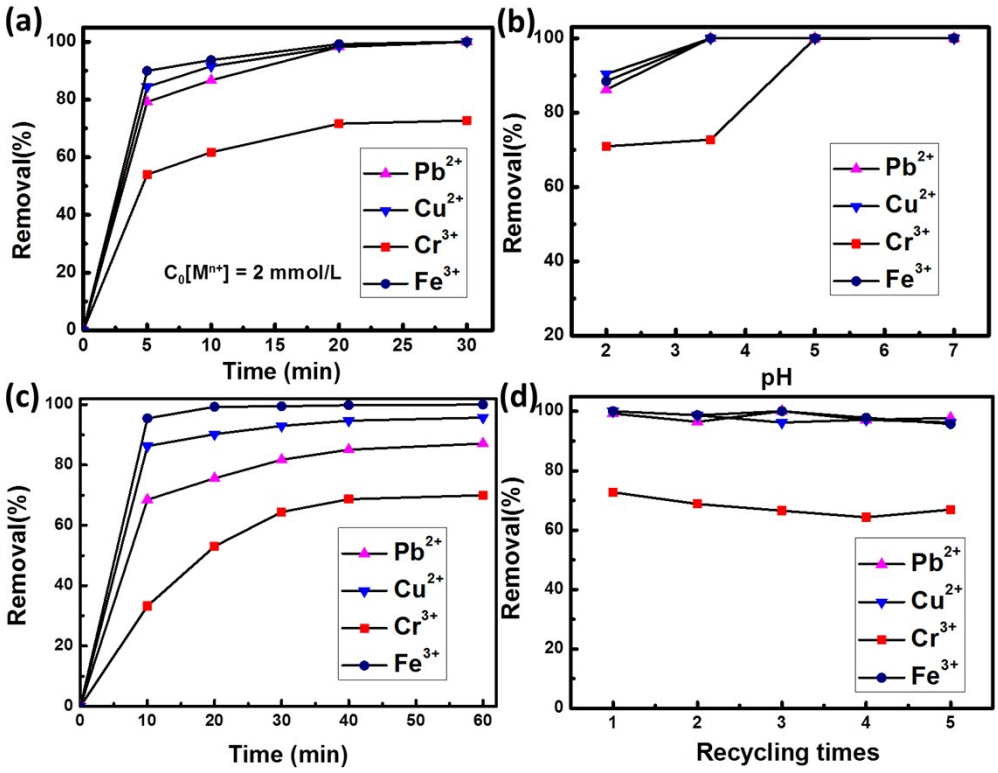

Figure S4. (a) Adsorption kinetics of 3D titania foam, pH = 3.5±0.1, $C_0[M^{n+}]$ = 2 mmol/L. (b) Same as (a) at different pH values at $C_0[M^{n+}]$ = 2 mmol/L. (c) Selected adsorption kinetics of M^{n+} on 3D titania foam, $C_0[Pb^{2+}]$ = 0.87 mmol/L (180 mg/L), $C_0[Cu^{2+}]$ = 2.81 mmol/L (180 mg/L), $C_0[Cr^{3+}]$ = 3.46 mmol/L (180 mg/L), $C_0[Fe^{3+}]$ = 3.21 mmol/L (180 mg/L), pH = 3.5±0.1. (d) Repeat performance of M^{n+} adsorption on recycled foam, at pH = 3.5±0.1 and $C_0[M^{n+}]$ = 2 mmol/L. All adsorption tests were performed at 293K, m/V =0.625 g/L.

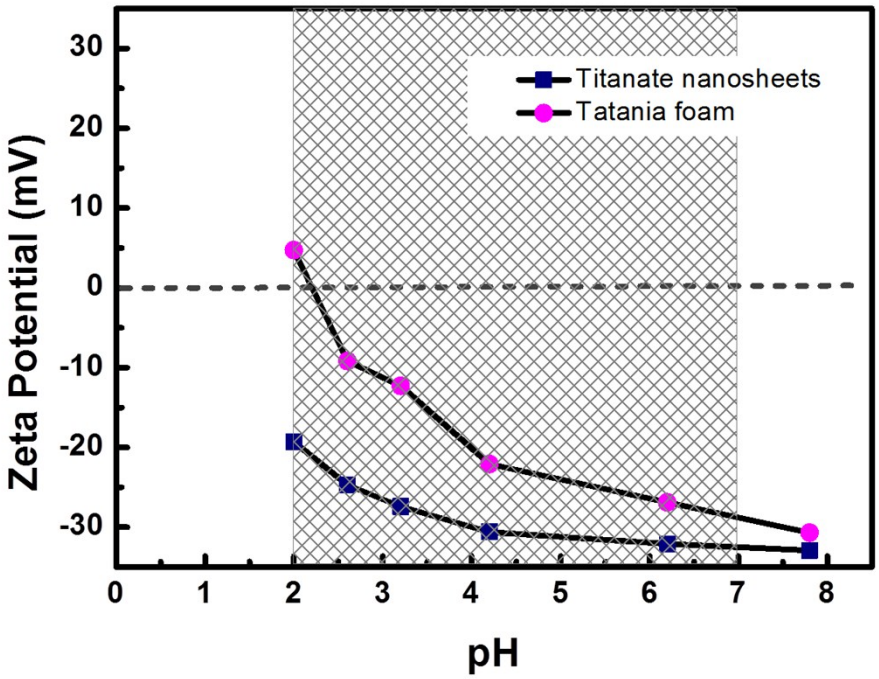

Figure S5. Zeta potential of titania foam and exfoliated titanate nanosheets as a function of pH of buffered solution. The isoelectric points (IEP) of titania foam is 2.2 and the exfoliated titanate nanosheets are more negatively charged than the foam.

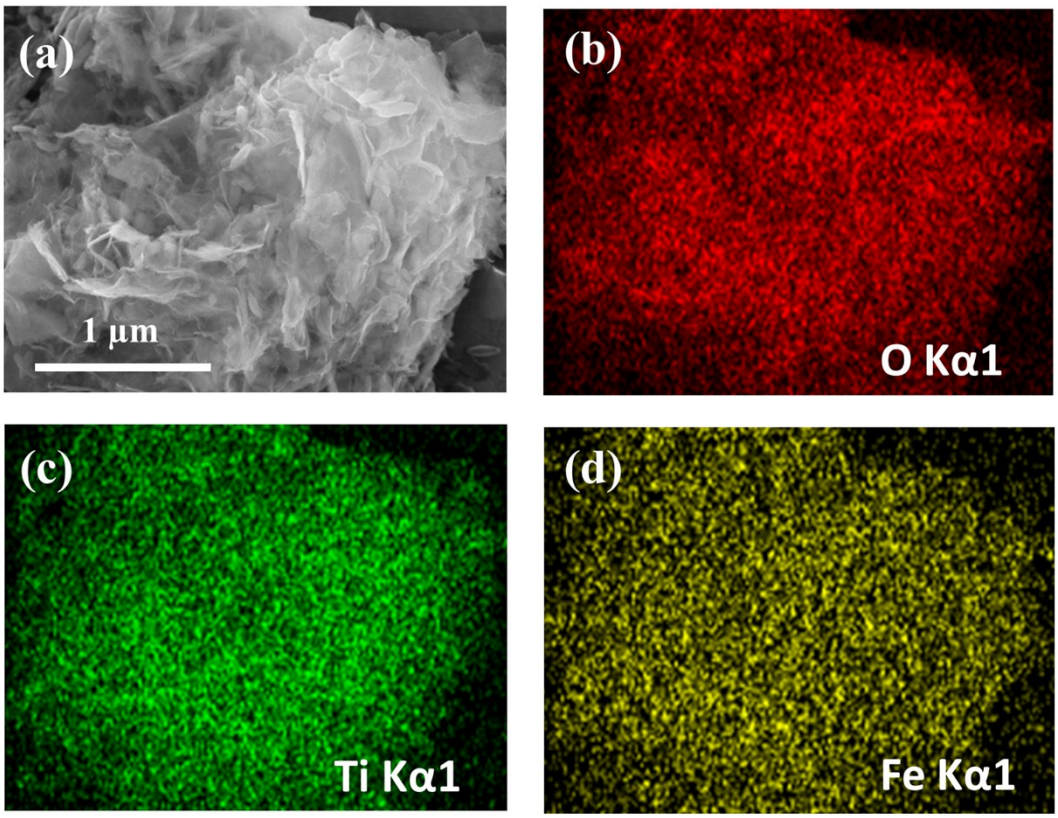

Figure S6. Elemental mapping of a region (a) for O (b), Ti (c) and Fe (d).

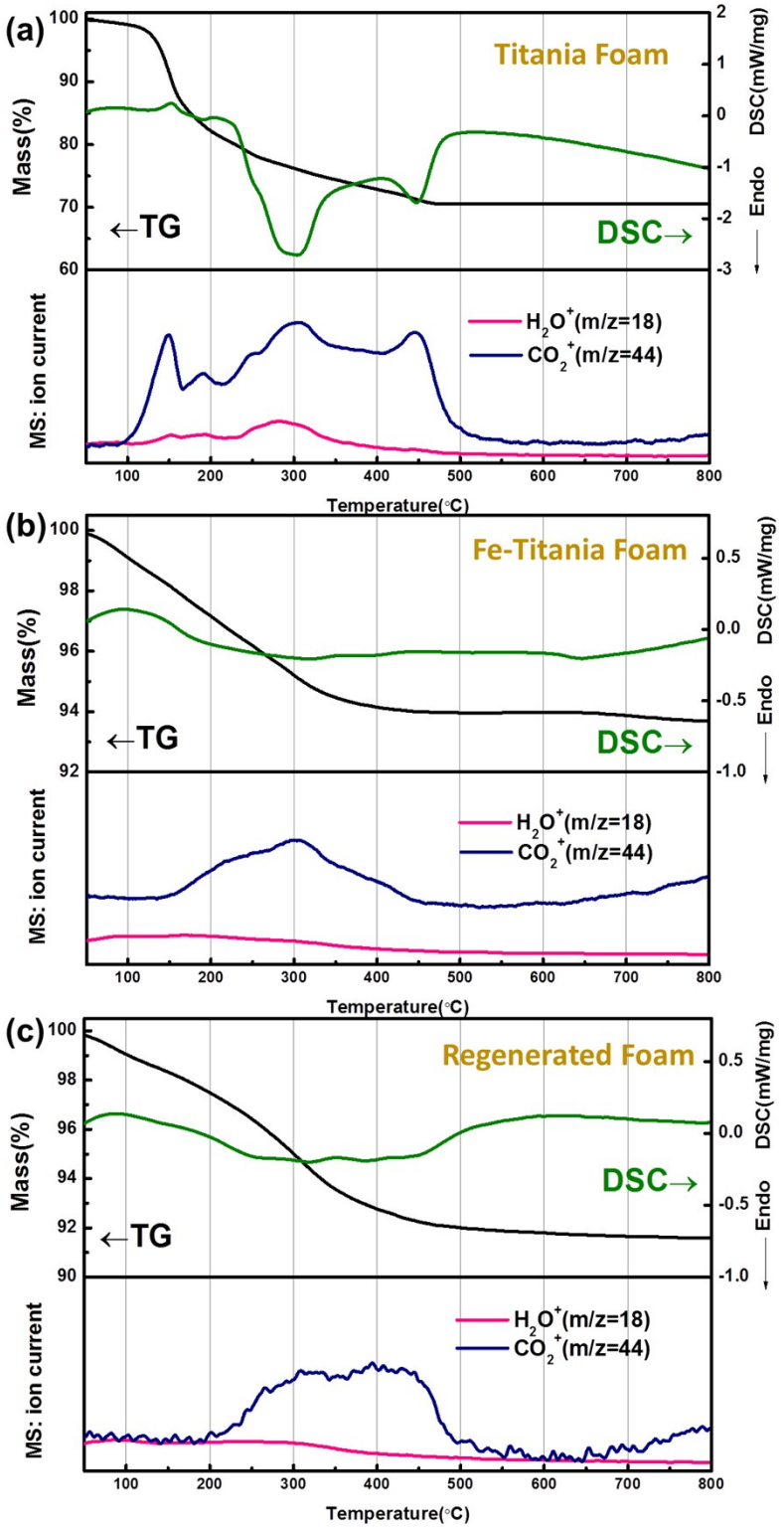

Figure S7. TG/DSC (top) and mass ion detection (MS, (bottom)) analysis curves of virgin titania foam(a), Fe^{3+}-adsorbed foam(b) and acid-washed (regenerated) foam(b). Low temperature (~150°C) weight loss is due to water and organic (TBA) evaporation plus organic oxidation. Middle temperature (150-350°C) weight loss comes from

hydroxyl and organic desorption/decomposition, giving off H_2O and CO_2. High temperature (350-500°C) weight loss in virgin foam and regenerated form is mostly due to burnoff of charcoal residue left by low-temperature organic burnoff. Lack of high temperature burnoff indicates very little TBA in Fe^{3+}-adsorbed foam. Heating from 50°C to 800°C at 10°C /min; atmosphere: O_2 /Ar, 20:80 vol.

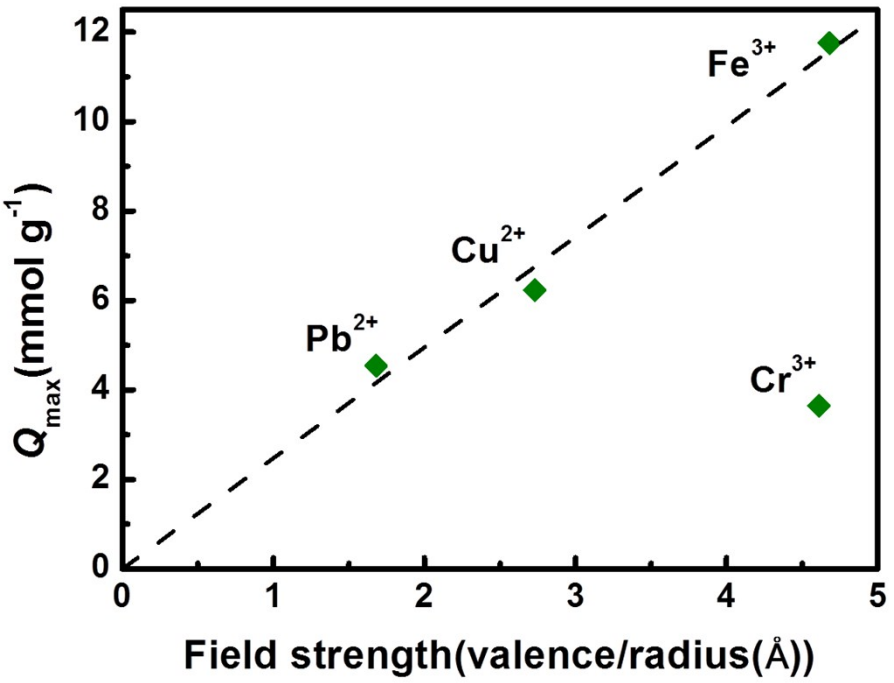

Figure S8. Q_{max} vs. field strength for M^{n+} using data shown in **Table S2** and **S4**.

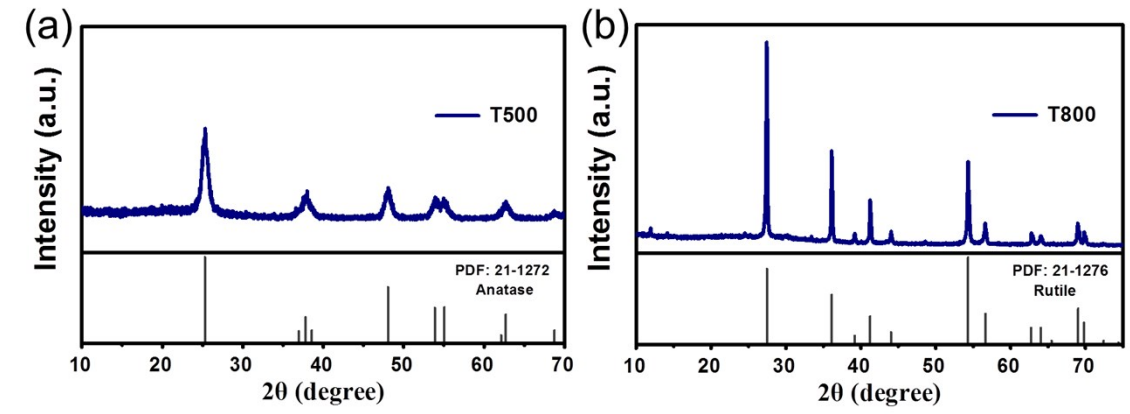

Figure S9. XRD patterns of titania foam calcinated in air for 2 h at 500°C (a) and 800°C (b). The XRD pattern indicates that the calcinated titania foam is transformed into an anatase phase at 500°C and a rutile phase at 800°C.