Supplementary information: Tuning the electronic band structure of microporous titanates with hollandite structure

Pouya Moetakef, Limin Wang, Annalise E. Maughan, Karen J. Gaskell, Amber M. Larson, Brenna C. Hodges, Efrain E. Rodriguez

Figure S1 represents density of states for TiO_2 hollandite structure obtained by first-principles density functional theory (DFT) calculation of nonmagnetic state. The band-gap estimated from DFT calculations is about 2.2 eV.

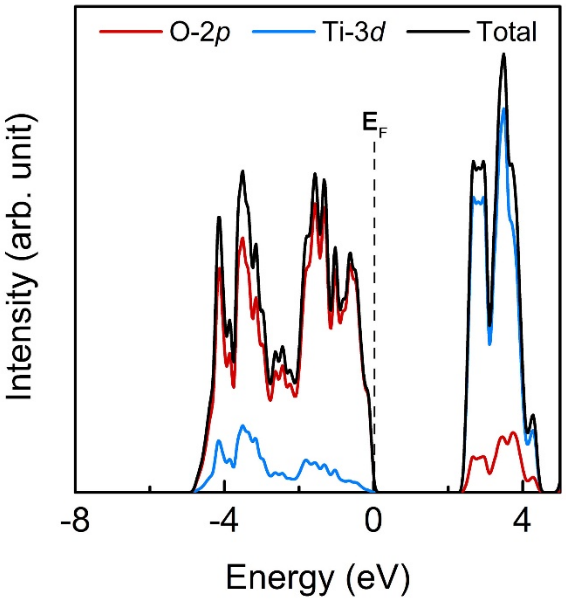

Fig. S1. Density of states for TiO_2 hollandite structure using Density Functional Theory (DFT) calculation.

Table S1. Relaxed lattice parameters and total system energy of titanate hollandite series, $K_x[Ti,M]_8O_{16}$, calculated by Wien2K. R_y is the energy unit in the Wien2k, and equals to 13.6 eV.

M	*a* (Å)	*c* (Å)	V (Å^3)	Energy * R_y
Sc	10.407904	3.013715	326.459	-9061.368
Ti	10.392179	2.994297	323.376	-9240.503
V	10.285900	2.975821	314.841	-9431.345
Cr	10.252551	2.971109	312.307	-9634.353
Mn	10.312801	2.958772	314.676	-9849.843
Fe	10.253730	2.973848	312.667	-10078.091
Co	10.277756	2.971006	313.834	-9779.968
Ni	10.268275	2.968587	313.000	-9907.301

The total energy of titanate hollandite series calculated in Wien2K are presented in Table 1S. This total energy represents the ground state property of the system, and includes the repulsive Coulomb energy of the fixed nuclei, the Kinetic energy of the non-interacting particles, the electron-electron repulsion, nuclear-electron attraction, and exchange-correlation energies. As it can be seen for the same valence substitution, there's a decreasing trend with increasing atomic number. Furthermore, it must be noted that for M^{3+}, the tetragonal symmetry is broken in the supercell consideration, $K_3M_3Ti_{13}O_{32}$, while for M^{2+}, the tetragonal symmetry remains unchanged, $K_6M_3Ti_{29}O_{64}$. Our calculations confirm that the symmetry breaking won't lead to any difference in the results of the calculation whether the supercell is tetragonal or orthorhombic.

Figure S2 shows the comparison between lattice parameters determined using X-ray diffraction and DFT relaxed lattice. As it can be seen the trend of changes with respect to the transition metal ion is similar in both cases.

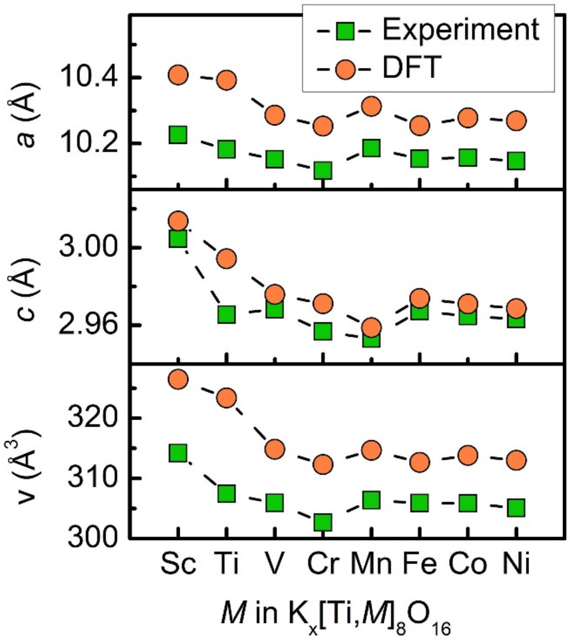

Fig. S2. Comparison on lattice parameters *a* and *c* as well as lattice volume between experimental measurements and relaxed DFT lattice.

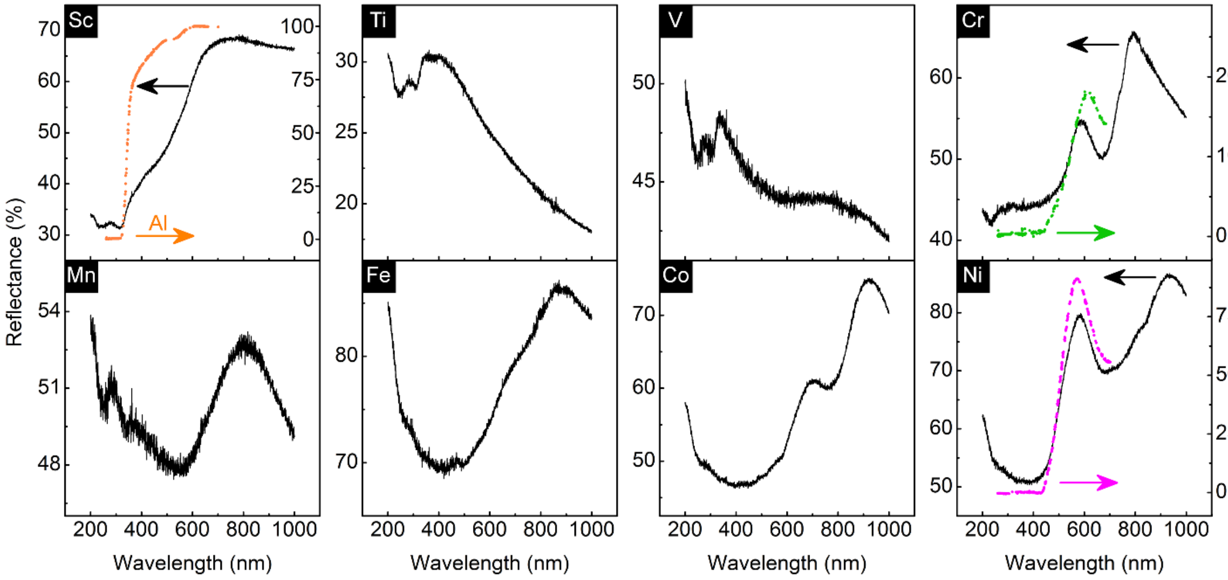

Fig. S3. Reflectance plots for $K_x[M,Ti]_8O_{16}$, where M = Sc – Ni, with 15 wt% dilution (except for M = Sc which is the 30 wt% dilution data). The dotted curves in M = Sc, Cr, and Ni, represent the reflectivity of $K_{1.8}Al_{1.8}Ti_{6.2}O_{16}$, $K_{1.8}Cr_{1.8}Ti_{6.2}O_{16}$, and $K_{1.8}Ni_{0.9}Ti_{7.1}O_{16}$, respectively, which are reproduced from Ref [1] for comparison.

Figure S3 represents the reflectance data for lower dilution (15 wt%) of hollandite series. It can be seen that the features in the spectra are similar to Fig. 4 in the manuscript, but a larger % Reflectance change is observed in Fig. 4.

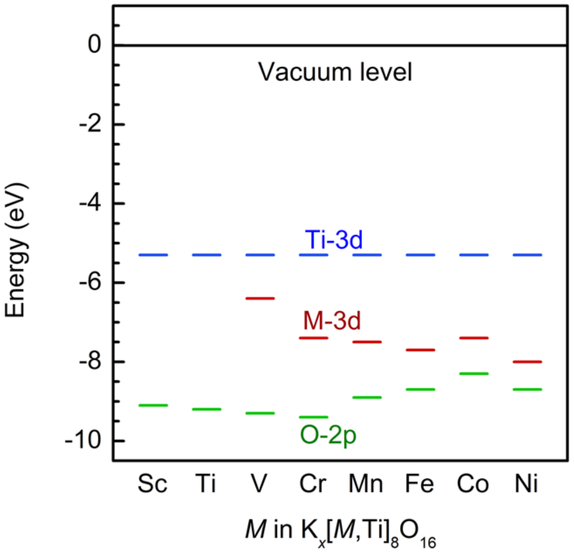

Fig. S4. Band diagram of $K_x[Ti,M]_8O_{16}$ series with respect to the vacuum level.

To determine a complete picture for the band diagram of the entire series, a measure of the work function is essential. However, our efforts to measure the work function using Ultraviolet Photoelectron Spectroscopy (UPS) did not yield in any meaningful results due to charging problems.

In another effort we tried to estimate the complete band diagram using calculation results presented by Buckeridge et al.[2] The results of their model presented in Ref. [2] is in good agreement with experimental band gap and work function energies of rutile and anatase. Furthermore, their band-gap prediction of hollandite TiO_2 is in good agreement with the band-gap energies determined in the present work. Hence, other calculated parameters including electron affinity in hollandites can be used as a good estimate to construct a complete band diagram. This band diagram is shown in Fig. S4. In this figure, the energy difference between Ti-3*d* and vacuum level ($E_{V\text{-}T}$) is estimated from electron affinity calculation.[2] Meanwhile it was assumed that the changes in $E_{V\text{-}T}$ is negligible as M is changed from Sc to Ni. Therefore, Fig. S4, can be used as a rough estimate for the titanate hollandite band diagram energy levels with respect to the vacuum.

References:

1. L. G. J. de Haart, G. R. Meima and G. Blasse, Materials Research Bulletin, 1983, 18, 203-210.
2. J. Buckeridge, K. T. Butler, C. R. A. Catlow, A. J. Logsdail, D. O. Scanlon, S. A. Shevlin, S. M. Woodley, A. A. Sokol, and A. Walsh, Chem. Mater. 2015, 27, 3844−3851