

ADVANCED ENERGY MATERIALS

Supporting Information

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Mn₂V₂O₇: An Earth Abundant Light Absorber for Solar Water Splitting

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$\text{Mn}_2\text{V}_2\text{O}_7$: An Earth Abundant Light Absorber for Solar Water Splitting

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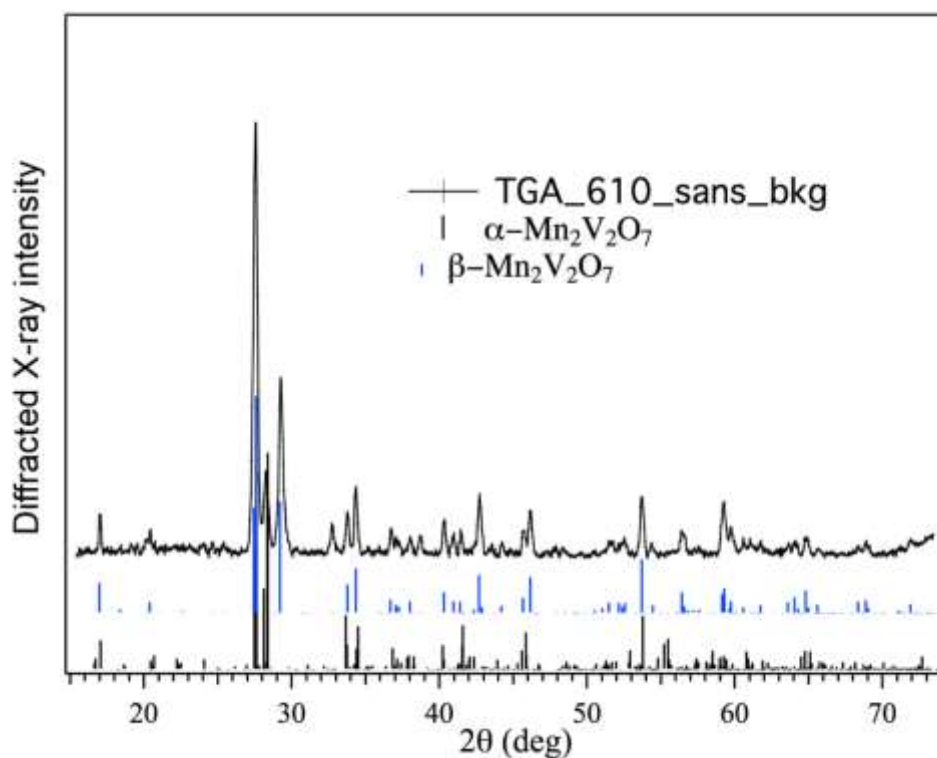


Figure S1. Experimentally measured (black line on the top) and theoretically simulated X-ray diffraction data for both $\alpha\text{-Mn}_2\text{V}_2\text{O}_7$ (in black) and $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ (in blue).

X-ray diffraction of $\beta\text{-Mn}_2\text{V}_2\text{O}_7$

The powder was characterized by X-ray diffraction (XRD, Bruker D8 with GADDS). The simulated patterns match that of the powder and demonstrate that the powder contains primarily $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ with a small fraction of $\alpha\text{-Mn}_2\text{V}_2\text{O}_7$. The equilibrium lattice parameters obtained from the HSE calculations are in excellent agreement with previous experimental data, with deviations of less than 0.5% in lattice constants (Table 1).

Magnetic properties of $\beta\text{-Mn}_2\text{V}_2\text{O}_7$

Due to the high-spin d^5 configuration of Mn^{+2} , $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ can in principle take up several possible magnetic states, and to identify the ground state we use both PBE+U and HSE functionals to calculate several ferromagnetic (FM) and antiferromagnetic (AFM) states. Our results show that the magnetism in $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ originates from the Mn atoms, with a magnetic moment of $4.58 \mu_B$ (HSE), and that the V^{+5} cations are nonmagnetic as expected. By comparing the total energies of different magnetic configurations obtained from both PBE+U and HSE methods, we find that the spins on Mn atoms favor FM interactions within the edge-sharing MnO_6 layer. The total energy of the AFM configuration with opposite spins on neighboring layers is very close to that of the FM phase (< 3 meV per Mn atom), indicating that the interlayer magnetic coupling is rather weak. This competing AFM phase exhibits similar structural and electronic properties as the FM phase; other AFM arrangements in the conventional cell are 0.04 eV higher in energy, and excluded from our analysis. As the $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ is paramagnetic at room temperature^[1], we restrict our study to the FM phase.

Electronic structure of $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ from first-principles calculations

We now turn to a discussion of the electronic properties of $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ relevant to solar photocatalysis. The band gaps produced by PBE and PBE+U calculations are 0.82 eV and 1.20 eV, respectively. For metal oxides, HSE band gaps have been reported to trend more closely to experiment in some cases^[2,3], and for $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ using a standard mixing parameter of 0.25, we find a gap of 2.35 eV, significantly lower than many oxides^[2] and near the desired range for a photocatalyst. Since DFT is not a rigorous theory of the band gap^[4], the quantitative nature of these predictions is limited. Many-body perturbation theory within the GW approximation can result in significantly more reliable gaps for many inorganic semiconductors^[5], despite its

neglect of excitonic effects and electron-phonon interactions. Yet standard implementations of the GW approximation—in particular one-shot G_0W_0 corrections—are challenging for transition metal oxides where d states feature prominently^[5, 6], possibly owing to insufficiently accurate mean-field Kohn-Sham starting points^[7].

Comparison with other semiconductors for photocatalysis

For efficient, solar-driven photoelectrochemical water oxidation, the 3 primary criteria for a promising photoanode light absorber are:

- (i) valence band maximum 0.1-0.5 V with respect to the OER potential (Valence band alignment)
- (ii) band gap between 1 and 2 eV to provide appreciable photovoltage and high absorption of solar radiation.
- (iii) electrochemical stability in pH 13 under illumination, particularly at the OER potential (measured as no dark- or photo-corrosion current)

Here we tabulate known semiconductors for photocatalysis [based on the information in Chem. Soc. Rev. 38, 253 (2009), Chem Mater. 24, 3659 (2012), and our measurements of photoelectrochemical stability noted by *] with these three criteria.

Table S1. Known semiconductors for photocatalysis.

	(i)	(ii)	(iii)
CdS	Y	N	N
CdSe	N	Y	N
GaP	Y	N	N
SiC	Y	N	N
MoS ₂	Y	Y	N
ZnSe	Y	N	N
Ta ₃ N ₅	Y	N	N
Cu ₂ O	Y	Y	N*
□-Fe ₂ O ₃	N	N	Y
BiVO ₄	N	N	N
NaTaO ₃	N	N	Y
SrTiO ₃	N	N	Y
TiO ₂	N	N	Y
WO ₃	N	N	N*
β-Mn ₂ V ₂ O ₇	Y	Y	Y

In this table, β-Mn₂V₂O₇ is the only semiconductor to meet all 3 criteria. Only Cu₂O and MoS₂ meet 2 of the criteria and are notoriously unstable materials in oxidizing conditions. The majority

of photoelectrochemically stable materials are wide band gap metal oxides, and $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ maintains the characteristic stability of oxides while exhibiting desirable band energetics.

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