**Supplementary Materials**

**Carrier-induced absorption as a mechanism for electrochromism in tungsten trioxide**

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**Contents:**

#### S1 Generation of Disordered Structures

#### S2 Atomic and Electronic Structure of Disordered Phases

#### S3 Determination of Fermi Level

#### References

### Supplementary Material

In this Supplementary Material, we describe our computational methodology for generating disordered structures and provide an overview of their atomic and electronic structure.

#### S1 Generation of Disordered Structures

To generate disordered structures, we use molecular dynamics simulations, following the general procedure outlined in Ref. [S1]. The disordered phase is constructed from a 3×3×3 supercell of the cubic structure (equivalent to 27 formula units). A k-point mesh of 2×2×2 is used; higher meshes of 3×3×3 were tested, leading to energy differences of less than 5 meV. The amorphous phase is quenched from a “melted” phase. This melted phase is achieved with a microcanonical ensemble that is allowed to equilibrate at T = 5000 K. The time step was Δt = 2.0 fs. In order to ensure any order has vanished, structures were sampled once atoms moved on average at least one nearest-neighbor distance. As the W atom is much more massive than the O atom, it moves more slowly in molecular dynamics simulations. This is circumvented by reducing the W mass to 40 amu.[S1] After equilibration, every 250 time steps a structure was taken and rapidly quenched to room temperature. We choose a structure every 250 time steps in order to ensure that structures are distinct from each other. Quenching occurred for 1000 time steps and the structure was then allowed to equilibrate at room temperature for an additional 500 steps.

GGA is used for molecular dynamics simulations, followed by a single self-consistent HSE calculation for calculating optical properties. We performed this procedure to obtain 3 structures, which we label as Structures A, B, and C. The range of bond lengths and angles for the structures generated are comparable to those reported in Ref. [S1].

#### S2 Atomic and Electronic Structure of Disordered Phases

We describe the atomic and electronic structure of the disordered structures generated. Our objective is to capture representative structural features of the disordered solid, not to provide a comprehensive description of the disordered phase. The disordered structure differs from the crystalline phases in that bond lengths have a wider distribution and deviations from 6-fold coordination become possible. In Fig. S1 we compare W-O and W-W bond lengths in the monoclinic and amorphous phases. Results for amorphous reflect values accumulated for Structures A, B, and C. The W-O distances peak at approximately 1.89 Å (the bond length in the cubic phase) and display a broadening that tails off around 2.3 Å; they show distinct broadening compared to the crystalline phase. Similar observations apply to the W-W distances, which peak around 3.78 Å (the lattice constant of the cubic phase).

The O-W-O bond-angle distribution is shown in Fig. S2. In the cubic phase the bond angles are 90∘; in the monoclinic phase the angles spread between approximately 80∘ and 100∘. This range is significantly broadened in the amorphous structures [Fig. S2(b)]. The wide range of possible O-W-O bond angles is indicative of the disrupted octahedral structure. These changes and distributions are consistent with those observed in previous studies of the amorphous phase.[S1]

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| **FIG. S1:** Distribution of W-O and W-W bond lengths in the (a) monoclinic and (b) disordered structures, using a cutoff of r = 2.30 Å for W-O and r = 5.5 Å for W-W distances. |

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| **FIG. S2:** Distribution of relative number of O-W-O bond angles for the (a) monoclinic and (b) disordered structures. |

Other major changes to the atomic structure occur upon amorphization. Melting disrupts the 6-fold coordination of W, leading to a distribution of possible coordinations. Unlike in the cubic and monoclinic phases where all W are 6-fold coordinated, 4-, 5-, and 6-fold coordinations are found in the amorphous structure. We consider W and O to be part of an octahedron if they are less than 2.3 Å apart from each other. Among the three structures sampled, around 33% of the possible W centers are 4-fold coordinated, 50% are 5-fold coordinated, and the remaining are 6-fold coordinated.

The changes in the crystal structure lead to significant changes in the electronic structure. We observe a band narrowing compared to crystalline phases. The band width of the W d states (combined t2g and eg states) is 13.2 eV in the cubic phase; 8.9 eV in the monoclinic phase; and 8.4 eV, 8.4 eV, and 7.3 eV for the amorphous structures. Similar band narrowing has been found previously for amorphous WO3.[S1]

Figure S3 shows the electronic density of states for the amorphous structures. As expected, states appear in the band gap, corresponding to localization and/or the formation of defects in the disordered structure. For purposes of analyzing the electronic structure and absorption spectra, we identify a band gap by checking the degree of localization of states. For both the VB and CB, we take the band edge to be the first electronic state not associated with any particular defect or localized state of the structure. Inspection of the charge density indicates whether a state is localized (on the scale of a few atoms) versus delocalized (distributed over a majority of atoms in the supercell). Our choice of band edges is shown in the shaded regions in Fig. S3.

Structure A is free of localized states far from the band edges, while Structures B and C have localized states throughout the gap. In Structure A, the localized states near the VB are primarily from undercoordinated O, and those near the CB come from edge-sharing octahedra or undercoordinated W. In contrast, in Structure B the states in the gap at slightly less than 1 eV above the VB arise from neighboring oxygen atoms in configurations with small W-O-W bond angles; these oxygens interact more strongly within the same octahedra

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| **FIG. S3:** Total density of states for the three disordered structures, (a) Structure A, (b) Structure B, and (c) Structure C. The zero of energy corresponds to the VB maximum. The edges of the shaded region correspond to the VB maximum and CB minimum; states within this region are ignored in calculated optical spectra. |

(smallest separation distance is 1.47 Å). They can also arise from interactions between oxygens in two separate octahedra. The gap state just above 1 eV is associated with several undercoordinated O, in addition to a pair of W-W separated by 2.77 Å in edge-sharing octahedra. This W-W distance is less than that in the bulk and leads to greater hybridization between the adjacent W, resulting in a gap state.

Like Structures A and B, the localized states in Structure C near the VB maximum are derived from undercoordinated oxygens and interactions of two oxygens in separate octahedra spaced closer than the typical O-O distance. The states near mid-gap arise from atoms positioned in edge-sharing octahedra and from undercoordinated W. While edge-sharing octahedra are also present in Structure A, the W of edge-sharing octahedra in Structure C are spaced closer together (by up to 0.1 Å). This smaller separation of edge-sharing W in Structure C leads to localized states further from the CB edge.

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| **Figure S4:** (a) Absorption coefficient for disordered Structure B for three different choices of conduction-band edge. (b) Choice of conduction-band edge illustrated within the total density of states for Structure B. The valence-band edge is kept fixed (and chosen as the zero of energy). Each colored box corresponds to a different choice of the CB edge. |

While it is informative to examine the character of these defect states, the concentration at which they occur in our simulations is much higher than expected in a realistic

disordered solid due to the limited size of our supercells. These defects would therefore have a spuriously large impact on the optical absorption. For purposes of analyzing the absorption spectra, we have therefore removed these localized states from our calculations, by omitting them from the sum over bands in Eq. (2).

The inclusion of localized states does not change our conclusions. We show an explicit calculation of CB → CB transitions for different choices of band edges for Structure B in Fig. S4. The detailed features that occur at specific energies are due to the specifics of the disordered structure (modeled in a modest-size supercell); on average, the absorption changes by less than a factor of 2. In a real system, the concentration of localized or defect states would be far smaller than in our models and would have an even smaller impact on absorption.

### S3 Determination of Fermi Level

In our calculations for both crystalline and disordered structures, we use the rigid band approximation. We adjust the Fermi level to achieve a particular electron concentration using the calculated density of states. We first fix what the target doping concentration is based on number of excess electrons per unit volume. Using the fact that the total electron concentration *n* in the system is



where is the density of states and is the Fermi-Dirac distribution, we find the corresponding Fermi level that gives the desired the target doping concentration. Tables S1 and S2 give the Fermi level for the structures considered and equivalent number of electrons per formula unit. For each of the disordered structures, the states within the grey region shown in Fig. S3 are omitted.

**Table S1:** Fermi level (eV) with respect to the conduction band minimum for crystalline structures. In parentheses is the corresponding number of electrons per formula unit.

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| *n* (cm-3) | Cubic | Monoclinic |
| 1018 | -0.14 (5.43 x 10-5) | -0.11 (5.51 x 10-5) |
| 1019 | -0.081 (5.43 x 10-4) | -0.047 (5.51 x 10-4) |
| 1020 | -0.0039 (5.43 x 10-3) | 0.034 (5.51 x 10-3) |
| 1021 | 0.17 (5.43 x 10-2) | 0.30 (5.51 x 10-2) |

**Table S2:** Fermi level (eV) with respect to the conduction band minimum for disordered structures at 1021 cm-3 doping. The equivalent number of electrons per formula unit is 5.43 x 10-2 e-/WO3.

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| Structure | (eV) |
| A | 0.047 |
| B | 0.32 |
| C | 0.051 |

### References

[S1]   G. A. de Wijs and R. A. de Groot: Structure and electronic properties of amorphous WO3. Phys. Rev. B 60, 16463 (1999).