Supporting Information

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S1. VO₂ Specimen
Polycrystalline VO₂ nanoparticles on graphene substrates were prepared by the sol–gel method as described elsewhere (35, 37). Fig. S1 shows a bright-field (BF) image of the VO₂ nanoparticles. The sample is found to be heterogeneous, with the average size of the VO₂ nanoparticles ~200 nm. A PINEM image of the same sample is shown in Fig. S1B. This image was acquired by energy filtering the ultrafast electron pulses to select only electrons that have gained quanta from the gating photon pulse.

S2. Time-Resolved Electron Diffraction Measurements
Time-resolved electron diffraction experiments have been conducted to investigate the ultrafast phase transition dynamics in VO₂ nanoparticles from initial (monoclinic) insulator phase to (tetragonal) metal phase, as explained and shown in Fig. 4 in the main text. As was reported earlier (35) for equivalently prepared specimens of VO₂ nanoparticles on graphene, even under high fluence the photoinitiated phase transition recovers in ~1–2 μs. Therefore, within the experimental repetition period of 10 μs used here, the system is fully recovered to the initial monoclinic phase before the succeeding pump pulse. As a contrast to the ultrafast dynamics of Bragg spot 2 shown in Fig. 4D in the main text, and assigned to the phase transition in VO₂ in Fig. S2B we have traced the intensity change in Bragg spot 5 (as shown in Fig. 4B and C in the main text and Fig. S2A), which is assigned to the graphene substrate. This Bragg spot intensity remains unchanged before, in the presence of, and after the second optical (pump) pulse. Other Bragg spots assigned to the graphene substrate (connected by yellow dashed lines in Fig. S2A) show the same behavior.

S3. Heat Distribution in VO₂ Nanoparticles Illuminated by Ultrafast Visible Laser Pulses
Investigation of the dependence on pump excitation fluence of the PINEM change of VO₂ nanoparticles by time-resolved PINEM measurement reveals an onset around 2 mJ/cm² (Fig. 5, main text). In these measurements, the first optical pulse, with fluence 1.3 mJ/cm², was synchronous with the probing electrons (τᵣ = 0 ps). Because the dynamic PINEM change has a picosecond rise time, energy absorbed from P₁ cannot contribute to the observed specimen response; therefore this energy is not included in the fluence calculation.

To interpret the behavior observed, we consider the nature and distribution of energy deposited in the specimen by our femtosecond optical pulse. For a thick absorbing medium, the light intensity attenuates exponentially with penetration depth x, depositing an energy per unit volume of

$$\Delta H(x) = F₀(1 - R)α \exp(-xα),$$

where F₀ is the excitation fluence, and R and α are the reflectivity and the absorbance, respectively. Previous studies have reported a range of values of the absorbance of the monoclinic phase of VO₂ at 519 nm (38–41) in most cases for polycrystalline specimens and without specification of the polarization dependence. These values are generally consistent with the range of α reported in the study of Verleur et al. (42) on polarization dependence of absorbance in a bulk specimen with oriented domains. There, the maximum value found was 1.31 × 10⁵ cm⁻¹ or 1/α = 76 nm (derived from ε = 9.11 + 3.33 i), for polarization parallel to the monoclinic crystal axis aᵣ (≈cᵣ, of rutile phase). For an assumed average nanoparticle thickness of ~200 nm and this value of α, the thick medium assumption is seen to be a good approximation, with only 5% transmission through a 200-nm particle on graphene. This maximum absorbance will apply to a fraction of the randomly oriented nanocrystals of our specimen that have a favorable orientation relative to our pump beam polarization.

In the thick specimen limit, the reflectance at normal incidence at the vacuum-VO₂ interface derived from the above optical constants is 0.272. With these values, ΔHₑ(x) for a fluence of 2 mJ/cm² attains a maximum value of 190 J/cm³ at the upper surface of the nanoparticle (x = 0). The values of heat capacity (Cᵥ), of 0.656 J/(g K) (22) and density (ρₐ) of 4.65 g/cm³ (43) of the monoclinic phase show that an energy of 3.05 J/(cm³ K) × 40 K = 122 J/cm³ is required to raise VO₂ from room temperature to the transition temperature of 340 K (21). In addition, latent heat of 237 J/cm³ (22) is needed to complete the thermal transformation. Thus, the calculated energy absorbed for excitation at 2 mJ/cm² is far below that required for any part of the VO₂ nanoparticle specimen to experience a thermodynamically stable transition to rutile phase, even the hottest surface layer. Moreover, Eq. 1 shows that the initial energy density drops by a factor of more than 10 through the specimen, so that, at 5 mJ/cm², the required thermal transformation energy threshold of 359 J/cm³ is reached only in a 30-nm surface layer of the most strongly absorbing nanocrystals. Heat diffusion calculations for the very low heat conductivity of VO₂ [κ = 3.5 W/(m K) to ~5.6 W/(m K) for monoclinic and rutile VO₂, respectively (44)] show that over the first few hundred picosecond time range of interest, there is only a noticeable cooling at the upper surface, without significant increase in the low temperatures in the particle interior. Therefore, we conclude that the changes in PINEM due to phase transition that we observe starting at fluence around 2 mJ/cm² (Fig. 4 in the main text) are induced by optical excitation of carriers and are not associated with a thermal phase transition or thermal equilibration.

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Fig. S1. VO₂ specimen. (A) BF (particles are shown as dark contrast) and (B) PINEM image of VO₂ nanoparticle sample under investigation. The PINEM electron counts are marked according to the scale shown, with yellow being the highest.

Fig. S2. (A) UEM diffraction pattern at $\tau_2 = -50$ ps for VO₂ specimen showing the Bragg spots assigned to the graphene substrate connected with dashed yellow line. (B) Tracing the change in intensity of the Bragg spot 5 in the electron diffraction pattern in Fig. 4 B and C in the main text as a function of the second (pump) pulse delay ($\tau_2$).