Electronic Supplementary Information

Two-component polymers embedded with tungsten oxide nanoparticles toward broadband and nonvolatile photomemory

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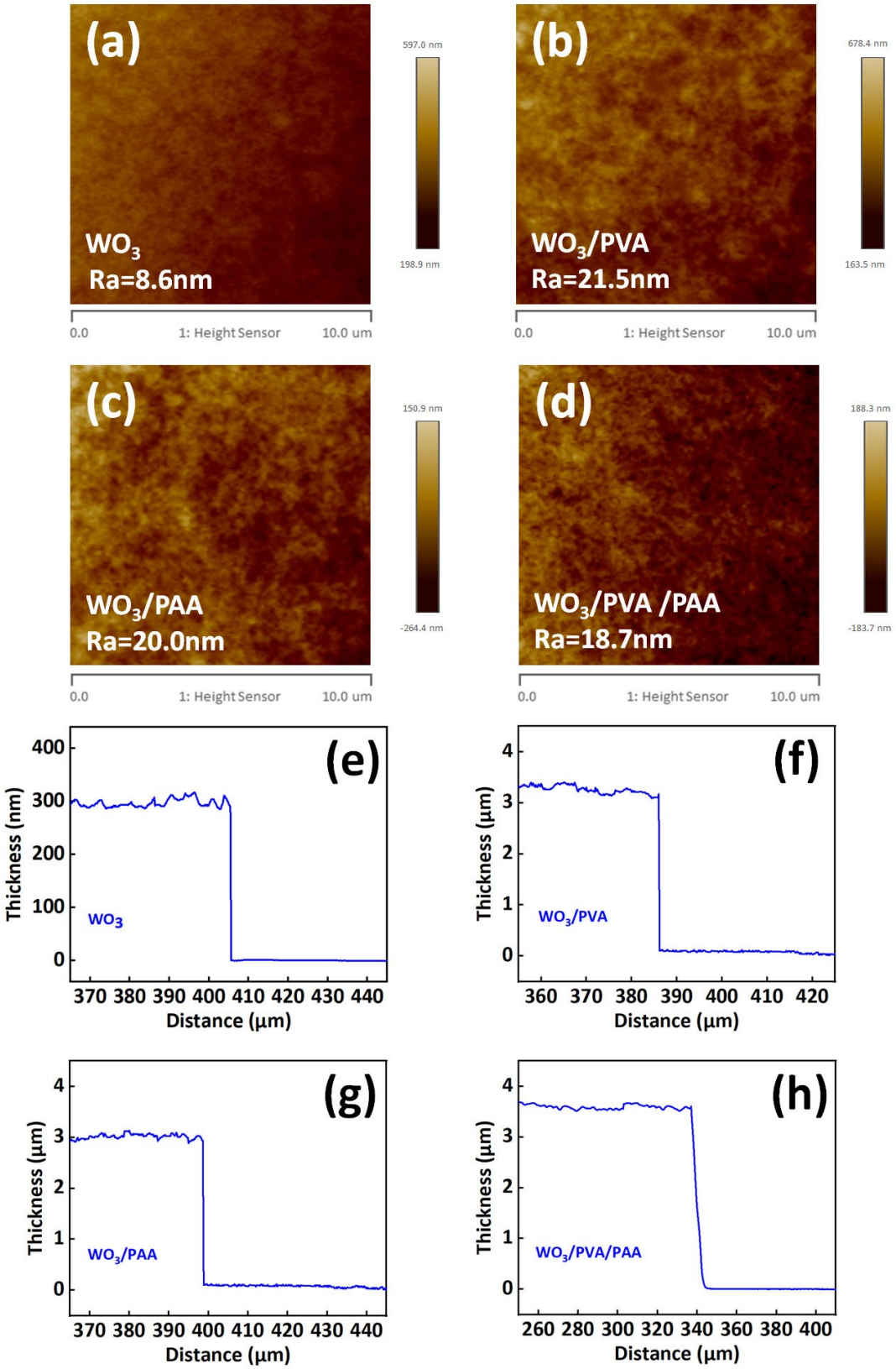

Figure S1. Surface flatness observed by AFM on (a) WO_3, (b) WO_3/PVA, (c) WO_3/PAA and (d) WO_3/PVA/PAA films. Thickness of (e) pure WO_3, (f) WO_3/PVA, (g) WO_3/PAA and (h) WO_3/PVA/PAA films determined by a probe optical profile-meter.

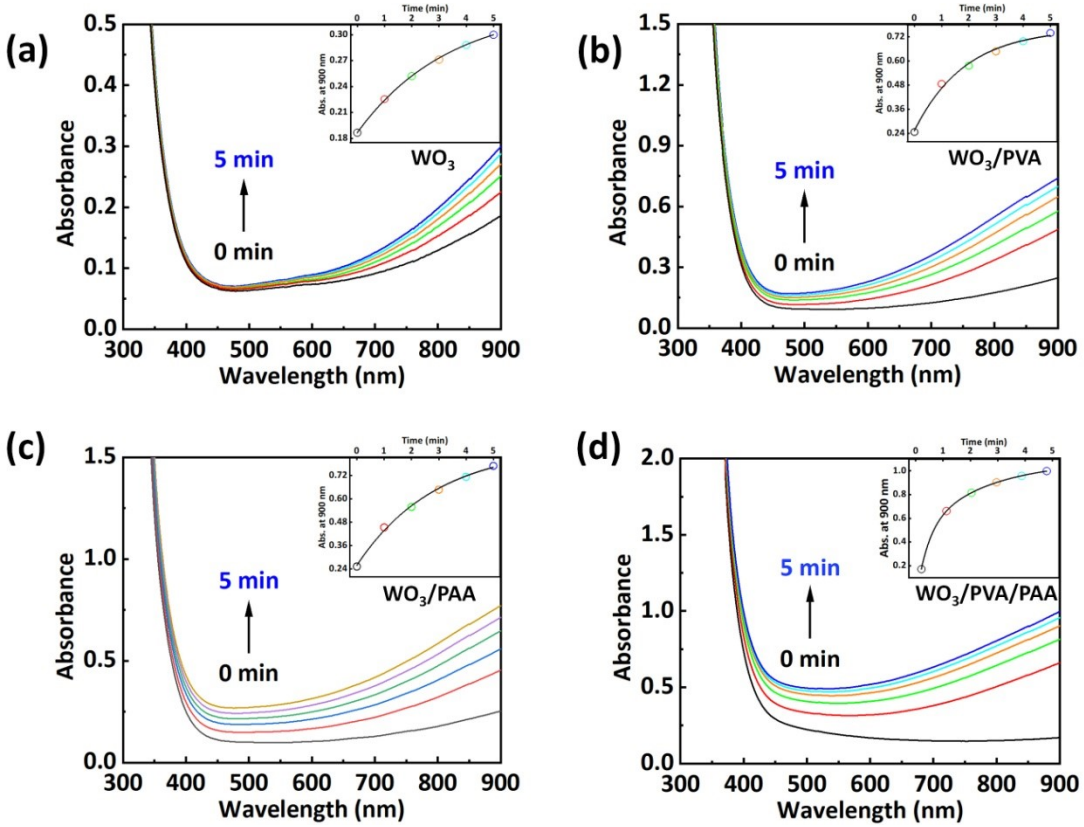

Figure S2. Absorption spectra of (a) WO_3, (b) WO_3/PVA, (c) WO_3/PAA and (d) WO_3/PVA/PAA films irradiated by blue-violet light. The insets show temporal evolution of absorbance at 900 nm and the corresponding theoretical fitting.

In-situ absorption spectra of the four kinds of nanocomposite films were measured under monochromatic irradiation. Absorption spectral curves at different irradiation times under blue-violet excitation for WO_3, WO_3/PVA, WO_3/PAA and WO_3/PVA/PAA films were obtained as shown in Figures S2. The absorbance of the four kinds of films increases gradually in the spectral range of 300-900 nm, and the color of the sample changes from colorless to blue. Temporal evolution of absorbance for WO_3, WO_3/PVA, WO_3/PAA and WO_3/PVA/PAA films was compared. Theoretical fitting to the absorbance at 900 nm with different irradiation times can be expressed as follows:

$$A(t) = [A(\infty) - A(0)] \cdot [1 - \exp(-kt)] + A(0) \quad \text{(S1)}$$

, where $A(t)$ is the absorbance at 900 nm versus time, $A(0)$ and $A(\infty)$ are the absorbance at t=0 and t=∞, respectively, k is the coloring rate constant. The theoretical fitting curves are shown in the insets of Figure S2 (solid lines). Here, k_{WO_3}=0.0049 s^{-1}, $k_{WO_3/PVA}$=0.0053 s^{-1}, $k_{WO_3/PAA}$=0.0073 s^{-1} and $k_{WO_3/PVA/PAA}$=0.11 s^{-1} were obtained. After introduction of PVA and PAA, the photo-response-time was shortened and the coloring process became faster.

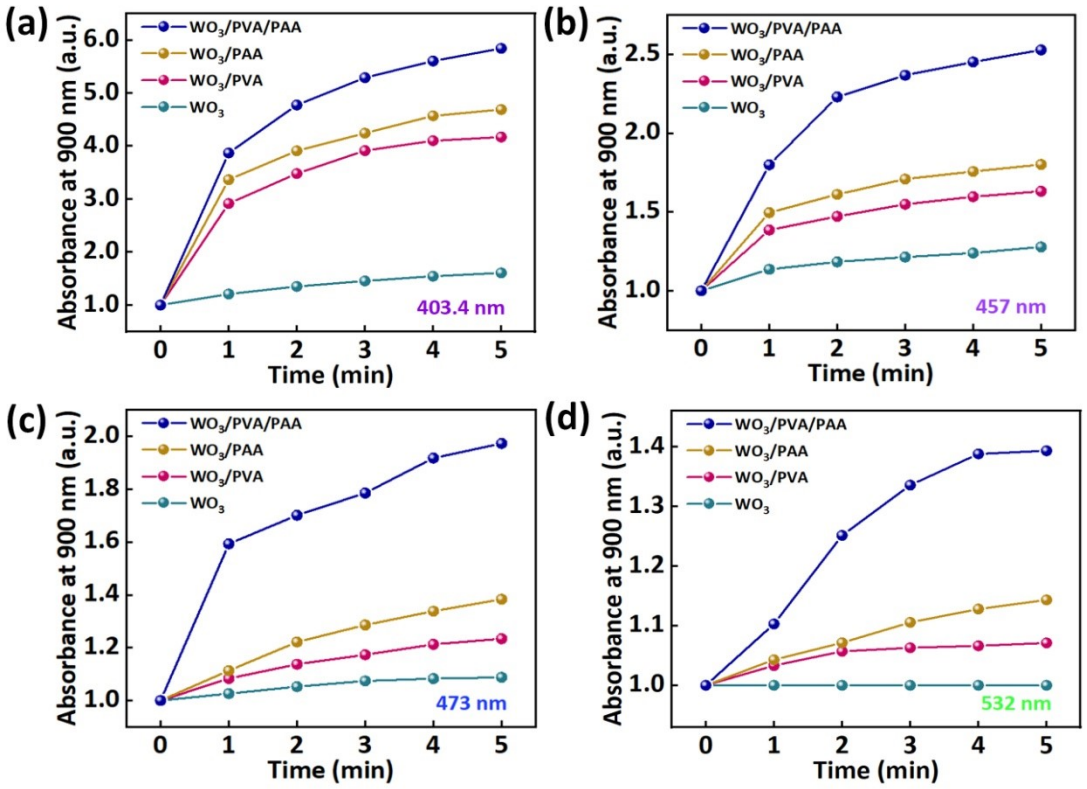

Figure S3. Absorbance at 900 nm versus irradiation time for WO_3, WO_3/PVA, WO_3/PAA and WO_3/PVA/PAA films with the exciting lights of (a) 403.4 nm, (b) 457 nm, (c) 473 nm and (d) 532 nm, respectively.

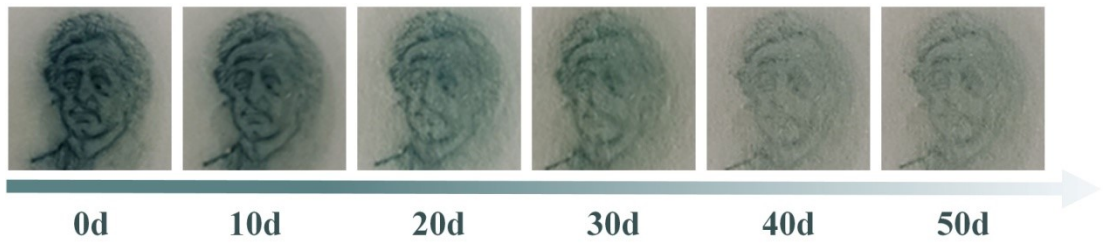

Figure S4. Long-term monitoring (0-50 day) of WO_3/PVA/PAA films loaded with optical information. The Einstein's image is optically printed by blue-violet light irradiation of 30 minutes.

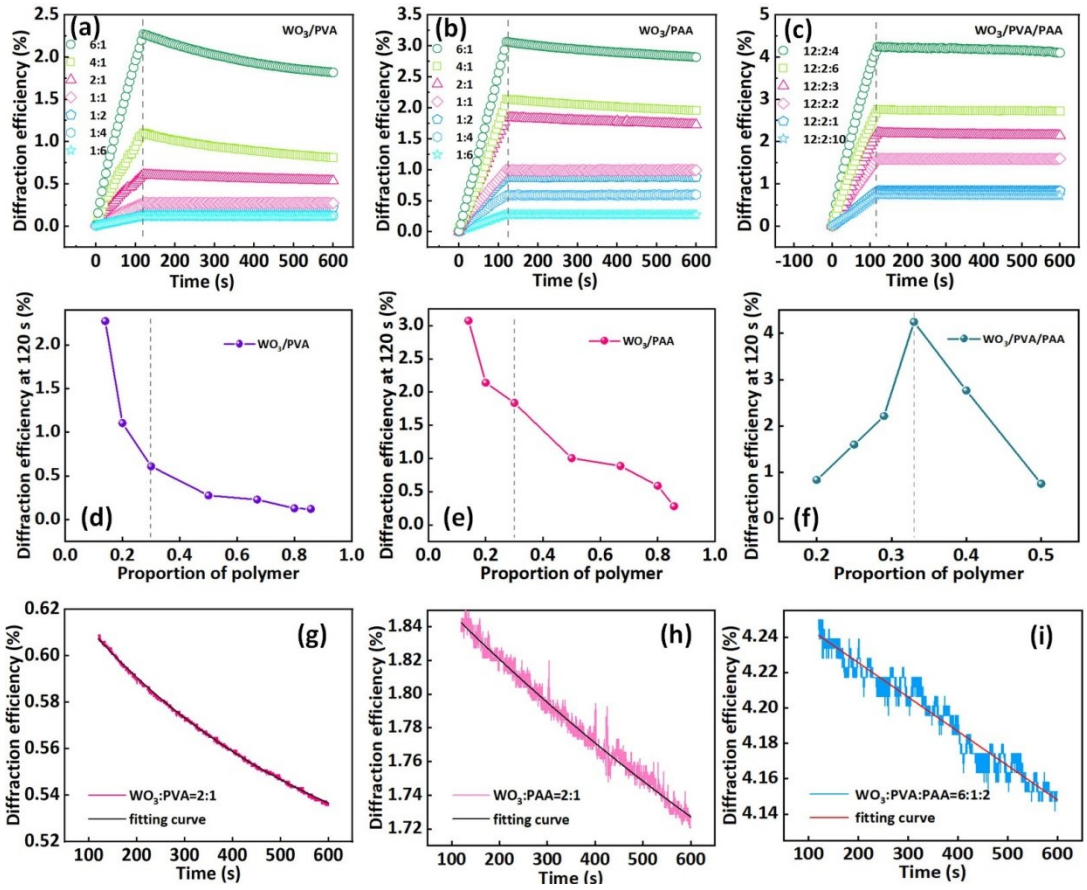

Figure S5. Diffraction efficiency versus time for (a) WO_3/PVA, (b) WO_3/PAA, and (c) WO_3/PVA/PAA films with different solution volume ratios. Diffraction efficiency at different proportions of polymer in (d) WO_3/PVA, (e) WO_3/PAA, and (f) WO_3/PVA/PAA films. For example, 0.33 on horizontal axis means that when the volume ratio of WO_3 ink to polymer solution is 2:1, the proportion of polymer is defined as $1/(2+1)\approx0.33$. Decay of holographic kinetics from 120s to 600 s for three kinds of samples of (g) WO_3:PVA =2:1, (h) WO_3:PAA=2:1, and (i) WO_3:PVA:PAA=6:1:2.

We precisely adjusted the parameters and carried out experiments on the effect of sample mixture ratio on optical storage performance. Firstly, WO_3 is mixed with PVA and PAA according to different volume ratios, and the setting ratios are 1:6, 1:4, 1:2, 1:1, 2:1, 4:1 and 6:1, respectively. Figures S5 (a) and (b) show the holographic dynamic curves of WO_3/PVA and WO_3/PAA films with different volume ratios, respectively. Obviously, with the increase of WO_3 volume fraction, the diffraction efficiency of WO_3/PVA and WO_3/PAA films is significantly improved under the irradiation of coherent lights. However, when the volume ratio of WO_3 to PVA or to PAA reaches 4:1, the issue of destructive readout from 120 s to 600 s appears. This phenomenon is explained as the increase of WO_3 content leads to monomer aggregation, light scattering and the insufficient number of protons and electrons. It is difficult for WO_3 nanoparticles to undergo a spatially-modulated photochromic reaction in different regions of interference fringes. Next, setting WO_3/PVA mixed

solution with a volume ratio of 6:1 as the basic sample, different volumes of PAA are added to make the volume ratios 12:2:1, 12:2:2, 12:2:3, 12:2:4, 12:2:6 and 12:2:10, respectively. As shown in Figure S5(c), the readout stability of interference fringes is significantly improved after adding PAA to the WO_3/PVA mixed solution with a volume ratio of 6:1. However, when adding a small amount of PAA, the diffraction efficiency of WO_3/PVA/PAA is much lower than that without PAA, which may be caused by the decrease of actual volume fraction of WO_3. When the volume ratio of WO_3/PVA/PAA is 12:2:4 (i.e. 6:1:2), the diffraction efficiency and readout stability of the hybrid film are both improved significantly. Then further adding PAA causes that the diffraction efficiency of WO_3/PVA/PAA hybrid film is weakened greatly. Therefore, we choose WO_3/PVA/PAA hybrid film with a ratio of 6:1:2 as the optimized recording medium of holographic grating.

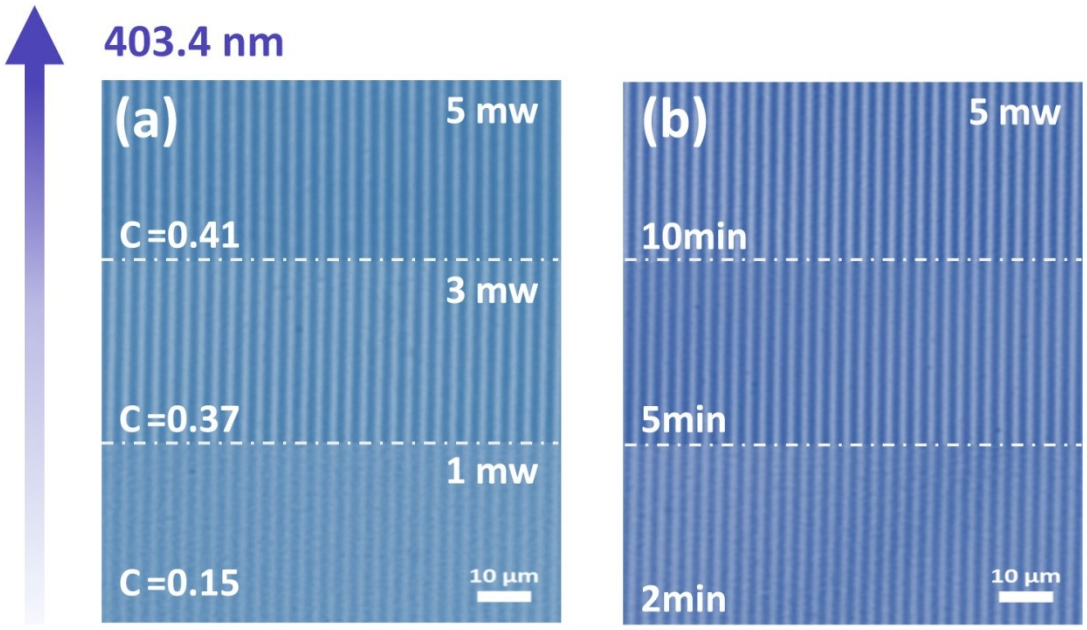

Figure S6. Polarized optical microscope image of holographic fringes in WO_3/PVA/PAA films at (a) different writing powers, and (b) different writing times.

Diffraction gratings were selectively recorded with two linearly *s*-polarized laser beams (403.4 nm, TOPTICA Photonics; 457 nm, 473 nm and 532 nm, Changchun New industries Optoelectronics Tech. Co. Ltd., respectively). The angle between the writing beams was fixed at 9°. Grating period was calculated according to the equation $\Lambda=\lambda/2\sin(\theta/2)$, where λ is the wavelength of writing beams. For example, $\Lambda=2.58$ μm for the holographic recording at 403.4 nm.

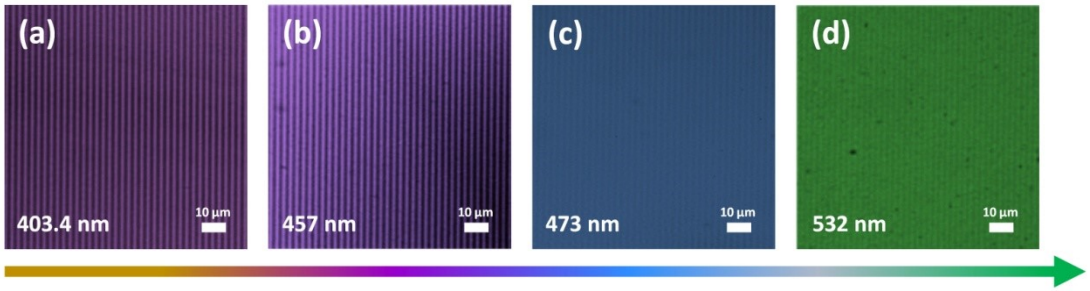

Figure S7. Holographic fringes formed in WO_3/PVA/PAA nanocomposite film under (a) 403.4 nm, (b) 457 nm, (c) 473 nm, and (d) 532 nm irradiations, respectively.

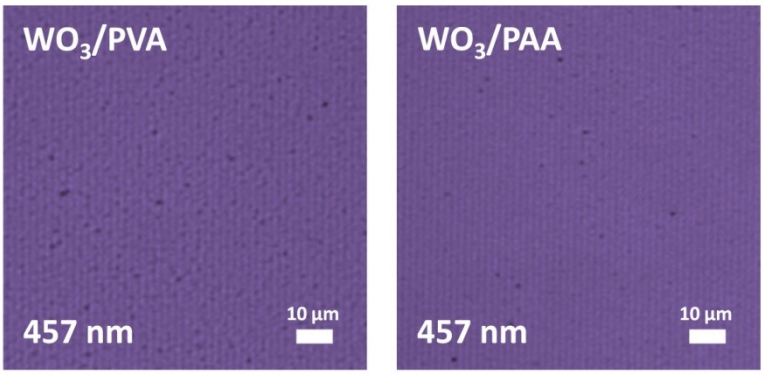

Figure S8. Holographic fringes formed in WO_3/PVA and WO_3/PAA nanocomposite films under the 457 nm irradiation.