

Electronic Supplementary Information

Synthesis and characterizations of Au nanorods, CsWO₃ and the composite/mixed fillers

Tungsten hexachloride (WCl₆), cesium hydroxide monohydrate (CsOH.H₂O), gold (III) chloride trihydrate (HAuCl₄.3H₂O), sodium borohydride (NaBH₄), and cetyltrimethylammonium bromide (CTAB) were supplied from Sigma-Aldrich Pty Ltd. Silver nitrate (AgNO₃), was purchased from Merck Co.Ltd.. Ascorbic acid was obtained from Tokyo Chemical Industry Co. Ltd. All these chemicals were analytical grade and used as received.

Synthesis of gold nanorods (Au_{NR})

Au nanorods were synthesized via a seed-mediated growth method.¹ The seed solution was firstly prepared by dissolving 0.01 M of HAuCl₄ in of CTAB solution (0.1 M) with gently stirring for 5 min. Then, an ice-cold solution of NaBH₄ (0.01 M) was added and the mixture was vigorously stirred for another 2 min. At this stage, change in color of the solution from yellow to brownish shall be noticed. The CTAB-stabilized seed solution was left at room temperature for 2 h without stirring. Next, the growth solution was prepared by mixing CTAB (0.1 M) with AgNO₃ (0.006 M) and HAuCl₄ (0.01 M) in an aqueous solution of hydrochloric acid (1.0 M) under a gentle stirring. Next, of an aqueous solution of ascorbic acid (0.1 M) was added dropwise, followed by addition of the CTAB-stabilized seed solution (10 μl). The whole mixture was gently stirred for another 10 sec and then left standing at room temperature for 18 h. The product was isolated by centrifugal and then washed with DI water to remove some excess CTAB. Finally, the obtained product was added to 5 ml of DI water and the suspension was kept at room temperature before use.

Synthesis of cesium tungsten oxide (CsWO₃) particles

In this study, the CsWO₃ particles were synthesized via a water-controlled release solvothermal process.² In a typical process, 1.0 mmol of WCl₆ powder and 0.5 mmol of CsOH.H₂O powder was dissolved in 40 ml of absolute ethanol under stirring. Next, 10 ml of acetic acid was added. The mixture (50 ml) was transferred into a Teflon-lined autoclave, and then heated at 240 °C for 20 h. The obtain product was centrifuged and washed several times with DI water and ethanol. Finally, the cleaned product was dried at 60 °C for 12 h.

Characterizations

The X-ray diffraction patterns of ATO, Au_{NR}, CsWO₃, Au_{NR}+CsWO₃ and Au_{NR}@CsWO₃ particles were examined by using a Bruker D8 Advance X-ray

diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ ranging from 20° - 90° . The crystallite size was also calculated by using the Scherrer's equation;

$$D=0.9\lambda/\beta\cos\theta$$

where D is the crystal size (nm)

λ is the X-ray wavelength (CuK $\alpha = 0.15406 \text{ nm}$)

β is the Line broadening (full width) at half maximum of the peak (radians)

θ is the Bragg angle ($^\circ$)

Morphological characterization of Au_{NR}, CsWO₃ and nanocomposites were analyzed by transmission electron microscopy (Thermo scientific, Talos) with an EDS attachment. TEM specimens were prepared by dropping an aqueous particle solution on a carbon-coated copper grid and then evaporating the solution at room temperature.

Length, diameter and L/D ratio of the fillers were evaluated by using SEM images with the ImageJ software (version 1.53V). In addition, the standard deviation values were determined by the following equation;

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n}}$$

Where x_i = individual sample value

\bar{x} = sample average

n = total number of sample

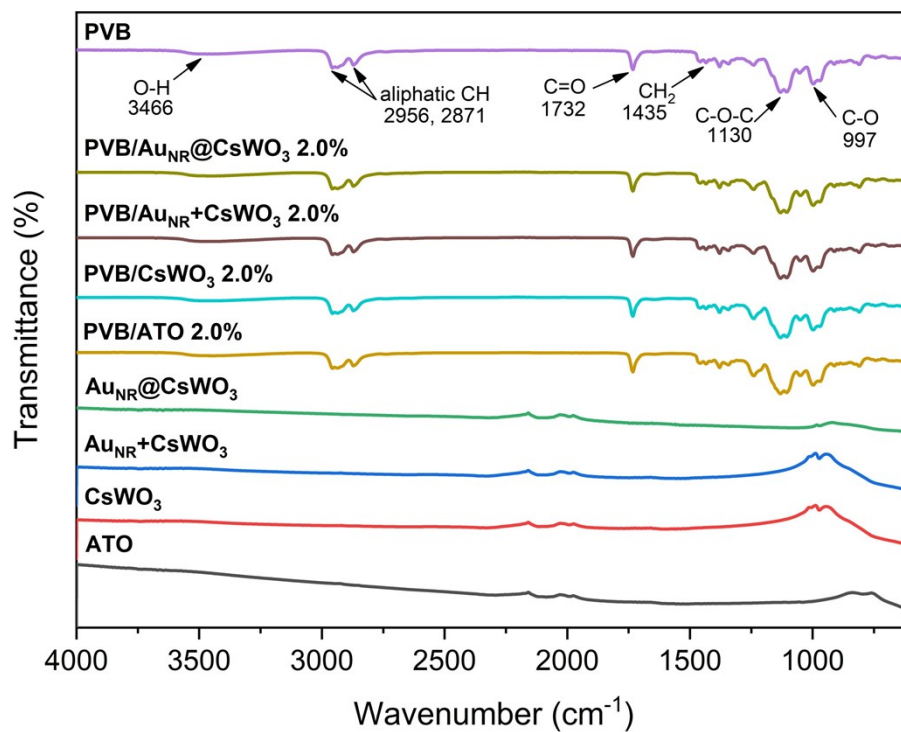


Fig. S1 FTIR spectra of PVB film.

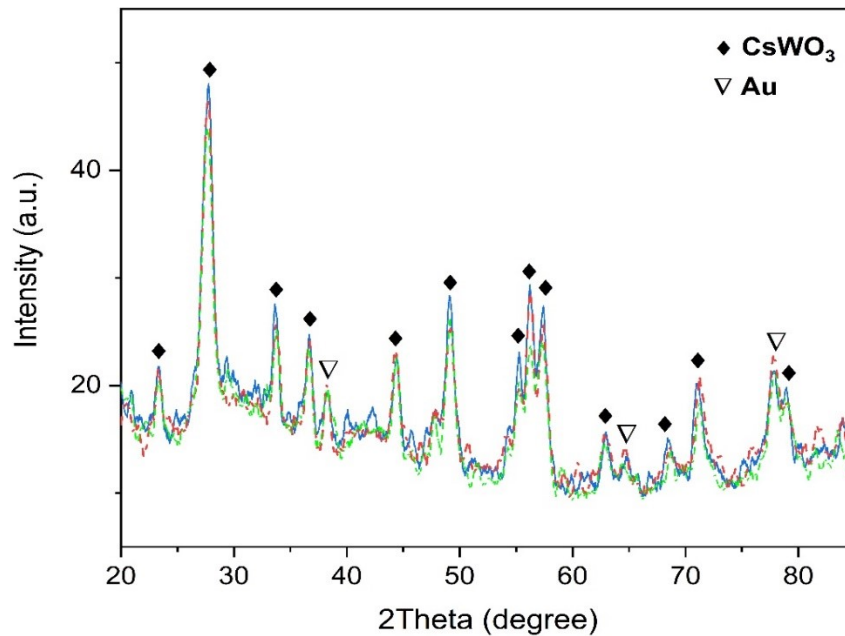


Fig. S2 Overlaid XRD patterns obtained by randomly sampling of the type-1 composite filler ($\text{Au}_{\text{NR}}+\text{CsWO}_3$).

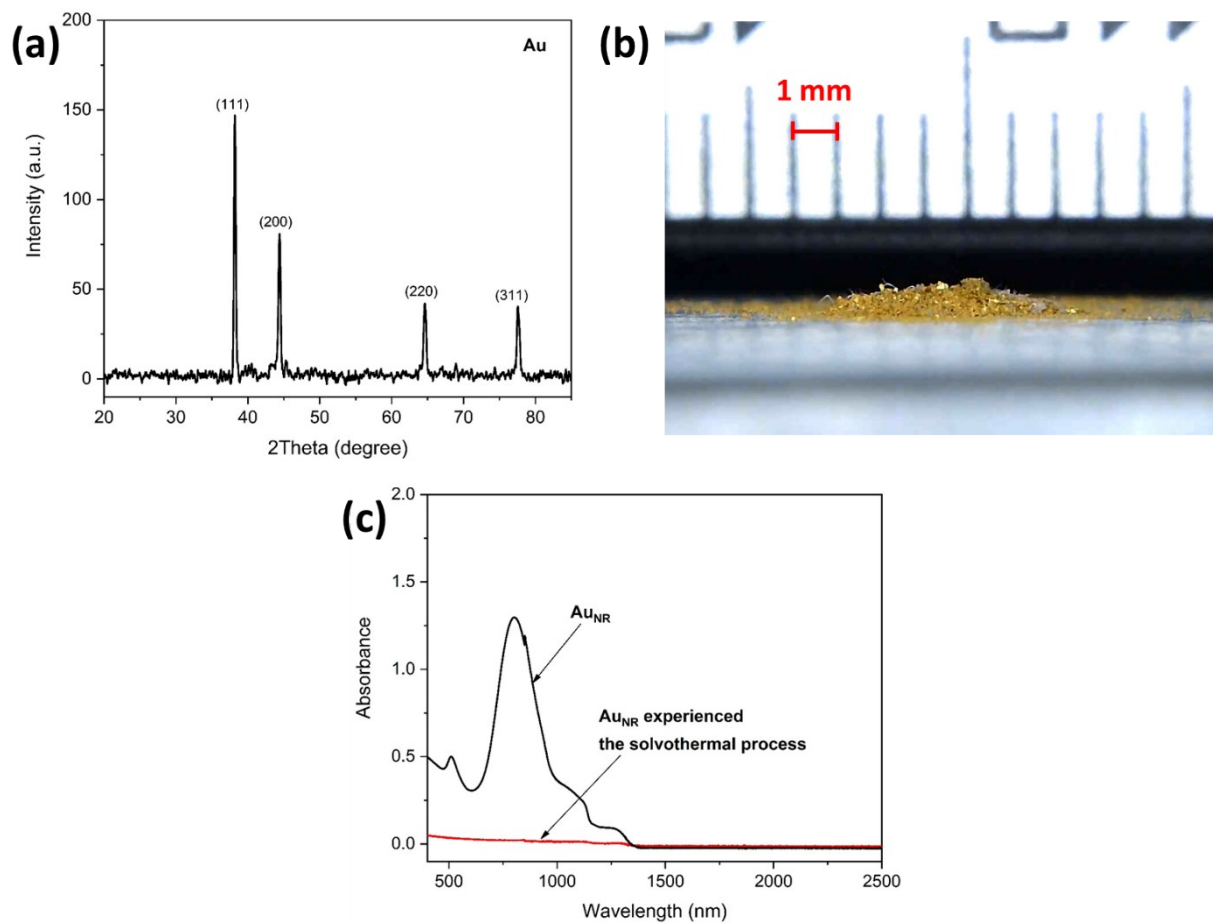


Fig. S3 (a) XRD pattern, (b) Microscope image and (c) UV/Vis/NIR spectrum of Au nanorods experienced the solvothermal process.

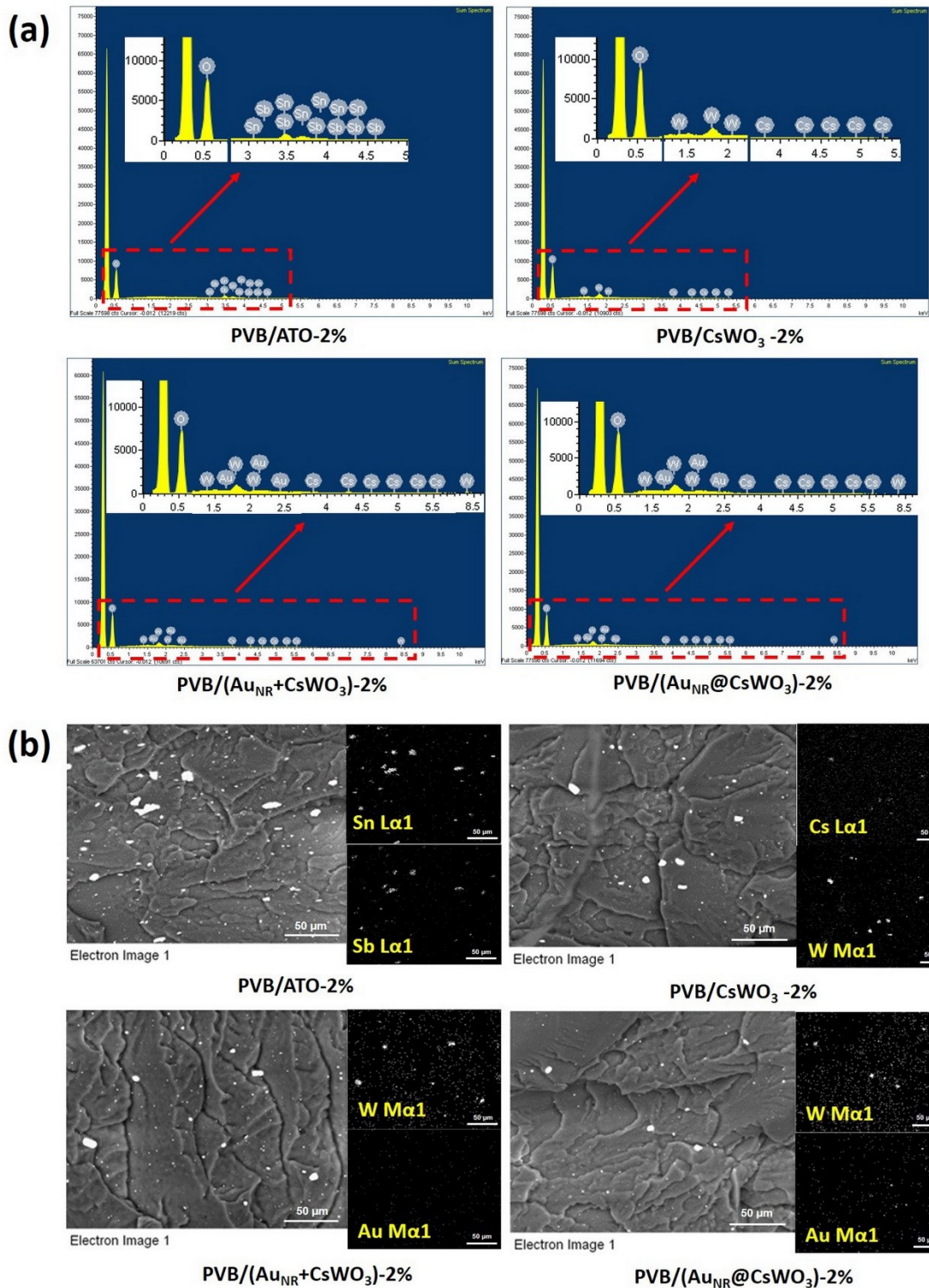


Fig. S4 (a) EDX patterns and (b) SEM images and EDX dot maps of PVB composite films load with 2.0 wt% of the different types of fillers.

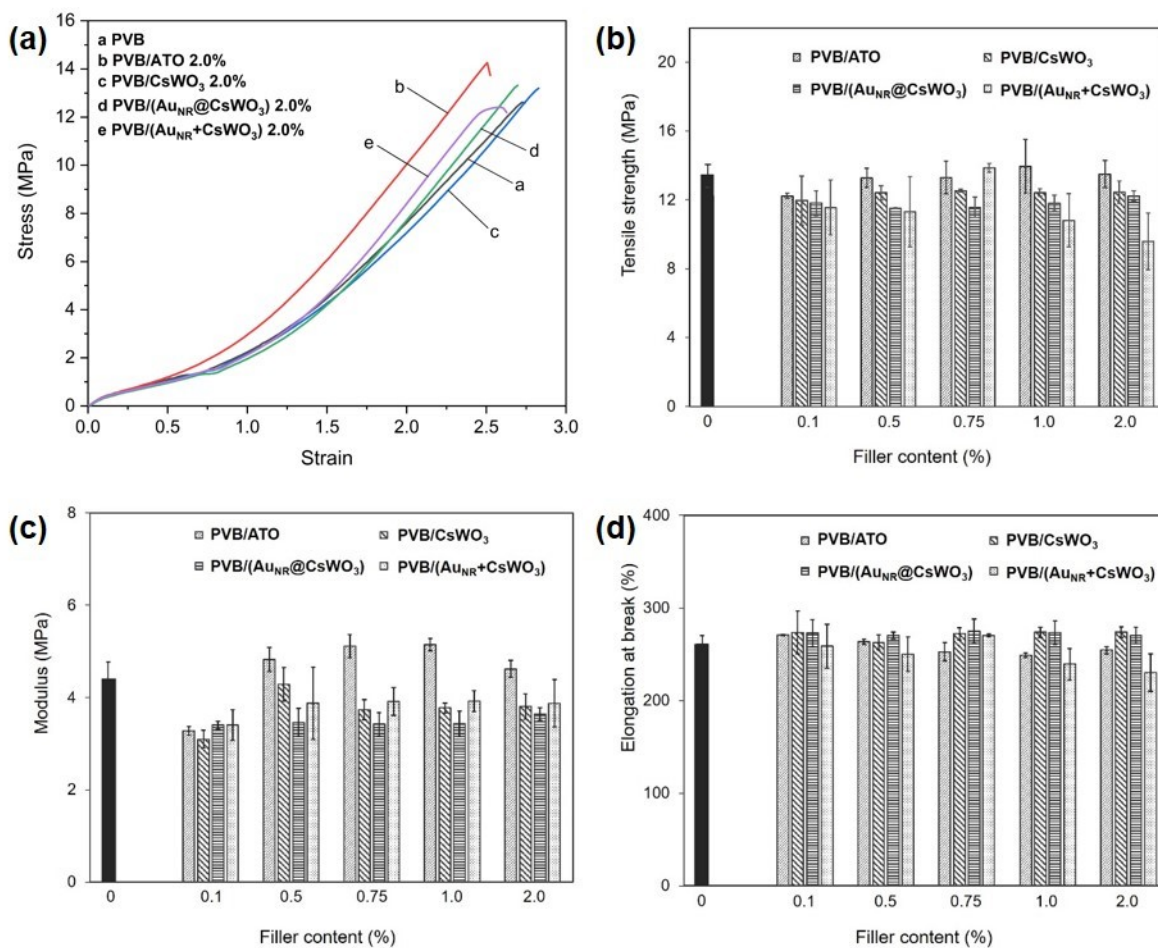


Fig. S5 (a) Overlaid stress-strain curves of PVB films loaded with 2.0 wt% of different fillers. (b) Tensile strength, (c) modulus, (d) elongation of PVB films containing different types and concentration of fillers.

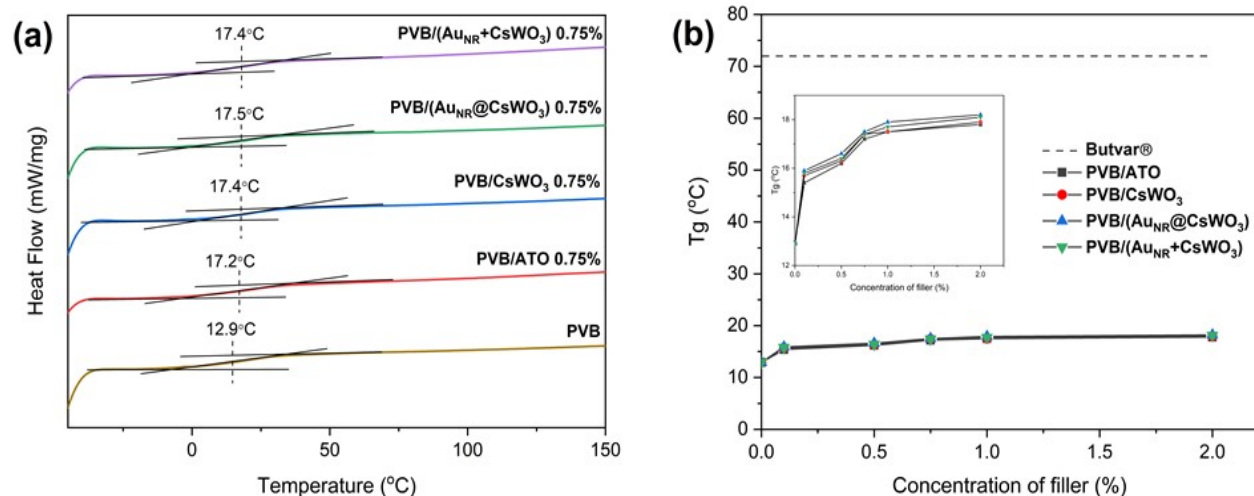


Fig. S6 (a) DSC thermograms (the second heating run) of PVB films mixed with different types of filler (0.75 wt%). (b) Changes in T_g values of PVB composite films with percentage loading of the filler.

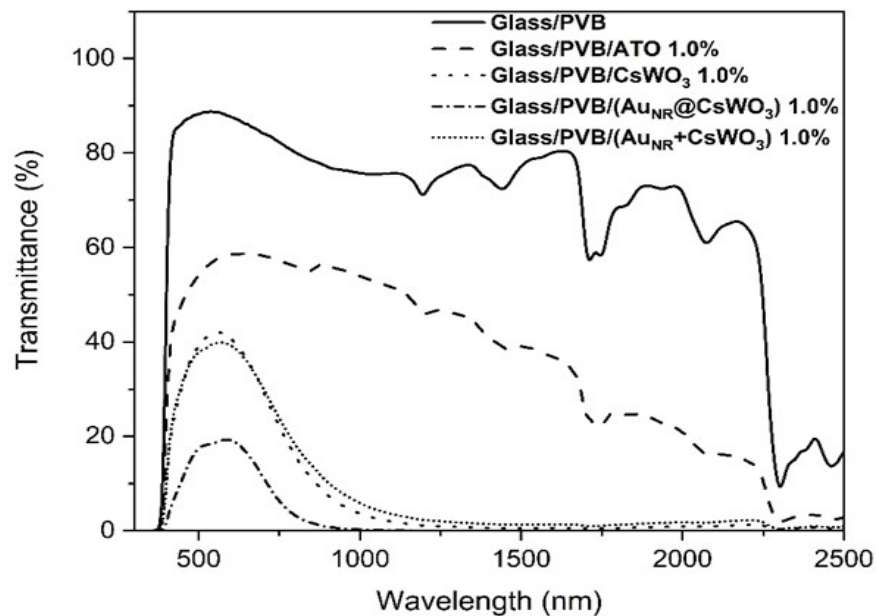


Fig. S7 UV/Vis/NIR spectra of the various glass/PVB laminates.

Table S1 Intensity data of Au_{NR}+CsWO₃ (Type 1) and Au_{NR}@CsWO₃ (Type 2)

Samples		<i>hkl</i>	2θ (degree)	Height (count)	Relative intensity (%)	
Au _{NR} +CsWO ₃ (Type 1)	CsWO ₃	002	23.6	56	14.4	
		200	27.7	390	100.0	
		112	34	45	11.5	
		202	36.7	48	12.3	
		212	44.4	31	7.9	
		220	49	44	11.3	
		204	55.8	19	4.9	
		312	56.3	35	9.0	
		400	57.6	25	6.4	
		224	71.3	11	2.8	
		420	79	13	3.3	
		Au _{NR}	111	38.2	12	3.1
			311	77.6	11	2.8
Au _{NR} @CsWO ₃ (Type 2)	CsWO ₃	002	23.6	189	31.4	
		200	27.7	602	100.0	
		112	34	134	22.3	
		202	36.7	202	33.6	
		212	44.4	72	12.0	
		220	49	124	20.6	
		204	55.8	62	10.3	
		312	56.3	96	15.9	
		400	57.6	110	18.3	
		224	71.3	57	9.5	
		420	79	40	6.6	
		Au _{NR}	111	38.2	45	7.5
			311	77.6	26	4.3

Table S2 Dimensions of the agglomerated particles

Samples	Dimensions		
	Length (μm)	Diameter (μm)	Aspect ratios (L/D)
PVB/ATO-2%	12.2 (± 4.7)	5.8 (± 1.6)	2.1 (± 0.7)
PVB/CsWO ₃ -2%	7.5 (± 1.4)	4.3 (± 1.2)	1.7 (± 0.5)
PVB/(Au _{NR} +CsWO ₃)-2%	9.5 (± 2.5)	5.2 (± 1.1)	1.8 (± 0.4)
PVB/Au _{NR} @CsWO ₃ -2%	6.9 (± 0.4)	4.2 (± 0.7)	1.6 (± 0.3)

Table S3 Cost analysis of the PVB/(Au_{NR}@CsWO₃) film compared with those of the commercial NIR shielding materials and the existing products.

Materials	Estimated Product Price	Optical properties	References
Au _{NR} @CsWO ₃	\$71.50 /g #	n/a	3-5
ATO	\$12.24 /g	n/a	6
PVB	\$ 6 /kg	n/a	7
PVB/(Au _{NR} @CsWO ₃) (0.05 wt% loading)	\$42.60 /kg	T _{NIR} = 55.33 %, T _{VIS} = 70.15 %	<i>This study,</i>
PVB/(Au _{NR} @CsWO ₃) (0.1 wt% loading)	\$78.36 /kg	T _{NIR} = 31.54 %, T _{VIS} = 57.38 %	<i>This study</i>
PVB/ATO (1.0 wt% loading)	\$129.12 /kg	T _{NIR} = 35.77 %, T _{VIS} = 30.73 %	<i>This study,</i>
PVB/ATO (untreated) (0.5 wt% loading)	n/a	T _{NIR} = 57 %, T _{VIS} = 68 %	8
PVB/ATO (silane treated) (0.5 wt% loading)	n/a	T _{NIR} = 47 %, T _{VIS} = 60 %	8
Coating based on a conductive metal oxide (APO)	\$524.88 /kg	NIR ray cut = 70% T _{Solar} = 68.6% T _{Vis} = 84.7%	9

based on prices of the precursors; HAuCl₄ (\$139.10 /g)³, CsOH (\$12.37/g)⁴, WCl₆ (\$3.66 /g)⁵

Table S4 Colorimetric parameters of various PVB composite films

Samples	L^*	a^*	b^*
Before exposure to the open air			
PVB/(Au _{NR} +CsWO ₃) 0.1%	87.22 ± 0.11	-1.66 ± 0.02	4.98 ± 0.02
PVB/(Au _{NR} +CsWO ₃) 0.5%	59.99 ± 0.15	-3.90 ± 0.02	10.86 ± 0.02
PVB/(Au _{NR} +CsWO ₃) 0.75%	56.51 ± 0.31	-4.28 ± 0.03	11.24 ± 0.10
PVB/(Au _{NR} +CsWO ₃) 1.0%	46.63 ± 0.15	-4.65 ± 0.01	11.69 ± 0.02
PVB/(Au _{NR} +CsWO ₃) 2.0%	22.19 ± 0.16	-4.38 ± 0.02	10.07 ± 0.04
After exposure to the open air			
PVB/(Au _{NR} @CsWO ₃) 0.1%	82.19 ± 0.18	-1.90 ± 0.02	6.30 ± 0.05
PVB/(Au _{NR} @CsWO ₃) 0.5%	51.50 ± 0.30	-4.41 ± 0.01	10.85 ± 0.06
PVB/(Au _{NR} @CsWO ₃) 0.75%	37.38 ± 0.24	-4.01 ± 0.04	10.43 ± 0.07
PVB/(Au _{NR} @CsWO ₃) 1.0%	27.27 ± 0.45	-3.92 ± 0.03	9.90 ± 0.09
PVB/(Au _{NR} @CsWO ₃) 2.0%	5.14 ± 0.12	-1.68 ± 0.07	3.96 ± 0.07
After exposure to the open air			
PVB/(Au _{NR} +CsWO ₃) 0.1%	87.25 ± 0.06	-1.69 ± 0.01	4.94 ± 0.04
PVB/(Au _{NR} +CsWO ₃) 0.5%	59.97 ± 0.10	-4.01 ± 0.03	10.78 ± 0.02
PVB/(Au _{NR} +CsWO ₃) 0.75%	56.39 ± 0.26	-4.41 ± 0.02	11.09 ± 0.02
PVB/(Au _{NR} +CsWO ₃) 1.0%	46.45 ± 0.05	-4.75 ± 0.03	11.55 ± 0.07
PVB/(Au _{NR} +CsWO ₃) 2.0%	21.83 ± 0.03	-4.50 ± 0.02	9.92 ± 0.04
PVB/(Au _{NR} @CsWO ₃) 0.1%	82.11 ± 0.18	-1.88 ± 0.01	6.24 ± 0.07
PVB/(Au _{NR} @CsWO ₃) 0.5%	51.21 ± 0.05	-4.47 ± 0.00	10.73 ± 0.03
PVB/(Au _{NR} @CsWO ₃) 0.75%	36.73 ± 0.23	-4.06 ± 0.03	10.40 ± 0.06
PVB/(Au _{NR} @CsWO ₃) 1.0%	26.7 ± 0.23	-4.06 ± 0.06	9.74 ± 0.02
PVB/(Au _{NR} @CsWO ₃) 2.0%	4.96 ± 0.13	-1.69 ± 0.04	3.81 ± 0.09

References

- 1 N. R. Jana, L. Gearheart and C. J. Murphy, *J. Phys. Chem. B*, 2001, **105**, 4065-4067.
 - 2 C. Guo, S. Yin, M. Yan and T. Sato, *J. Mater. Chem.*, 2011, **21**, 5099-5105.
 - 3 <https://www.sigmaaldrich.com/TH/en/product/aldrich/520918>, (accessed July 2023).
 - 4 <https://www.sigmaaldrich.com/TH/en/product/aldrich/516988>, (accessed July 2023).
 - 5 <https://www.sigmaaldrich.com/TH/en/product/aldrich/241911>, (accessed July 2023).
 - 6 <https://www.sigmaaldrich.com/TH/en/product/aldrich/549541>, (accessed July 2023).
 - 7 https://www.alibaba.com/product-detail/Manufacturers-Polyvinyl-Butyral-Pvb-Powder-Chemicals_1600332940238.html?s=p, (accessed July 2023).
 - 8 S. Pizzanelli, C. Forte, S. Bronco, T. Guazzini, C. Serraglini and L. Calucci, *Coatings*, 2019, **9**, 247.
 - 9 <https://www.zauba.com/import-fumin+coating-hs-code.html>, (accessed July 2023).
-