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Supporting Information

Spectrally Tunable Nanocomposite Metamaterial as Near-perfect Emitters for Mid-

infrared Thermal Radiation Management

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S1. Experimental section

AZO Nanoparticles Synthesis.^[1] All chemicals were used without further purification. Zinc acetate dihydrate $(Zn(CH_3COO)_2 \cdot 2H_2O)$, Aluminium nitrate nonahydrate $(Al(NO_3)_3 \cdot 9H_2O)$, (3-Glycidyloxypropyl)trimethoxy silane (KH-560), Ethyl cellulose (EC) and Hydroxypropyl methylcellulose (HPMC) were supplied by Sigma-Aldrich Corporation. 4.39 g of $Zn(CH_3COO)_2 \cdot 2H_2O$ and 0.15 g of $Al(NO_3)_3 \cdot 9H_2O$ were mixed with 60 ml of ethanol, and 1.6 g NaOH was dissolved in 65 ml of ethanol. Then NaOH solution was slowly added to the mixed solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$. After the above solution was fully reacted at 60 °C, 0.324 g of modifier KH-560 was added for continuous modification over two hours, maintaining a reaction temperature of 60 °C. Finally, the reaction precipitate was washed 4-6 times with deionizes water and ethanol, and the dried to obtain the AZO nanoparticle powder.

Absorber Fabrication. The nanocomposite structures were fabricated by spin-coating on the reflecting aluminum substrates that were deposited via sputtering on silicon wafers. The slurry of the dielectric layer was composed of Al_2O_3 powder, HPMC and deionizes water. The slurry of the AZO layer was made of AZO powder, EC and ethanol. Al_2O_3 powder was purchased from Strem Chemicals, and AZO powder was synthesized by the aforementioned method. Thin films were prepared by spin-coating these slurries at 1000-4000 rmp for 30 s and dried on a hot stage at 100 °C for 10 min.

Characterization techniques. The optical absorption spectra of the broadband absorber were measured using a Lamda 950 UV/ VIS/ NIR Spectrophotometer in the 300-3000 nm range. The infrared spectral reflectivity measurement was performed using a Microscopes Fourier Transform Infrared Spectrometer (NicoletiN10 MX) over a spectral range of 3-14um. XRD measurement was carried out by a Bruker D8 diffractometer equipped with Cu Kα radiation source at 40 mV and 40 mA. Transmission electron microscopy (TEM) images were collected using a JEM-2100F microscopy operating at 200 KV, and the scanning electron

microscope (SEM) images were taken using a S-4800 microscope. The surface roughness of the absorbers was measured with a VARTAN model 3100 atomic force microscope (AFM). Thermal imaging camera was used to collect the infrared thermal images operating in windows of 8-14 um (FLIR T420).

Numerical simulation. The simulated spectra and electromagnetic field distribution of nanocomposite structures were calculated by finite-difference time-domain (FDTD) method, on the software OptiFDTD. All of the simulations were performed in three-dimensional layouts, with plane waves propagating along -z direction and power monitors collecting the reflective light energy. A unit cell of nanocomposite absorber is covered by periodic boundary conditions along x and y axes, and 32 perfectly matched layers (PML) along z axis. The specific simulations parameters are shown in Table S1.

Performance measurements. The radiative cooling performance of selective absorber is tested using the setup presented in Figure S13.^[2] Since the selective absorber has a low emissivity in the atmospheric window band, and the temperature reduction is achieved by heat exchange with the surrounding air through a 5-8 um non-atmospheric window, the cooling test is carried out in an indoor environment. The sample is placed on a hot stage kept at a constant temperature, and the temperature on the sample is recorded over a certain period of time by a thermocouple. For broadband absorber, the overall design of thermal measurement apparatus is shown in Figure S14.^[3] The low-density polyethylene (PE) film working as a wind shield to reduce both convection and conduction to the broadband absorber under solar irradiation. The wooden frame is covered by Aluminum foil that reflected the sunlight to prevent heating of it. Absorbers are placed on a polystyrene block that is wrapped by Al foil, and they are supported by a clear acrylic box. This real-time, continuous radiative cooling measurement was carried out over a series of hours on a cloudless day around solar noon, and we recorded the surface temperatures of absorber and reference using the thermocouple.

S2. Imaginary part selection method supplement



Figure S1. Absorbance map of nanocomposite structure at different wavelengths (from 3 µm to 20 µm).

Absorption (ε_{top}) maps at different wavelengths (Figure S1) are calculated in order to obtain the relationship between ε_{perf} and wavelength. The results show that both the real and imaginary parts of ε_{perf} increase monotonically with the wavelength.



Figure S2. a,b) Real part of perfect-absorbance permittivity (ε_{perf}), AZO nanocomposite permittivity (ε_{NPs}) and AZO slab permittivity (ε_{slab}) as a function of wavelength.

Real part of perfect absorbance (Im(ε_{perf})) at different wavelengths were calculated, and the result is the red region shown in Figure S2a. As a result, there is a big gap between Re(ε_{perf}) and Re(ε_{top}).



S3. Effect of nanocomposite layer parameters on absorbance

Figure S3. a-c) Calculated effective permittivity spectrum maps of AZO nanocomposite at different matrixes (ϵ_0), AZO carrier concentrations (Nh) and filling factors (FF). Here, h = d = 1 μ m, and ϵ_{dielec} = 2.67.

The effects of these three parameters on $\text{Re}(\varepsilon_{\text{top}})$ are shown in Figure S3a-c. It can be seen from the figures that the real part has no decisive effect on absorption.



Figure S4. a) Real (dash line) and imaginary (solid line) parts of effective permittivity (ɛtop) as a function of wavelength with different filling factors (i.e., larger than, equal to, and smaller than the percolation threshold).b) Calculated absorptance spectrum at different filling factors.

To further illustrate the effect of percolation threshold on absorptance, we selected three cases where the volume fraction is less than the threshold (0.1), equal to the threshold (0.33) and greater than the threshold (0.6), and calculated Im[ɛtop], Re[ɛtop] and total absorptance in these cases, as presented in Fig. S4(a, b). When the filling factor is close to fperc, the average

absorptance is larger than 80% from 5 μ m to 20 μ m; on the contrary, when the filling factor is far away from fperc, the absorptance becomes considerably narrower and lower. It is noticed that there is still considerable discrepancy between Re[ϵ_{top}] and Re[ϵ_{perf}] at the fperc.

Figure S5. a-f) Calculated imaginary part of perfect-absorbance permittivity ($Im(\epsilon_{perf})$) as a function of three parameters at different wavelengths.

We separately calculated the parameter range when the $Im(\varepsilon_{top}) = Im(\varepsilon_{perf})at$ different wavelength, and the results are shown in FigureS5.

S4. Summary of relevant simulations parameters

Parameter	Value
FDTD-simulation region	$1 \ \mu m \times 1 \ \mu m \times 17 \ \mu m$
Boundary conditions	Bloch in X- and Y- direction
	Perfect matching layer PML with 32
	layers in Z-directions

Table S1. Summary of relevant simulations parameters^[4]

Minimum mesh size	1nm
Source	Linear polarized light in the X-Z-plane
Frequency domain power monitors	Transmission is recorded at $z = -6 \ \mu m$
	Reflection is recorded at $z = 6 \ \mu m$
Early shutoff	1E-6

Table 1 summarizes all relevant parameters that are used for simulations. The mesh's spatial resolution is set to 1 nm in and around the spheres. This high resolution was selected to assure good convergence of the solution.

S5. Simulation results of absorption spectra with diverse structural parameters

Figure S6. a-f) Simulated absorptivity of absorber as a function of the volume fraction of AZO nanoparticles (v), free-carrier density of AZO nanoparticles (Nh), the thickness of top layer (h) and dielectric layer (d), electric permittivity of dielectric (ϵ_3), and angle of incidence (θ).

In order to verify the accuracy of the results shown in Figure 3a, we simulated the corresponding absorption spectra of absorbers with different parameters (Figure S6a-f) using FDTD solutions under the same conditions as in Figure 3a. Although the calculation and simulation process are based on different theories, the simulation results are in good agreement with the calculation results.

S6. Thicknesses of the dielectrics for selective absorbers

Figure S7. Simulated selective absorption spectra of ten absorbers with calculated thicknesses of dielectrics.

Dielectric material	Simulated thickness (um)	Calculated thickness (um)
Ge	0.37	0.45
Si	0.42	0.53
GaAs	0.45	0.57
ZnSe	0.64	0.78
ZnS	0.68	0.82
Si ₃ N ₄	0.70	0.85
TiO ₂	0.78	0.94

Table S2. Thicknesses of different dielectrics for selective absorber

AIN	0.80	1.08
ZnO	0.90	1.11
Al ₂ O ₃	1	1.2

Table 2 exhibits the simulated and calculated thicknesses of the dielectrics of selective absorber for selective absorption at 6.5 μ m. The calculated thicknesses of the dielectrics are larger than the simulated ones, which means a slight red-shift of the calculated absorption. This can be demonstrated by the simulated selective absorption of absorbers with calculated thicknesses of dielectrics (Figure S7). The absorption peaks are located at around 7.8 μ m, which is a 1.3 μ m-red-shift than the simulated thicknesses.

S7. Influence of the dispersion of dielectric materials on absorption

Figure S8. a, b) The calculation and simulation absorption spectra of selective and broadband absorber. The value of Al2O3 in calculation process is constant, and that in simulation process is dispersive.

S8. Characterizations of the AZO nanoparticles

Figure S9. a) Picture of dry powder of AZO. b) SEM image in top view of the deposited AZO films. c,d) TEM images of AZO nanoparticles. e,f) Element maps of the deposited AZO films.

Figure S10. XRD pattern of the dried powder of AZO.

Figure S11. a) FTIR spectrum of AZO nanoparticle films deposited on Si substrates.

Figure S9 shows the topographical features of the synthesized AZO. As shown in Figure S8a, the dried AZO powder was pale yellow. The XRD results shown in Figure S9 illustrates that AZO powder possesses the wurtzite ZnO phase (ICDD No. 16-1451) with no additional crystalline phases observe. Using the FTIR spectroscope, we evaluated the SPR feature of AZO nanoparticles, identifying broad plasmon peaks centered at about 7μ m (Figure S11a). Based on the modified Drude-Lorentz theory, the SPR frequency can be calculated using the following equation:^[5]

$$\omega^2 = \frac{Nh \cdot e^2}{m_e \cdot \varepsilon_0(\varepsilon_\infty + 2\varepsilon_m)} \tag{1}$$

where *Nh* is the free-carrier density of nanoparticles, *e* is the electron charge, m_e represents the effective mass of electron (0.24 times of the free electron mass), ε_0 , ε_∞ , ε_m are the permittivity of vacuum, high-frequency and of the surrounding medium. Based on this function, free electron concentrations of ~0.9 × 10²⁰ cm⁻³ is estimated for AZO.

S9. Characterizations of nanocomposite absorbers

Figure S12. a) AZO slurry for spin-coating and corresponding SEM image. b) Al₂O₃ slurry for spin-coating and corresponding SEM image.

Figure S13. a) Simulated absorptivity of selective absorber with different Al_2O_3 layer. b) Simulated absorptivity of broadband absorber with different Al_2O_3 layer.

In the preparation process, Al_2O_3 nanoparticles are prepared into dielectric layer by spincoating. While in the calculation, we regard the dielectric layer as a slab structure. To illustrate the difference between nanoparticle and slab structure of dielectric layer, we simulated the absorption spectra of selective and broadband absorbers with nanoparticle and slab dielectric layer. It can be seen from the results shown in Figure S13 that the influence on this difference is negligible. Figure S12a, b shows the photos of slurry of Al_2O_3 and AZO.

Figure S14. Characterizations of absorber. a, b) SEM images of AZO and Al₂O₃ nanoparticles. c) Atomic force microscopy (AFM) image of absorber fabricated by spin-coating. d, e) Histograms of Al₂O₃ and AZO size distribution evaluated from SEM images (Figure S14 a, b). f) Experimental absorptivity for normal incidence, normalized to the absorbers, for different thicknesses of dielectric layer (d) with the thickness of top layer (h) is 0.5 µm. Insert, simplified schematic of the structure model. g) Experimental absorptivity for normal incidence, normalized to the absorbers, for different thicknesses of top layer (h) with the thickness of dielectric layer (d) is 1.0 µm. Insert, simplified schematic of structure model.

After evaluating the underlying absorption mechanisms and tunability of the absorber, we now try to implement the concept experimentally using chemically synthesized 23.6 ± 3.0 nm AZO (Figure S14b, e) nanoparticles and commercial 24.9 ± 1.9 nm Al₂O₃ (Figure S14a,d) nanoparticles that are randomly arranged with controlled thickness above an aluminum film. The spacer layer and nanocomposite layer are both fabricated via spin-coating, and the serous fluid consists of solvent, nanoparticles, and binder. The solvent and binder for Al₂O₃ serous fluid are deionized water and hydroxypropyl methylcellulose (HPMC), and those for AZO serous fluid are ethanol and ethyl cellulose (EC). The purpose of this design is to prevent these two layers dissolving into each other during spin-coating. We note that that diffuse reflection (surface scattering) occurs when a beam of light hits a rough surface, which can be negligible as the roughness of the surface is much smaller than characterizing wavelength. The measured surface roughness (Figure S14c) of absorber here is 40.25nm, so the surface scattering effect is negligible. Absorption spectra generated from absorbers with various thicknesses of top layer (h) and dielectric layer (d) are exhibited in Figure S14f and g, which reveal the absorption tunability and agrees well with calculated results. It should be pointed out that the absorption difference between absorbers with nanoparticle and slab spacer layer is negligible, and the result are presented in Figure S13.

S10. Thermal measurement apparatuses

Figure S15. Schematic of the thermal measurement apparatus for selective absorber.

Figure S16. Schematic of the thermal measurement apparatus for broadband absorber.

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