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Largely lowered transition temperature of VO₂/carbon hybrid phase change material with high thermal emissivity switching ability and near infra-red regulations

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Abstract: Vanadium oxide (VO₂) as a phase changing material possesses abrupt infrared (IR) transmission and thermal emissivity changing during the metal-insulator transition (MIT) across transition temperature (τ_c) of 68 °C. However, the high τ_c , moderate IR transmission and emissivity regulating ability limits its applications in various fields. We report a VO₂/carbon hybrid phase change material fabricated via homemade plasma enhanced chemical vapor deposition (PECVD). The material shows a best reported thermal emissivity contrast (0.44) among the experimental value, a largely lowered τ_c (45 °C), promising near IR-regulation ability with enhanced photothermal effect in smart windows applications. The theoretical calculation results proved that the improvement of emissivity contrast is due to the hybridization of carbon. This work provides a new approach to synthesis VO₂ hybrid material which have wide application in camouflage, sensing and smart windows.

1. Introduction

VO₂ is a well-known phase change material because of its near room-temperature metal-insulator transition (MIT) at the transition temperature (τ_c) of 68 °C.^[1, 2] Accompanied with the phase changing, the crystal structure of VO₂ transfers between monoclinic [P2₁/c, namely VO₂(M)] and rutile [P4₂/mmm, namely VO₂(R)] together with abrupt changes of infra-red (IR) transmittance^[3] and emissivity.^[4] Above τ_c , the thermal emissivity at the region of 8-13 μ m (mid-IR, MIR) and near-IR (NIR) transmittance will decrease dramatically while maintaining the transmittance over the visible region.^[5] This makes VO₂ an ideal candidate for the applications of both MIR camouflages and NIR regulation devices.^[6-8]

Camouflages is the dream of human beings from ancient time. Inspired by chameleons and cephalopods, researchers invented several types of camouflages.^[9-11] However, as any object with the temperature above absolute zero will emit electromagnetic wave as thermal radiation.^[12] IR camera is able to identify the IR emissions by hot bodies from the environment and limit the application of conventional camouflages. Therefore, IR camouflage has attracted the interest of researchers. One important type of IR camouflage is based on the phase changing materials and the working principle of the camouflage is based on the switching of emissivity as shown in **Figure S1**. Currently, the intensively researched phase change material for camouflage application includes Ge-Sb-Te (GST) chalcogenide phase-change material^[13], perovskite manganese oxide,^[14] tungsten oxide (WO₃),^[15] and the most importantly, vanadium dioxide (VO₂). Although the VO₂ is naturally a candidate with the emissivity contrast of ~ 0.3 ^[16, 17] for camouflage applications due to its unique MIT phenomenon, there are formidable challenges to limit its effectiveness. On one hand, the ideally maximized difference in the emissivity is 1 at the various temperatures, however so far the highest reported experimental value was only 0.39 by using a complicated VO₂/CNT/graphene stacking structures.^[18]

On the other hand, τ_c of VO₂ have to be reduced for room temperature applications together with insufficient NIR regulating capability.^[19, 20] Currently there are a few methods to address these two issues, i.e. chemical doping,^[21, 22] nanothermochromism,^[23] nanoporous structure,^[24] core-shell structure,^[25, 26] multi-layered structure^[27] and so forth. In this paper, we proposed a facile VO₂/carbon composite structures synthesised by plasma enhanced chemical vapor deposition (PECVD). Our experimental measurement shows that such a composite material can possess a much lower τ_c of 45 °C, higher emissivity contrast of 0.44 and interesting enhanced photothermal effect compared to the pure VO₂. A theoretical model was also performed to validate our approach that has an agreement with the experiment.

Noteworthy, the VO₂/carbon hybrid structures were also employed for energy storage devices such as the electrode material of battery^[28-30] and supercapacitor^[31-33] due to the enhanced conductivity of carbon. Nevertheless, the present fabrication approach was mainly hydrothermal,^[34, 35] our proposed fabrication method based on the plasma enhanced process could be utilized in those applications that offers the advantages of fast deposition time (~100-200 nm min⁻¹).

2. Results and discussion

2.1. Fabrication of VO₂/carbon hybrid structures

The phase diagram for the deposition of VO₂/carbon hybrid structures associated with oxygen flow rate and deposition temperature was shown in **Figure 1(a)**. There are four possible process windows to be outlined: amorphous mixture, low crystalline VO₂/carbon mixture, high crystalline VO₂/carbon hybrid material and VO₂/V₂O₅/carbon mixing phases.

As shown in the Figure 1(b), as increasing the oxygen flow rate from 0 sccm to 20 sccm, the structural states of the samples changed from amorphous, to VO₂ and VO₂/V₂O₅ mixture, which are all hybridized by carbon. Figure 1(e) shows the weight-temperature and weight derivation-temperature curve of VO(acac)₂ during the TGA testing the decomposition of VO(acac)₂ occurred at approximately 180 °C and reached the highest rate at ~260 °C. The structure of

VO(acac)₂ molecule was illustrated in Figure 1(f) and the deposition process can be divided into two parts [Figure 1(g)]. At the decomposing stage, the carbon contained chelate rings detaches from the molecule and further decomposes to form carbon. Subsequently, oxygen oxidized V-O to form crystalline VO₂ and some carbon from precursor remained in the composite [36]. At the low oxygen flow rate range, the VO₂ shows a very low crystallinity or even being amorphous. It should be noted that a large amount of oxygen will promote the formation of V₂O₅, which is the most thermodynamic form of vanadium oxides. Therefore, the optimized oxygen flow rate was 10 sccm when the deposition temperature was set at 450 °C. Meanwhile, the deposition temperature can also significantly affect the composition. At the oxygen flow rate of 10 sccm, by changing the deposition temperature from 350 to 450 °C, VO₂ can be evolved from the amorphous, low crystallinity to high crystallinity [Figure 1(c)]. By increasing the oxygen flow rate to 20 sccm, a similar trend could be observed with the formation of V₂O₅ at 450 °C [Figure 1(d)]. This temperature influence can be explained by the higher amount of energy that prompts the diffusion and rearrange of atoms to form high crystallinity which is essential to form high performance VO₂.

2.2. Characterization of VO₂/carbon hybrid material

Based on the phase diagram summarized in previous section [Figure 1(a)], the sample was synthesised with oxygen flow rate of 10 sccm and temperature at 450 °C by PECVD method and the XRD [Figure 2(a)] pattern shows that monoclinic phase of VO₂ is synthesised. To our knowledge, it is the first time to successfully synthesis of VO₂(M) through PECVD method.[37] In Figure 2(b), the FTIR of both produced sample and pure commercial VO₂ powders further provides the information of VO₂ and carbon in the material. The peaks at 422, 530, and 715 cm⁻¹ attribute to the V–O–V octahedral bending modes [38] and coupled vibration of V=O bond [39] belongs to the typical VO₂(M). On the other hand, the peak at 1606 cm⁻¹ origins from the vibration of C=C stretching and the peak at 1411 cm⁻¹ represents the vibration of C=O

stretching.^[40, 41] The FTIR and XRD results confirmed that the thin film synthesised is in the form of VO₂/carbon composite.

It can be observed that the continuous film consists of sub-micron grains with large inter-grain pores [Figure 2(c)]. This morphology is similar to that deposited by other CVD techniques such as atmospheric pressure CVD (APCVD) and metal-organic chemical vapor deposition (MOCVD).^[37] At the same time, the EDX mapping [Figure 2(d)] shows that the carbon coexists in the VO₂ film, which proves that the carbon is hybridized into VO₂ with no phase segregation. The morphology of one typical grain was then examined by AFM showing that the grain size is 400-500 nm and the height is around 100 nm [Figure 2(e)].

2.3. The emissivity switching performance analysis

The VO₂/carbon hybrid material can switch the emissivity in the MIR region from 8 to 13 μm . **Figure 3(a)** visualise the MIR emissivity switching process of the material. At the room temperature, there is no temperature difference between the sample and the background (carbon black tape with an emissivity of 0.95). By increasing the temperature to 50 °C, the VO₂/carbon sample shows a lower temperature than the background, due to the phase change of VO₂ induced by MIT. During the cooling down process, such a change occurs at 40 °C, caused by the MIT hysteresis.

Figure 3(b) and (c) summarise the emissivity switching for both the VO₂/carbon composite and pure VO₂. Figure 3(b) shows that the emissivity of VO₂/carbon composite changes from 0.95 (20 °C) to 0.51 (100 °C) thus leading to an emissivity contrast of 0.44 between the high and low temperatures. This is higher than the emissivity difference of 0.39 observed in the VO₂/carbon nanotube (CNT)/ graphene multi-layered composite.^[18]

Moreover, compared to the pure VO₂, such a hybrid material has a much better performance of emissivity switching capability [pure VO₂ 0.19, dotted line Figure 3(b)]. The temperature differences between the samples and background show the similar trending [Figure 3(c)]. When the actual temperature was set at 100 °C, the IR temperature of the VO₂/carbon composite is

36 °C lower than the background; however, the pure VO₂ only shows a 14 °C difference. The insets show the IR camera image of the composite and pure VO₂ at 100 °C. By fine tuning the oxygen flow rate, the different content of carbon sample has been fabricated (**Figure S3, S4**). As shown in Figure 3(d), both emissivity and temperature differences are proportional to the carbon concentration: the largest emissivity (0.44) and temperature (35.7 °C) differences are achieved in the carbon rich sample (V:C atomic ratio 1.5). In contrast, the vanadium rich sample (V:C atomic ratio 3.8) shows the smaller emissivity (0.38) and temperature difference (27.5 °C). The trending of calculated thermal emissivity differences matched the measured ones [Figure 3(d), dotted line]. The variation of measured emissivity from calculation could be partially due to the simplification of modeling which supposed a new flat and perfect films. Moreover, the emissivity was measured in the far-field using IR camera, while in the simulations, the reflectance and transmittance were simulated in the near-field of the films, which may also cause differences between the experiment and the simulation. Moreover, the emissivity was measured in the far-field using IR camera, while in the simulations, the reflectance and transmittance were simulated in the near-field of the films, which may also cause differences between the experiment and the simulation.

The numerical models adopt the experimental measured permittivity for VO₂ and carbon that consider losses. The complex permittivity of carbon was taken from Ref.^[42]. The real, $\epsilon_{v_real}(\omega)$ and imaginary $\epsilon_{v_imag}(\omega)$ parts of the permittivity of VO₂ at low and high temperatures were achieved from the experimental data in Ref.^[43] and for the entire NIR and MIR spectral regions the dielectric permittivity is shown in **Figure 4(a)**. As was observed, the permittivity [$\epsilon_{VO_2}(\omega) = \epsilon_{v_real}(\omega) + i * \epsilon_{v_imag}(\omega)$] of VO₂ was dispersive and had a large $\epsilon_{v_imag}(\omega)$ showing a high absorptance. **Equation 1** represents the effective permittivity ($\epsilon_{vc}(\omega)$) of VO₂/carbon composite material by the Lorentz-Lorenz model,^[44]

$$\frac{\epsilon_{vc}(\omega) - 1}{\epsilon_{vc}(\omega) + 2} = j \times \frac{\epsilon_{carbon}(\omega) - 1}{\epsilon_{carbon}(\omega) + 2} + (1 - j) \times \frac{\epsilon_{VO_2}(\omega) - 1}{\epsilon_{VO_2}(\omega) + 2} \quad (1)$$

where $\varepsilon_{\text{carbon}}(\omega)$ is effective permittivity of carbon, $\varepsilon_{\text{VO}_2}(\omega)$ effective permittivity of VO_2 , and j the proportion of carbon. Therefore, one can tune the refractive index of the $\text{VO}_2/\text{carbon}$ composite by controlling the ratio of carbon doping (j). Figure 4(b)-(d) present the $\varepsilon_{\text{vc}}(\omega)$ at the different carbon doping ratios of 1.5, 1.75, and 3.8 for both high (shown in red lines) and low (shown in blue lines) temperatures. It shows that the imaginary parts of permittivity of $\text{VO}_2/\text{carbon}$ composite [$\varepsilon_{\text{vc_imag}}(\omega)$] for the various doping ratios are smaller than the pure VO_2 [$\varepsilon_{\text{v_imag}}(\omega)$]. This leads to the lower absorptance of the composite, that in turn, produces the smaller thermal emissivity compared to the pure VO_2 planar film.

Table 1 summarises the performance of IR camouflage with different working principles, in which the hybrid structure reported in this work shows an outstanding emissivity regulation performance.

2.4. The NIR regulating capability and thermochromic performance

The hybrid structure shows a largely lowered τ_c of $\sim 45^\circ\text{C}$ [**Figure 5(a), (b)**]. Both phase change temperature for heating ($\tau_{\text{c,Heating}}$) and cooling ($\tau_{\text{c,Cooling}}$) show decreasing. For example, the $\tau_{\text{c,Heating}}$ is decreased from 70°C to 55°C , and the $\tau_{\text{c,Cooling}}$ is decreased from 55°C to 30°C . As shown in Figure 5(c), compared with the peak of (0 1 1) plane for pure VO_2 , the peak of the same plane for $\text{VO}_2/\text{carbon}$ hybrid material shifts left for $\sim 0.2^\circ$, which indicates the presence of compressive strain along the c-axis of VO_2 .^[49] On the other hand, the Raman peaks of $\text{VO}_2/\text{carbon}$ hybrid material showed blue shifting compared to the peak of bulk VO_2 (**Figure S5**). The blue shifting of Raman peak attributes to the presence of compressive strain,^[50-52] which agrees the result of XRD. As the compressive strain has been reported able to lower the τ_c by stabilizing the $\text{VO}_2(\text{R})$ high temperature phase and prompt the phase change,^[53-55] it can be concluded that the compressive strain is the main reason that contributes to the decreasing of τ_c in $\text{VO}_2/\text{carbon}$ hybrid material.

We compared the thermochromic performance between the $\text{VO}_2/\text{carbon}$ composite and the pure VO_2 . The $\text{VO}_2/\text{carbon}$ hybrid structure shows a deeper colour and lower luminous transmittance

(T_{lum}), due to the absorption of carbon in the visible light range [Figure 5(d), (e)]. However, as carbon is transparent in NIR region,^[56] the hybrid material maintains a promising NIR switching performance: When temperature increases from 20 °C to 90 °C, the transmittance of the hybrid material for 2500 nm decreases from 40.7% to 5.0% [Figure 5(e)] with the transmittance difference for hybrid material of 36% which is comparable to that of the pure VO₂ (~45%). Moreover, as the **Table 2** summarises, the hybrid material achieves a combination between low τ_c and promising NIR switching devices. At the same time, surface temperature of VO₂/carbon hybrid increases faster and the final temperature is higher compared to the pure VO₂ and glass (hybrid sample: 107.1 °C; pure sample: 89.9 °C; glass: 65.8 °C) [Figure 5(f)]. From the previous reported case of photothermal effect in VO₂/carbon composite, the higher final temperature and faster heating speed are attributed to the visible light absorption by carbon.^[57, 58] Furthermore, the porous surface of the hybrid material could also contribute to the improving of photothermal performance by improving the absorption of light.^[59] Therefore, the improved photothermal performance could be due to both carbon and pore effects which makes the hybrid material a candidate for the energy saving window in colder region, as the increased surface temperature is able to effectively lower the U-factor and prevent the heat loss from the window.^[60, 61]

3. Conclusion

The VO₂/carbon hybrid structure was deposited by PECVD method for the first time and the integrated emissivity of the sample for the MIR spectral region (8-13 μ m) decreases from 0.95 to 0.51 by heating it up from 20 °C to 100 °C. This shows greater emissivity difference than pure VO₂ and other thermal induced phase-change emissivity regulation device. Also, the transition temperature ($\tau_c = 45$ °C) of the hybrid material is lower than that of the pristine VO₂. Moreover, the hybrid material shows a promising NIR-regulation property. Its transmittance contrast at 2500 nm between 20 °C and 90 °C is ~36%, which is comparable to the pure VO₂. Moreover, this material shows better photothermal performance than pure VO₂. The VO₂/carbon hybrid achieves a combination of low τ_c , good emissivity switching capability, and

moderate thermochromic properties with enhanced photothermal effects, this hybrid material has a potential of being the candidate for camouflage, IR-switching devices and energy saving window

4. Experimental Section

The PECVD system: A homemade PECVD system was employed to synthesis the material (**Figure S6**), where the plasma source is a 13.56 MHz RF-plasma generator. Two mass flow controllers (Sevenstar CS200) were used to precisely control the flow rate of gas. Two heaters were set at different temperature for precursor and substrate, accordingly.

Chemicals: Vanadyl acetylacetonate [VO(acac)₂] was used as vanadium and carbon source without further purification, and the oxygen source was oxygen gas. Argon (99.999%, Leeden NOX) was carrier gas for VO(acac)₂ vapor. The quartz substrate was cleaned by piranha solution (H₂SO₄:H₂O₂ = 3:1 in volume) before deposition.^[62]

Experimental procedure: The reaction chamber was evacuated, and the argon gas was introduced into chamber at a flow rate of 200 sccm. The furnace for precursor was set at 200 °C, and the furnace for substrate was set at 350, 400 and 450 °C for evaluate the effect of temperature to the composition of product. When the temperature reached the specified value, power generator was switched on and the plasma was ignited. Oxygen gas was straightaway introduced into the system to react with VO(acac)₂ vapor. The reaction time was four minutes. Afterwards, the oxygen flow and the power generator were switched off. The samples were cooled down in argon flow to room temperature, and then were taken out from the chamber for further characterization.

Characterization: The thermogravimetric analysis (TGA) was conducted by TGA Q500 thermogravimetric analyser in the gas flow of argon. The crystal phases are identified by X-ray diffraction (XRD, Panalytical Empyrean) with Cu K α X-ray. The Fourier transform infrared (FTIR) testing was conducted using Parkin Elmer Frontier spectrometer with transmission mode. The surface morphology of the samples was characterized using the field-emission

scanning electron microscope (FESEM, JEOL JSM-7600F) and tapping mode of atomic force microscope (AFM, Bruker Nanoscope). The carbon concentration in the hybrid structure was estimated by energy dispersive spectrometer (EDX, Oxford INCA) with semi-qualitative method. The thermochromic properties were tested by UV-Vis high-sensitivity spectrometer (AvaSpec). The Raman spectra were obtained by using the confocal Raman spectrometer (WiTec alpha300) with a 532 nm laser source. The integrated emissivity was measured by an IR camera (FLIR) with the method reported elsewhere.^[18] The sample was attached to black tape with emissivity of ~ 0.95 that serves as background. Subsequently, the sample and the black tape were placed on a heating plate that controlled by a temperature controller. The temperature of sample was measured by a thermocouple. The integrated emissivity was measured by adjusting the emissivity value of thermal camera until the temperature display of camera is the same as the display of thermal couple.

FDTD simulations: The thermal emissivity [$\varepsilon(\omega)$] of the object equals to its absorptivity [$A(\omega)$] based on Kirchhoff's law of thermal radiation.^[67, 68] The proposed film behaves as a black body with $\varepsilon(\omega) = A(\omega)$, showing the identical feature to the absorptivity. Calculation was carried out using the commercial Finite Difference Time Domain (FDTD) solver.^[69] Perfectly matched layer boundary conditions were used in the model. The structure was illuminated by a plane wave normal to the VO₂/carbon composite film. The reflectance [$R(\omega)$] and transmittance [$T(\omega)$] were recorded with the power monitors. The thermal emissivity can thus be obtained by $\varepsilon(\omega) = A(\omega) = 1 - R(\omega) - T(\omega)$. A 2 nm FDTD square mesh was chosen to reduce numerical error during the FDTD approximation. The thickness of the films was set to those measured ones i.e. 1 μm for the VO₂/carbon film. The calculations validate the varying direction of emissivity difference by tuning the doping level of carbon. In the model, we ignored the surface roughness and fabrication imperfections.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. (a) Phase diagram for the deposition of VO₂/carbon hybrid structures. The points indicate the experimental results discussed in this section. The four regions are established based on the experiment results showed in **Figure S2**. (b), (c), and (d) XRD patterns to illustrate the phase change accompanies the parameter changing. (b) XRD pattern to show the effect of oxygen flow rate along the line 1. (c) XRD patterns to show the effect of deposition temperature along the line 2. (d) XRD pattern to show the effect of deposition temperature at high oxygen flow rate along the line 3. (e) TGA analysis result for VO(acac)₂. The red line represents the weight of sample and the blue line represents the derivation of weight during heating up. (f) Structure of VO(acac)₂ molecule, the balls stand for different atoms and rods stand for the chemical bond between atoms. (g) Schematic illustration of the reaction happened during the deposition.

Figure 2. (a) XRD pattern of deposited material. The background was removed for the ease of illustration. The peak that labelled by asterisk belongs to the quartz substrate. (b) FTIR spectrum of produced material and pure VO_2 . (c) FE-SEM image of the hybrid structure produced with oxygen flow rate of 10 sccm. (d) EDX mapping of the sample for vanadium (in blue color), carbon (in yellow color) and its overlapping. (e) Tapping mode AFM image of the hybrid material. The curve of cross section along the dash line shows the thickness of the individual island is ~ 100 nm.

Figure 3. (a) IR camera images for the sample at different temperatures to show the emissivity switching phenomenon of VO_2 /carbon hybrid material. (b) Hysteresis loop of integrated emissivity for the hybrid material and the pure VO_2 . The solid lines are the curve for the sample, and the dash lines are for the pure VO_2 , respectively. (c) Hysteresis loop for the temperature difference between the sample/ VO_2 film and the background. Inserted photos are the IR camera photos for the sample/ VO_2 at 100°C . The coloured squares at the centre are the samples, the surrounded white region is background. (d) Curves to show the relationship between the carbon concentration and emissivity/temperature difference.

Figure 4. NIR–MIR complex permittivity of the (a) pure VO₂ film, and VO₂/carbon composite films for the carbon doping ratios of (b) 1.5, (c) 1.75, and (d) 3.8. at the low (shown in blue lines) and high (shown in red lines) temperatures. The measured refractive index data of VO₂ were extracted from Ref. [46].

Figure 5. (a) Hysteresis loop for the transmittance at 2500 nm to show the τ_c of hybrid structure and pure VO₂. (b) Transmittance derivation curves for the hybrid structure and pure VO₂ during the heating and cooling process. The sharpest point on the curve stands for the temperature that phase transition occurred. (c) XRD pattern for the (0 1 1) plane of hybrid structure and pure VO₂. (d) Optical image of VO₂/C hybrid and VO₂, respectively. (e) Transmittance and absorbance spectra for the hybrid structure at 20 and 90 °C. (f) Temperature-time curve for VO₂/C sample, VO₂ sample, and glass substrate under the irradiation of quartz heating lamp.

Table 1. Performance comparison of emissivity switching ability of different materials and devices.

Type of mechanism	Material	Emissivity difference	Temperature difference	Reference
Thermal induced phase change	VO₂/carbon hybrid structure	0.44	36 °C at 100 °C Averaged 6.5 °C at 50 °C	This work
	VO ₂ /CNT/graphene multi-layered composite	0.37	~10 °C at 90 °C	[18]
	VO ₂ /ZnS core-shell structure	0.28	20.8 °C at 95 °C	[45]
	1%W-doped VO ₂	0.13	n.a.	[46]
Biomimetic IR-reflecting device	Al coated controllable IR-reflecting device	n.a.	~4.4 °C at 48 °C	[47]
UV-activated metamaterial	Au/ZnO/ITO metamaterials	~0.2	~4 °C at room temperature	[48]

Table 2. Performance comparison of τ_c and transmittance difference for different structures of VO₂.

Material	τ_c (°C)	$\Delta T\%$ at 2500 nm	Reference
VO₂/carbon composite	45	36	This work
Photonic structure	68	24-55	[62]
Biomimetic structure	68	35-60	[63]
Mg/W co-dope	~30	~20	[64]
Nanothermochromism	35-65	~30	[65]
Anti-reflection coating	68	~40	[66]

A novel multifunctional VO₂/carbon hybrid material is fabricated by PECVD with fast deposition rate. Reduced transition temperature, the highest reported emissivity contrast and interesting enhanced photothermal effect make it a good candidate for Infrared (IR) camouflage, near IR regulation device, and smart window applications.

Keyword: vanadium dioxide, hybrid materials, camouflages, near infra-red regulations, smart windows

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Largely lowered transition temperature of VO₂/carbon hybrid phase change material with high thermal emissivity switching ability and near infra-red regulations

Supporting Information

Largely lowered transition temperature of VO₂/carbon hybrid phase change material with high thermal emissivity switching ability and near infra-red regulations

Shancheng Wang, Guowei Liu, Peng Hu, Yang Zhou, Yujie Ke, Chuanchang Li, Jian Chen, Tun Cao and Yi Long**

Figure S1. Working principle of IR camouflage. Upper: MIR image (left) and schematic diagram (right) of hot object without camouflage. The red arrows represent the IR thermal radiation emitted from the object. The hot object emits large amount of IR radiation. As the result, the object shows bright white color compared to the blue colored background. Lower: MIR image and schematic diagram of hot object with camouflage. The dark colored region at the centre of MIR image is camouflage. The phase change material lowers its emissivity upon heating via phase change. As the result, less IR being emitted from the hot object and the camouflage covered part of hot object have smaller contrast to background in IR camera

Figure S2. XRD patterns for the data points taken to construct the phase diagram showed in Figure 2(a). The growth conditions of samples are labelled at the left bottom corner of patterns. Due to the limit of space, more patterns will be displayed in the next page.

Figure S2. (Continue) XRD patterns for the data points taken to construct the phase diagram showed in Figure 2(a). The growth conditions of samples are labelled at the left bottom corner of patterns.

Figure S3. EDX spectra for the hybrid material samples with different carbon content. (a). V:C atomic ratio 1.5. (b). V:C atomic ratio 1.8. (c). V:C atomic ratio 3.8.

Figure S4. SEM (left side) and AFM (right side) images for the hybrid material samples with different carbon content. (a). V:C atomic ratio 1.5. (b). V:C atomic ratio 1.8. (c). V:C atomic ratio 3.8.

Figure S5. Raman spectra for VO₂/carbon hybrid material and bulk VO₂. The black solid lines indicate the peak position of hybrid material. The black dotted lines indicate the respective peak of bulk VO₂.

Figure S6. The scheme of PECVD system. The alumina boats in the heaters are containers for precursor and substrates, respectively. The purple light in this scheme represents the plasma produced by generator.