Article

Carbon Aerogel Based Waterborne Ultra-Black Coatings with High Light Absorption

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Abstract: In this paper, we wish to report the preparation of ultra-black films via spraying coatings composed of waterborne binders and low-cost carbon aerogels on pre-treated tinplate. The CAs were prepared by annealing resorcinol-formaldehyde resin (RF resin) and the following CO₂ activation, of which the reflectance was less than 0.4% in a wide wavelength range. The reflectance of different coatings, which using CAs as functional pigments, ranged from 1.8% to 4.3% in the visible light region (400–760 nm), while it ranged from 1.9% to 4.2% in the near-infrared region (760–1100 nm). Further studies revealed the relationship between the pigment-to-binder ratio and reflectance and found the best ratio to be 0.96, and the minimum reflection was less than 1.8%. Outstanding adhesion to the tinplate substrate was also achieved using a two-component polyurethane binder after the thermal cycling test carried out from −100 °C to 100 °C. The fabrication process of ultra-black coatings is particularly convenient to remove the constraints of high costs and complex processes, making it instructive guidance for industrial production.

Keywords: carbon aerogels; high light absorption; ultra-black coating; waterborne binder; outstanding adhesion

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1. Introduction

Since the ‘black body’ theory was first introduced into thermodynamics by Kirchhoff and the law of black body radiation was proposed by Planck [1,2], the interest in the research of ideal electromagnetic absorbers [3] to simulate a black body gradually arose [4]. Great efforts have been made toward the design, synthesis, and optimization of such materials because of the outstanding optical and thermal properties introduced by their high light absorptivity [5,6]. Therefore, various materials based on metal, carbon, silicon, etc., were reported to possess excellent light absorbing property [7–12] and applied to different fields, such as photothermal conversion [13,14], optical instrumentation [15,16], aerospace applications, as well as satellites [17–19]. As far as we know, the properties of high light absorbing of ultra-black materials originate from the periodic structures endowed by nature or by artificial designing [7,20–23], such as needle-like ‘forest’ or inverse V-type structures. Steglich et al. managed to fabricate an ultra-black silicon absorber with needle-like forest morphology to process an absorptance of more than 99.5% [11]. Through bionics, Zhao et al. pyrolyzed the scale wings of *Ornithoptera goliath* butterfly at 650 °C and finally obtained the ultrathin inverse V-type structure anti-reflection materials entirely consisting of carbon and having a reflectance of <1% in the visible light region [24]. In recent years, carbon materials, for instance, carbon nanotubes (CNTs) [25–27], carbon aerogels (CAs) [28,29], carbon foam [30], carbon fiber composites [31], and carbon spheres (CSs) [32], as research hotspots, were reported to possess not only good capacitive performance [33,34] but also great light absorptivity in both visible and infrared regions, which was attributed

to the peculiar porous structures, large conjugated system and moderate free-electron density of carbon [35]. Moreover, low density and a wide source of raw materials are excellent advantages of these materials in industrial applications compared with other element-based materials [36]. Therefore, multiple carbon materials have been applied to produce ultra-black coatings with extremely low reflectance. Magdassi et al. reported carbon nanotube black coating using multi-walled carbon nanotubes (MWCNTs) mixed with a silicon-based binder to obtain a reflectance of <4% in the visible light region and <5% in the near-infrared region [26]. Theoretically, a subwavelength structure was demonstrated by Sun et al., in which light absorption resulted from the reduced electron mean free path in subwavelength micropores [37]. This conclusion helped us in designing coatings with subwavelength structures in order to reduce diffuse light reflection. Additionally, by adjusting the ratio of the reactants and catalyst in precursor solutions, various preparation processes have been developed and improved for fabricating artificial CAs with three dimensional porous subwavelength structures since first synthesized by Pekala [38–41]. Therefore, we tried to apply the subwavelength structured CAs as functional fillers to prepare coatings with high light absorption.

In this study, an appropriate ratio of resorcinol, formaldehyde, and sodium carbonate in the precursor was determined to fabricate hydrosol. The resorcinol-formaldehyde solution was dissolved in deionized water (DIW) with sodium carbonate as base catalyst. Then, a hydrothermal process was performed to obtain the hydrogel. The final CAs with hierarchical porous nanostructures were derived from the pyrolysis of such hydrogel and a subsequent CO₂ activation process. Coatings of different binder types composed of these carbon aerogels show a reflection of <2.1% in the visible region and <2.2% in the NIR region at the best experimental conditions. The mechanical properties of adhesion and thermal cycling tests prove that the coating is reliable enough for applications in extreme situations. Furthermore, the convenience of preparation and commercial availability of raw materials enable the facile realization of industrial production of such ultra-black coatings.

2. Experimental

2.1. Materials

Sodium carbonate, formaldehyde (37% in water), resorcinol, and all other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCR, Shanghai, China) and used as received without further purification. Anionic polyacrylate dispersion along with aliphatic isocyanate (2K-WPU), anionic polycarbonate modified polyurethane dispersion (DLC-F), and aliphatic anionic acid modified polyurethane dispersion (PUD) were purchased from Covestro Polymers (Shanghai, China) Co., Ltd. The two-component ceramic coating Sunactive CD200 (2K-CERA.) was purchased from Shanghai Kinlita Chemical Co., Ltd. (Shanghai, China) Other additives, wetting agents, flattening agents including dispersing agents were purchased from BYK-Chemie GmbH (Tongling, Germany). Both resin and additives were used as received.

2.2. Synthesis of CAs Through the Sol-Gel Process

The carbon aerogels were obtained via the carbonization of resorcinol-formaldehyde (RF) gels, which derived from the addition reaction and polycondensation reaction under alkaline condition provided by sodium carbonate. The molar ratio of formaldehyde to resorcinol (F/R) was adjusted to 2, and this mixture was dissolved in a certain amount of deionized water. Subsequently, as a base catalyst, alkaline sodium carbonate (C) was added, with the molar ratio of formaldehyde to the catalyst (F/C) being fixed at 600. This aqueous solution was denoted as the precursor solution, the total weight of resorcinol and formaldehyde (W%) was set at around 5%. Typically, 3 g of resorcinol was added in a round bottom beaker containing 135 mL deionized water (DIW). Then, 4.2 g of formaldehyde was added dropwise under stirring. The resulting solution was stirred for 15 min and subsequently 9.6 mg of sodium carbonate was added. After stirring for another 20 min, the precursor solution was transferred into a polytetrafluoroethylene (PTFE) mold and

sealed in a steel hydrothermal reactor. The reactor was cured in a constant temperature humidity chamber at 85 °C for 72 h. The resulting gel was soaked in acetone for 24 h for a few times to completely remove residual solvents and water. After the solvent exchange process, the wet gel was subsequently transferred into a fridge at −16 °C, stored for 3 h to keep the structure robust, and then dried in a freeze-dryer for 24 h. The dried sol was carbonized at 900 °C under a nitrogen atmosphere for 2 h. The resulting black cylindrical materials were the target product of CAs and named CA-S.

2.3. Activation of CAs with CO₂

CA-S were annealed in a tubular furnace at 1000 °C for 2 h under the mixture gas environment (N₂ flow of 75 mL·min^{−1} and CO₂ flow of 75 mL·min^{−1}). The heating rate was set at 10 °C per minute from room temperature to the target temperature, and the natural cooling process was followed. Both the heating and cooling processes were performed under a nitrogen atmosphere at a flow rate of 250 mL·min^{−1}. The obtained CAs activated by CO₂ were denoted as ACA.

2.4. Preparation of Ultra-Black Coating

In the primary formulation, the CA aqueous dispersion was mixed with various ratios of different binders to fabricate different polymer-based ultra-black coatings. For a typical experiment, a certain amount of dispersing agent (10 g) was added to 70 mL deionized water, which was stirred using a laboratory mill for 10 min in a plastic beaker at ambient temperature. With a stirring speed of 400 rpm, 20 g ACA was added gradually to avoid splashing due to the low pile density. On completely adding ACA, the stirring speed was increased to 2000 rpm and maintained for 1 h to acquire the ACA aqueous dispersion. A certain amount of resin (2K-WPU/PUD/2K-CERA./DLC-F) was added in another plastic beaker, followed by the dropwise addition of additives with a stirring speed of 700 rpm. Then, the ACA aqueous dispersion was added, and the resulting solution was dispersed using a laboratory mill at a speed of 700 rpm for 60 min to obtain the ultra-black coatings.

2.5. Characterization

The microscopic structures of the carbon aerogels were investigated using scanning electron microscopy SEM (JSM-7800F, Japan Electronics Corporation, Tokyo, Japan). The crystal structure of the sample was examined on an X-ray diffraction instrument (XRD, Bruker D8 Advance, Leipzig, Germany), with Cu target (0.154 nm) as the radiation source, tube voltage of 40 kV, tube current of 40 mA, and scanning speed of 5 °min^{−1}. Absorbance was identified indirectly by measuring the reflectance of the film at wavelengths ranging from 1100 nm to 400 nm using a U-4100 Spectrophotometer (HITACHI). Thermogravimetric analysis (TGA) was performed on TA Q500 (TA Instruments, New Castle, CA, USA) under a nitrogen atmosphere. Raman spectra (ThermoFisher Scientific DXR2xi, Waltham, MA, USA) were recorded from 600 cm^{−1} to 2500 cm^{−1} under 532 nm excitation. The pore size distribution and specific surface area were measured via the N₂ adsorption method at 0 °C in a magnetic suspension balance using the Brunauer-Emmett-Teller (BET) nitrogen adsorption/desorption technique (ASAP 2020 V4.0 from Micromeritics, Norcross, GE, USA). Film thickness was measured using a SURFIX B thickness gauge from PHYNIX GmbH & Co. KG, Neuss, Germany. The adhesion properties were measured through an ISO2409/ASTM D3359 [42,43] cross-cut test and evaluated using the above standards.

3. Results

The synthesis of the RF aerogels is schematically illustrated in Figure 1. Commercially available raw materials of resorcinol and formaldehyde can easily co-dissolve in deionized water and form a semi-opaque hydrosol using sodium carbonate as the base catalyst under alkaline conditions. The obtained precursor solution was sealed in a PTFE mold and subjected to a low-temperature hydrothermal process at 85 °C for 72 h. The resulting hydrogel was soaked in acetone for 24 h, the process was replicated 3 times to remove

the residual water and solvent. After the freeze-drying process, the cylindrical product was pyrolyzed at 900 °C in a tubular furnace for 2 h. In this process, to protect the morphological structure of CAs from collapsing, a heating rate of 10 °C/min from ambient temperature to 400 °C and 5 °C/min from 400 °C to 900 °C was engaged under a nitrogen environment. During the activation procedure, we controlled the flow rate of carbon dioxide and nitrogen to maintain an appropriate etching efficiency in order to stabilize the original three-dimensional structure.

Figure 1. Fabrication and morphology of carbon aerogels. (a) Schematic illustration of the fabrication process. Resorcinol and formaldehyde hydrosol were converted into hydrogel by hydrothermal process, freeze-dried for 24 h, and annealed at 900 °C to form the porous carbon aerogels, and the activating process built more nanostructure pores resulting in a lower reflectance. SEM images of (b) CA-S and (c) ACA. The scale bar is 400 nm.

Subsequently, the process to prepare CAs with subwavelength structures was performed, as illustrated in Figure 1. According to its morphology, more pores and microstructures exist in ACA than in CA-S on comparing the SEM images (Figure 1b,c). For the purpose of analyzing the type of carbon in these two samples (CA-S and ACA), Raman spectra were recorded and shown in Figure 2a. The spectrum of both samples shows two characteristic peaks located at approximately 1355 cm^{-1} and 1585 cm^{-1} , which are ascribed to the D band and G band, respectively. The D band results from disordered carbon and other defects, whereas the G band is assigned to the zone center E_{2g} mode, which is the consequence of the ordered sp^2 bonded carbon [44]. Moreover, X-ray diffraction analysis was performed, and the results are shown in Figure 2b. The XRD pattern of both CA-S and ACA exhibits two diffraction peaks at 2θ of around 24° and 44° , corresponding to the (0 0 2) and (1 0 1) planes, respectively. These data imply that carbon aerogels are composed of both graphite carbon and amorphous carbon [45,46]. Nevertheless, the activation step shows a limited effect on the major structure and the type of carbon due to the similar curves. To further study the difference in physical properties after activation, more measurements were performed.

Figure 2. (a) Raman spectra of ACA and CA-S. (b) X-ray diffraction patterns of ACA and CA-S. (c) Isotherms of ACA and CA-S. (d) BJH pore distribution of ACA and CA-S.

The pore structures of CA-S and ACA were investigated via low-temperature N₂ absorption-desorption measurements. Brunauer-Emmett-Teller specific surface areas as high as 1544.7 m²/g and 649.7 m²/g were measured for ACA and CA-S, respectively. Using the *t*-plot method, the micropore surface area and mesopore/macropore surface area of CA-S and ACA were calculated to be 448.22 m²/g and 201.42 m²/g and 911.52 m²/g and 633.13 m²/g, respectively. The activated process produced twice the micropores and thrice the mesopores, which was in good accordance with the isotherms shown in Figure 2c. The isotherm curve of ACA can be classified as type IV, while that of CA-S can be classified as type II, according to the IUPAC classification of adsorption isotherms [47]. The black line in Figure 2c for CA-S rapidly elevates at a low relative pressure (P/P₀), indicating the formation of abundant micropores. The absorption continues to increase without a plateau near P/P₀ of 1.0, suggesting the presence of mesopores and relative macropores. In contrast, the hysteresis loop of the red line for ACA in Figure 2c is associated with capillary condensation taking place in its mesopores, and the initial part of the isotherm is attributed to monolayer-multilayer adsorption [48]. Furthermore, the BJH absorption pore-size distribution was determined, which showed the expected results (Figure 2d). The corresponding pore-size distribution of both the samples before and after activation samples shows a high-intensity peak at the abscissa of 1–5 nm, especially 1–2 nm, and the slope of ACA is more precipitous than that of CA-S during the micropore range, indicating that the samples, particularly ACA, had abundant micropores with diameters of 1–2 nm on the nanostructure framework. Notably, the average pore size decreased significantly in the range of 10 to

100 nm, demonstrating the transformation from micropores to mesopores, which is in accordance with the isotherm curve results and changes in BET specific surface area.

The absorption rate was measured indirectly by testing the reflectance of the materials, and the reflectance of CA-S and ACA is shown in Figure 3. The average reflectance of CA-S ranged from 0.78% to 0.60%, while that of ACA was less than 0.40%, indicating that the activation process has a positive effect in decreasing the reflectance due to the presence of more micropores and mesopores. The line chart shown almost a relatively flat slope ranging from 1100 nm to 400 nm, which indicates uniform absorption in both visible and NIR regions. This feature helps in forming a uniform film, providing steady light absorbance in desired applications.

Figure 3. Reflection of CA-S and ACA.

Herein, we used ACA as the light-absorbing materials of the ultra-black coatings. In our primary formulation of coatings, four different types of binders were mixed well along with ACA aqueous dispersions, and the black coatings were formed by airbrush spraying such mixture onto pretreated Aluminum plate. For a typical preparation, 12 g of ACA aqueous dispersion was added into one-component, two-component, polycarbonate-modified waterborne polyurethane and silicon-based binder, and the pigment-to-binder (PB, the weight of pigment to the weight of resin in the dried film) ratio was set as 0.58. The reflectance of the four types of coatings acquired by spraying was measured at the visible-NIR light region (400–1100 nm) and presented in terms of wavelength-to-reflectance. As shown in Figure 4a, the primary formulations of coatings exhibit some differences in the range of 400 nm to 1100 nm. Moreover, the reflectance of the 2K-ceramic coating is about 1.8%, while that of DLC-F is 4.3%, which represented the best and the worst result, respectively. Furthermore, the average reflectance of 2K-WPU and PUD is 2.3% and 3.6%, respectively. We assumed that the overall reflected light of the coating is composed of interfacial reflection due to the refractive index mismatch and backward scattering inside the coating film. To figure out whether the interfacial reflection plays an important role in the overall reflectance of different coatings, a pure resin film without any additive or pigment was brushed on a PET membrane with a coating rod (from RD Specialties, 100 μ m), baked, and subjected to optical tests. Fortuitously, the results reveal almost the same reflectance curve (Figure 4b), and the deviation between the curves was less than 4%; therefore, we can assume that the pure resins are basically similar. Interestingly, the DLC-F shows a lower reflectivity in the form of pure resin but the highest value was obtained on applying the ultra-black coating, suggesting that the reflectance of the clear coating itself has an extremely minor effect on the overall reflectance in the ultra-black coating. Moreover,

SEM was performed to investigate the surface morphology of these four types of coatings in order to find out the reason for the difference in optical properties (Figure 5). Interestingly, the surface morphology of both 2K-ceramic coating and 2K-WPU seems more complicated than that of the other two samples (PUD and DLC-F) that presented lower reflectance. The differences may be due to the morphology change resulting from the polymerization of the two-component system, which is further enhanced with the presence of pigments. Accordingly, we can infer that a more complex surface morphology rather than a flat surface helps in decreasing the interfacial reflection of the dried film.

Figure 4. (a) Reflectance of primary coating formulations. (b) Reflectance of pure resin.

Figure 5. SEM of PUD, DLC-F, 2K-WPU, and 2K-CERA. film. The scale bar represents 10 μm.

Considering the practical applications of the material in aerospace optical auxiliary equipment, maintaining a steady weight is particularly important because weight is directly proportional to the orbital coefficients, so any change in weight under the weightlessness condition will result in changes in the orbit. Thus, TGA of the dry film was performed to determine the binder with the best thermal stability. To simulate the application situation, the coating film was heated to and maintained at 125 °C and 150 °C for 30 min each, and a heating rate of 10 °C per minute from 50 °C to 150 °C was used during the heating process. As shown in Figure 6, the 2K-WPU binder hardly lost any weight, with the weight loss

ratio being less than 0.5%, and was hence inferred to be the best. In contrast, the 2K-ceramic coating showed a 1% weight loss ratio, while both PUD and DLC-F have ratios significantly larger than 1%. The slight increase in weight during the heating-up period is due to the adsorption of N_2 at the surface of the porous CAs. Clearly, the thermal stability of two two-component coatings behaved better than the single component ones, indicating the better intermolecular combination of the two-component system, which can lead to better physical and chemical properties.

Figure 6. TGA analysis of PUD/DLC-F/2K-WPU/2K-CERA. film.

The adhesion property of the coatings to the substrates was evaluated using the ISO 2409/ASTM D3359 tape test with cross-cuts. The adhesion property is marked by the fraction of detachment of the coating. Typically, the film thickness should be less than 60 μm , and the cross-cutting spacing was set to 1 mm, using adhesive tape to stick the cutting parts several times after cross-cutting. The results were evaluated via naked-eye observations and classified according to a standard scale (class 0 is the best with no detachment, class 5 is the worst with more than 65% detachment for ISO 2409, class 5B is the best with no detachment, class 0B is the worst with more than 65% detachment for ASTM D3359). The typical adhesion results are presented in Figure 7.

Figure 7. Typical adhesion images of (a) DLC-F, (b) 2K-CERA., (c) PUD, (d) 2K-WPU.

The 2K-WPU coating shows the best adhesion as ISO class 0/ASTM class 5B, while both the 2K-ceramic coating and PUD present ISO class 1/ASTM class 4B adhesion. In contrast, DLC-F shows the worst grade with ISO class 3/ASTM class 3B adhesion. We expected that the 2K-ceramic coating would exhibit good adhesion due to its good optical performance, but the result seems contrary. The low adhesion level would cause the loose

combination of the coating and substrate, which resulted in a tiny interspace between the film and substrates. This interspace provided room for air bubbles, steam, or a trace amount of water, and the impurities will slowly increase and finally break through the coating film, forming micro-tunnels to let more impurities in, which will further enlarge the size of the tunnels. Considering the combined influence of poor adhesion in anti-corrosion, mechanical properties and weather resistance, we decided to use the 2K-WPU resin as the final binder for ultra-black coating.

The samples of different PB ratios ranging from 0.58 to 1.15 were brushed using a wire rod of 60 μm onto polished aluminum plate and dried at room temperature for 20 min before being placed in an oven at 50 $^{\circ}\text{C}$ for another 2 h, to finally obtain the dried film with a thickness of about 34 μm . As we expected, the sample of the lowest PB ratio (PB 0.58) shows the highest reflectance of 2.5%, which decreases as the PB ratio increases (Figure 8). However, when the PB ratio reaches 0.96, the reflectance reaches the lowest value (red line in Figure 8.). On increasing the PB ratio (1.06 and 1.15), negative results were acquired, i.e., the reflectance starts to increase. Although samples with a high PB ratio (less than 1) show better absorption properties, the adhesion property decreases as the PB ratio increases (Table 1). The samples with a PB ratio of 0.96 and below exhibit ISO class 0/ASTM class 5B adhesion, while those over 0.96 show ISO class 1/ASTM class 4B adhesion. In summary, the larger the PB ratio, the worse would be the adhesion. Therefore, in this study, a PB ratio of 0.96 was selected as the optimal choice for both good reflectance and adhesion.

Figure 8. Reflectance of different PB ratio samples.

Table 1. Adhesion classification of different PB ratios according to ASTM and ISO standard methods.

PB Ratio	Coatings as Prepared		After Thermal Cycling Test	
	ISO 2409	ASTM D3359	ISO 2409	ASTM D3359
1.15	Class 1	Class 4B	Class 2	Class 3B
1.06	Class 1	Class 4B	Class 1	Class 4B
0.96	Class 0	Class 5B	Class 0	Class 5B
0.87	Class 0	Class 5B	Class 0	Class 5B
0.77	Class 0	Class 5B	Class 0	Class 5B
0.67	Class 0	Class 5B	Class 0	Class 5B
0.58	Class 0	Class 5B	Class 0	Class 5B

Ultra-black coating with high light absorption can be used not only for optical devices but also in aerospace applications such as satellites. For aerospace applications, coatings will be exposed to vacuum and starkly bear the extreme environment, where the temperature may be more than 150 $^{\circ}\text{C}$ for long periods. When the satellites travel around the earth, the surface temperature will rise significantly where the equipment is

directly exposed to sunlight and will drop significantly when traveling through shadow areas [49]. Thus, the thermal cycling test was performed to simulate the space environment. The European Space Agency standard (ESA ECSS-Q-70-04A, 2008) and National Military standard of PRC (GJB 2052.8-2006) recommend a test where 100 heating-cooling ($100\text{ }^{\circ}\text{C}$ for heating and $-100\text{ }^{\circ}\text{C}$ for cooling) cycles are performed with a dwell time of 5 min. We performed the test strictly according to this standard. The samples were first placed in an oven at $100\text{ }^{\circ}\text{C}$ for 10 min and then transferred into a freezing pump at $-100\text{ }^{\circ}\text{C}$ within 10 s for another 5 min. This cycling was repeated 100 times. After the thermal cycling test, the surface states were examined using the naked eyes for flaking and using an optical microscope for morphological damage. As we expected, there was hardly any change in the morphology compared with initial samples, indicating good stability of coatings in extreme environments. Light absorption property (%R) and adhesion grade were also tested. The reflectance remained the same, while the adhesion slightly decreased in high PB ratios samples. The samples having PB ratios above 0.96 show the worse adhesion test results, while the others exhibit the class 0/ASTM class 5B adhesion (Table 1, Figure 9). The good adhesions in extreme cold and hot condition may be due to the moderate intramolecular flexibility of the polyurethane bond [50].

Figure 9. Typical adhesion test image of thermal cycling test of PB 0.96 samples. (a,c) Morphology and cross-cuts image before thermal cycling test. (b,d) Morphology and cross-cuts image after thermal cycling test.

4. Conclusions

In summary, in this study, we succeeded in preparing waterborne coatings composed of home-made activated CAs, which possess good adhesion and high optical absorption. In addition, the formulations for the preparation are commercially available and the process is reliable for large-scale production. The CAs were derived from resorcinol-formaldehyde resin (RFR) via sol-gel using a hydrothermal method, annealed, and reactivated using CO_2 . The ultra-black coatings of CAs comprising two-component waterborne polyurethane containing waterborne additives can be applied using different wet deposition methods, for example, spray coating, painting, and coil coating, which allow them to flatten and form a uniform film.

The adhesion properties and optical properties can be modified by adjusting the CAs/binder ratio, and we found the optimal ratio between absorption and adhesion to be 0.96. For the sample with the adhesion grade as class 0 after the thermal cycling test, an average reflectance of 2.1% within the visible and NIR regions was achieved.

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References

1. Korb, A.R.; Salisbury, J.W.; D'Aria, D.M. Thermal-infrared remote sensing and Kirchhoff's law: 2. Field measurements. *J. Geophys. Res. Solid Earth* **1999**, *104*, 15339–15350. [\[CrossRef\]](#)
2. Revzen, M.; Opher, R.; Opher, M.; Mann, A. Kirchhoff's theorem and the casimir effect. *Europhys. Lett.* **1997**, *38*, 245–248. [\[CrossRef\]](#)
3. Watts, C.M.; Liu, X.; Padilla, W.J. Metamaterial electromagnetic wave absorbers. *Adv. Mater.* **2012**, *24*, OP98–OP120. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Jones, A.C.; O'Callahan, B.T.; Yang, H.U.; Raschke, M.B. The thermal near-field: Coherence, spectroscopy, heat-transfer, and optical forces. *Prog. Surf. Sci.* **2013**, *88*, 349–392. [\[CrossRef\]](#)
5. Song, J.; Hao, X.P.; Yuan, Z.D.; Liu, Z.L.; Ding, L. Research of ultra-black coating emissivity based on a controlling the surrounding radiation method. *Int. J. Thermophys.* **2018**, *39*. [\[CrossRef\]](#)
6. Salimian, S.; Zadhoush, A.; Naeimirad, M.; Kotek, R.; Ramakrishna, S. A review on aerogel 3D nanoporous structured fillers in polymer-based nanocomposites. *Polym. Compos.* **2017**, *39*, 3383–3408. [\[CrossRef\]](#)
7. Jackson, J.J.; Poretzky, A.A.; More, K.L.; Rouleau, C.M.; Geohegan, D.B. Pulsed growth of vertically aligned nanotube arrays with variable density. *ACS Nano* **2010**, *4*, 7573–7581. [\[CrossRef\]](#)
8. Zhai, M.; Liu, Y.; Huang, J.; Wang, Y.; Chen, K.; Fu, Y.; Li, H. Efficient suspension plasma spray fabrication of black titanium dioxide coatings with visible light absorption performances. *Ceram. Int.* **2019**, *45*, 930–935. [\[CrossRef\]](#)
9. Xing, F.; Zhao, B.; Shi, W. Study on tunable fabrication of the ultra-black Ni-P film and its blacking mechanism. *Electrochim. Acta.* **2012**, *100*, 157–163. [\[CrossRef\]](#)
10. Hadobás, K.; Kirsch, S.; Carl, A.; Acet, M.; Wassermann, E.F. Reflection properties of nanostructure-arrayed silicon surfaces. *Nanotechnology* **2000**, *11*, 161–164. [\[CrossRef\]](#)
11. Steglich, M.; Lehr, D.; Ratzsch, S.; Käsebier, T.; Schrepel, F.; Kley, E.-B.; Tünnermann, A. An ultra-black silicon absorber. *Laser Photonics Rev.* **2014**, *8*, L13–L17. [\[CrossRef\]](#)
12. Wang, Y.F.; Fu, W.G.; Feng, M.; Cao, X.W. Investigation of the structure and the physical properties of nickel-phosphorus ultra-black surfaces. *Appl. Phys. A* **2007**, *90*, 549–553. [\[CrossRef\]](#)
13. Panagiotopoulos, N.T.; Diamanti, E.K.; Koutsokeras, L.E.; Baikousi, M.; Kordatos, E.; Matikas, T.E. Nanocomposite catalysts producing durable, super-black carbon nanotube systems: Applications in solar thermal harvesting. *ACS Nano* **2012**, *6*, 10475–10485. [\[CrossRef\]](#)
14. Zha, Z.; Yue, X.; Ren, Q.; Dai, Z. Uniform polypyrrole nanoparticles with high photothermal conversion efficiency for photothermal ablation of cancer cells. *Adv. Mater.* **2013**, *25*, 777–782. [\[CrossRef\]](#)
15. Jain, P.K.; Huang, X.; El-Sayed, I.H.; El-Sayed, M.A. Cheminform abstract: Noble metals on the nanoscale: Optical and photothermal properties and some applications in imaging, sensing, biology, and medicine. *Acc. Chem. Res.* **2007**, *41*, 1578–1586. [\[CrossRef\]](#)
16. Kaul, A.B.; Coles, J.B.; Eastwood, M.; Green, R.O.; Bandaru, P.R. Ultra-high optical absorption efficiency from the ultraviolet to the infrared using multi-walled carbon nanotube ensembles. *Small* **2013**, *9*, 1058–1065. [\[CrossRef\]](#)
17. De Rosa, I.M.; Sarasini, F.; Sarto, M.S.; Tamburrano, A. EMC impact of advanced carbon fiber/carbon nanotube reinforced composites for next-generation aerospace applications. *IEEE Trans. Electromagn. Compat.* **2008**, *50*, 556–563. [\[CrossRef\]](#)
18. Saxena, V.; Rani, R.U.; Sharma, A.K. Studies on ultra high solar absorber black electroless nickel coatings on aluminum alloys for space application. *Surf. Coat. Technol.* **2006**, *201*, 855–862. [\[CrossRef\]](#)
19. Arunnellaippan, T.; Rama Krishna, L.; Anoop, S.; Uma Rani, R.; Ramesbabu, N. Fabrication of multifunctional black PEO coatings on AA7075 for spacecraft applications. *Surf. Coat. Technol.* **2016**, *307*, 735–746.
20. Mousinho, A.P.; Mansano, R.D. Micropatterning of single-walled carbon nanotube forest. *Prog. Org. Coat.* **2011**, *70*, 326–329. [\[CrossRef\]](#)
21. Sun, Y.; Evans, J.; Ding, F.; Liu, N.; Liu, W.; Zhang, Y.; He, S. Bendable, ultra-black absorber based on a graphite nanocone nanowire composite structure. *Opt. Express* **2015**, *23*, 20115–20123. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Wilson, S.J.; Hutley, M.C. The Optical Properties of 'Moth Eye' Antireflection Surfaces. *Opt. Acta: Int. J. Opt.* **2010**, *29*, 993–1009. [\[CrossRef\]](#)
23. Yu, K.; Fan, T.; Lou, S.; Zhang, D. Biomimetic optical materials: Integration of nature's design for manipulation of light. *Prog. Mater. Sci.* **2013**, *58*, 825–873. [\[CrossRef\]](#)
24. Zhao, Q.; Fan, T.; Ding, J.; Zhang, D.; Guo, Q.; Kamada, M. Super black and ultrathin amorphous carbon film inspired by anti-reflection architecture in butterfly wing. *Carbon* **2011**, *49*, 877–883. [\[CrossRef\]](#)
25. Yang, Z.P.; Hsieh, M.L.; Wilthan, B.; Bur, J.A.; Ajayan, P.M.; Ci, L.; Lin, S.Y.; Hanssen, L.M. Experimental observation of extremely weak optical scattering from an interlocking carbon nanotube array. *Appl. Opt.* **2011**, *50*, 1850–1855. [\[CrossRef\]](#)

26. Azoubel, S.; Cohen, R.; Magdassi, S. Wet deposition of carbon nanotube black coatings for stray light reduction in optical systems. *Surf. Coat. Technol.* **2015**, *262*, 21–25. [[CrossRef](#)]
27. Sun, X.; Wei, Y.; Li, J.; Zhao, J.; Zhao, L.; Li, Q. Ultralight conducting PEDOT:PSS/carbon nanotube aerogels doped with silver for thermoelectric materials. *Sci. China Mater.* **2017**, *60*, 159–166. [[CrossRef](#)]
28. Wang, B.; Li, D.; Tang, M.; Ma, H.; Gui, Y.; Tian, X.; Quan, F.; Song, X.; Xia, Y. Alginate-based hierarchical porous carbon aerogel for high-performance supercapacitors. *J. Alloys Compd.* **2018**, *749*, 517–522. [[CrossRef](#)]
29. Zeng, F.Y.; Sui, Z.Y.; Liu, S.; Liang, H.P.; Zhan, H.H.; Han, B.H. Nitrogen-doped carbon aerogels with high surface area for supercapacitors and gas adsorption. *Mater. Today Commun.* **2018**, *16*, 1–7. [[CrossRef](#)]
30. Farhan, S.; Wang, R.; Jiang, H.; Li, K.; Wang, C. A novel combination of simple foaming and freeze-drying processes for making carbon foam containing multiwalled carbon nanotubes. *Ceram. Int.* **2016**, *42*, 8980–8989. [[CrossRef](#)]
31. Li, H.; Chen, Y.; Wang, P.; Xu, B.; Ma, Y.; Wen, W.; Yang, Y.; Fang, D. Porous carbon-bonded carbon fiber composites impregnated with SiO₂-Al₂O₃ aerogel with enhanced thermal insulation and mechanical properties. *Ceram. Int.* **2018**, *44*, 3484–3487. [[CrossRef](#)]
32. Sun, X.; Li, Y. Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 597–601. [[CrossRef](#)]
33. Pilch-Pitera, B.; Czachor, D.; Kowalczyk, K.; Pavlova, E.; Wojturski, J.; Florczak, Ł.; Byczyński, Ł. Conductive polyurethane-based powder clear coatings modified with carbon nanotubes. *Prog. Org. Coat.* **2019**, *137*, 105367. [[CrossRef](#)]
34. Sun, W.; Du, A.; Gao, G.; Shen, J.; Wu, G. Graphene-templated carbon aerogels combining with ultra-high electrical conductivity and ultra-low thermal conductivity. *Microporous Mesoporous Mater.* **2017**, *253*, 71–79. [[CrossRef](#)]
35. Guo, J.; Li, D.; Zhao, H.; Zou, W.; Yang, Z.; Qian, Z.; Yang, S.; Yang, M.; Zhao, N.; Xu, J. Cast-and-use super black coating based on polymer-derived hierarchical porous carbon spheres. *ACS Appl. Mater. Interfaces* **2019**, *11*, 15945–15951. [[CrossRef](#)]
36. Xie, P.; Sun, W.; Liu, Y.; Du, A.; Zhang, Z.; Wu, G.; Fan, R. Carbon aerogels towards new candidates for double negative metamaterials of low density. *Carbon* **2018**, *129*, 598–606. [[CrossRef](#)]
37. Sun, W.; Du, A.; Feng, Y.; Shen, J.; Huang, S.; Tang, J.; Zhou, B. Super black material from low-density carbon aerogels with subwavelength structures. *ACS Nano* **2016**, *10*, 9123–9128. [[CrossRef](#)]
38. Yu, Z.L.; Wu, Z.Y.; Xin, S.; Qiao, C.; Yu, Z.Y.; Cong, H.P.; Yu, S.H. General and straightforward synthetic route to phenolic resin gels templated by chitosan networks. *Chem. Mater.* **2014**, *26*, 6915–6918. [[CrossRef](#)]
39. Li, F.; Xie, L.; Sun, G.; Kong, Q.; Su, F.; Cao, Y.; Wei, J.; Ahmad, A.; Guo, X.; Chen, C.M. Resorcinol-formaldehyde based carbon aerogel: Preparation, structure and applications in energy storage devices. *Microporous Mesoporous Mater.* **2019**, *279*, 293–315. [[CrossRef](#)]
40. Pekala, R.W.; Alviso, C.T.; Kong, F.M.; Hulsey, S.S. Aerogels derived from multifunctional organic monomers. *J. Non Cryst. Solids* **1991**, *145*, 90–98. [[CrossRef](#)]
41. Illera, D.; Mesa, J.; Gomez, H.; Maury, H. Cellulose aerogels for thermal insulation in buildings: Trends and challenges. *Coatings* **2018**, *8*, 345. [[CrossRef](#)]
42. ISO 2409, Paints and Varnishes—Cross-cut Test. 2013.
43. ASTM Standard D 3359, *Standard Test Methods for Measuring Adhesion by Tape Test, Method A*; ASTM: Philadelphia, PA, USA, 2017.
44. Xu, Y.; Wang, S.; Yan, M.; Zhang, L.; Liu, Z. Synthesis, characterization and electrochemical properties of S-doped carbon aerogels. *Solid State Ionics* **2018**, *321*, 91–97. [[CrossRef](#)]
45. Xu, Y.; Ren, B.; Wang, S.; Zhang, L.; Liu, Z. Carbon aerogel-based supercapacitors modified by hummers oxidation method. *J. Colloid Interface Sci.* **2018**, *527*, 25–32. [[CrossRef](#)] [[PubMed](#)]
46. Li, X.; Liu, G.; Liu, S.; Ma, K.; Meng, L. The relationship between volatile fatty acids accumulation and microbial community succession triggered by excess sludge alkaline fermentation. *J. Environ. Manag.* **2018**, *223*, 85–91. [[CrossRef](#)]
47. Sing, K.S.W. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.* **1985**, *57*, 603–619. [[CrossRef](#)]
48. Xu, S.J.; Qiao, G.J.; Wang, H.J.; Li, D.C.; Lu, T.J. Preparation of mesoporous carbon derived from mixtures of phenol-formaldehyde resin and ethylene glycol. *Mater. Lett.* **2008**, *62*, 3716–3718. [[CrossRef](#)]
49. Bartosik, L.G.; Babel, H.W. Space environmental effects on spacecraft thermal control coatings. In *Proceedings of the Space Simulation Conference: Confirming Spaceworthiness Into the Next Millennium*, Albuquerque, NM, USA, 5–8 November 1990.
50. Li, M.; Qiang, X.; Xu, W.; Zhang, H. Synthesis, characterization and application of AFC-based waterborne polyurethane. *Prog. Org. Coat.* **2015**, *84*, 35–41. [[CrossRef](#)]