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# Absorption enhancement and shielding effect of brown organic coating on black carbon aerosols

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This study explores how the mixing structures and coating compositions of black carbon (BC) particles influence their light absorption, focusing on liquid-liquid phase separation (LLPS), which separates organic and inorganic phases and redistributes BC from the inorganic core (lcore) to the organic coating (Ocoating). Using transmission electron microscopy and 3D-modeling, we found that the BC core's position significantly impacts its light absorption. A BC core embedded within the lcore shows stronger light absorption at wavelengths below 600 nm compared to the same core in the Ocoating. When Ocoating is considered as brown carbon (BrC), it reduces BC core's light absorption at 350 nm due to shielding effect, but its overall impact on the entire BC particle is minimal (–3.0%  $\pm$  1.6%). The result indicates that in LLPS particles, the BrC coating primarily enhances light absorption, emphasizing the need to consider both mixing structures and coating compositions of BC in atmospheric models.

Black carbon (BC, also known as soot), emitted from incomplete combustion of biomass and fossil fuel, influence global climate by absorbing solar radiation, altering cloud properties, and accelerating the melt of ice cover<sup>1-3</sup>. Due to the strong light absorption and heating properties, BC became the major warming agent after greenhouse gases. The IPCC report "Climate Change 2021" showed that the effective radiative forcing of BC is +0.11 W m<sup>-2</sup> with the uncertainty ranges from -0.20 to +0.42 W m<sup>-2</sup> over the global<sup>4</sup>. Significant uncertainties are primarily attributed to size distributions, chemical compositions, and mixing states of BC particles, which depend on the chemical and microphysical evolution during atmospheric processes<sup>5-8</sup>. Climate models typically assume that BC particles are spherical and divide them into uncoated (external-mixing structure) or concentrically coated (core-shell structure)<sup>9</sup>. However, these simplified assumptions fail to effectively explain the observed optical properties of BC particles<sup>10-13</sup>, with uncertainties in light absorption enhancement (Eabs) ranging from 14% to 150%<sup>2,14,15</sup>. The reason is that the actual BC particles have three-dimensional agglomerates with tens to hundreds of monomers and their position embedded within the host particle is complicated, such as in the center or at the surface of host particle 16,17.

Recent advancements in BC morphology and its mixing structures have provided new insights into the complex interactions within

aerosols<sup>8,11,18</sup>. Once BC cores were internally mixed with other aerosols, their morphology became more compact, leading to significant changes in their optical properties and radiative forcing<sup>11,19,20</sup>. The coatings and embedding materials of BC particle were often considered as secondary inorganic matters (e.g., nitrates and sulfates). When BC cores are coated by these nonlight-absorbing aerosols, their  $E_{abs}$  fluctuates from 1.06 to  $3.5^{14,21}$  due to the "lensing effect". However, this assumption may not be true in ambient air, where abundant organics mixing with secondary inorganic species can be coating. Secondary organic aerosol (SOA) is a major component of PM2.5, contributing 30-77% of the total mass during heavy pollution events<sup>22,23</sup>. It is known that a large part of SOA behaves optical absorption in short wavelength (<400 nm) to near infrared, which has been called as secondary brown carbon  $(SOA_{BrC})^{24-26}$ . Some studies found the  $E_{abs}$  of BC core decreases due to the "shielding effect," as the light-absorbing coating blocks more photons from reaching the BC core<sup>27–29</sup>. Lack et al.<sup>30</sup> showed that the shielding effect can reduce the Eabs by 25% across the visible spectrum, and specifically by 40% at 400 nm. They also found that coating thickness or imaginary part of complex refractive index (RI) of the BrC control their shielding effect<sup>28,31</sup>. However, previous studies primarily focused on the core-shell structure and assumed the coating to be light-absorbing materials

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to account for shielding effects. This assumption cannot reflect the real mixing structure of BC and  $SOA_{BrC}$  in the atmosphere.

Many studies well recognized inorganic and organics coatings on BC particles in ambient air<sup>16,32,33</sup>. Under relative humidity (RH) < 90%, the unique phenomenon of liquid-liquid phase separation (LLPS) that organic and inorganic species separating in individual particles can frequently occur in ambient air<sup>34</sup>. Recent studies found that the LLPS can further cause BC redistribution in individual particles<sup>32,34</sup>. In other words, position of BC within individual particles responses to the LLPS, driven by its higher affinity for the nonpolar organic phase compared to the electrolytic inorganic phase<sup>34</sup>. The scientific question here is: how are the optical properties of BC influenced by double-layers coating (hereinafter referred to as LLPS) and BC redistribution? Zhang et al.<sup>32</sup> showed that the optical absorption of the LLPS increased 8.2–9.4% compared with core-shell structure. Furthermore, BC redistributing from inorganic to organic coating reduced 28–34% of light absorption at 550 nm<sup>32</sup>. Until now, no study has examined the coating mixture of inorganic and brown organic aerosols (i.e., SOA<sub>BrC</sub>).

In this study, we analyzed transmission electron microscope (TEM) images of individual particles to determine the actual mixing structures between BC and SOA in ambient air. A novel 3D modeling approach (Electron-Microscope-to-BC-Simulation, EMBS<sup>11</sup>) was employed to measure how the different microphysical properties (i.e., variations in BrC coating thickness and the position of BC) influence the optical absorption of aged BC particles. Based on the unique phenomenon of LLPS, our study aims to investigate the optical properties of actual mixing structures of BC/ inorganic/organic during atmospheric aging. The focus is primarily on the shielding effects of SOA<sub>BrC</sub> on aged BC particles with LLPS.

#### Results

#### Optical properties of BC coated by non-light-absorbing SOA

The LLPS significantly influences the microstructure of aerosol particles by separating organic from inorganic materials, which even redistributes BC from the Icore (Fig. 1A-iii) to the Ocoating (Fig. 1A-iv). The BC redistribution significantly alters the optical absorption of aged BC particles, reducing light absorption by 28–34% at 550 nm<sup>32</sup>. Figure 1A shows these transformations through four distinct mixing structures: BC, CS, PS-CS,

and R-CS models. To understand the non-light-absorbing SOA (SOA<sub>clean</sub>)/SOA<sub>BrC</sub> effects on light absorption of individual particles, three various thicknesses—thin, moderate and thick—were applied to both PS-CS (1.2, 7.0 and 12.8 nm) and R-CS (69.6, 139.2 and 208.8 nm) models.

While our study fixed BC morphology to isolate the effects of LLPS, previous study has shown that BC particles undergo morphological compaction during atmospheric aging<sup>35</sup>. Specifically, the capillary forces, induced by the interaction of BC with liquid coating, can lead to the compaction of BC aggregates<sup>36</sup>. This restructuring, driven by the surface tension of the coating material, reduces the voids between monomers, potentially altering the internal structure of the BC aggregates and influencing their optical properties. Therefore, future work should explore how surface tension gradients, induced by phase separation, might further influence BC morphology and its subsequent optical behavior.

The Absorption Ångström Exponent (AAE) reflects how light absorption of aerosol varies with wavelength<sup>37</sup>. Here we adopted wavelength at 400 nm as the starting point, which is commonly used in field observations of aerosol optical properties<sup>30</sup>. Figure 1B displays the variations of the AAE from 400–700 nm across four particle structures with the increased SOA thicknesses. For the CS structure, the AAE increased by 45.2% compared with the bare BC. When CS is coated by SOA<sub>clean</sub>, the AAE of PS-CS particle is positively correlated with the coating thickness, resulting in an increase of 45.9%–50.6% compared to BC. When BC is redistributed in organic coating, its AAE exhibits a reduction ranging from 37.6% to 91.9% compared to that of PS-CS particles.

The R-CS<sub>moderate</sub> particle, which experiences the most significant reduction in AAE, has an AAE that is only 12% of that of bare BC particle. Figure 1B shows that BC core coated by the sulfate or multi-coatings of sulfate and SOA<sub>clean</sub> increase the AAE, suggesting that the difference of light absorption between short and long wavelengths becomes greater. On the contrary, BC core embedded in organic coating shows one minimal AAE, suggesting that the BC redistribution either blocks short-wave absorption or enhances long-wave absorption, thereby equalizing light absorption across 400–700 nm and reducing AAE.

Once the ratio of SOA coating thickness to BC core size  $(T_{OD}/D_{BC})$  is greater than  $0.24^{32}$ , the BC redistribution due to LLPS can be observed. To





and hollow columns indicating the scenario of SOA<sub>clean</sub> and SOA<sub>BrC</sub>, respectively. C The absorption cross sections of PS-CS<sub>moderate</sub> and R-CS<sub>moderate</sub> models.  $\Delta C_{abs}$  are designed to eliminate intrinsic absorption of SOA<sub>BrC</sub>.

confirm how this impact of BC position changes its optical absorption, we compared the light absorption of PS-CS<sub>moderate</sub> and R-CS<sub>moderate</sub> particles across 350-700 nm. The dashed line shown in Fig. 1C represents the scenario where the SOA does not absorb radiation. The light absorption of R-CS particle is weaker than that of PS-CS particle in the near ultraviolet band, amounting for only 84.5% of PS-CS at 400 nm. Meanwhile, the light absorption of R-CS particle at 700 nm is 1.7 times that of PS-CS particle (Fig. 1C). This Cabs change trend of R-CS particle is similar to that of "bull horn", which leads to a notably smaller difference in the light absorption of R-CS particle between 400 nm and 700 nm compared to the PS-CS particle (Fig. 1C). The result confirms our conjecture that the BC redistribution blocks short-wave absorption and enhances long-wave absorption. The Cabs of PS-CS and R-CS particles intersect at approximately 580 nm (Fig. 1C). This indicates that the light absorption of BC core centered in Icore is stronger below 600 nm, while the light absorption of BC core in the Ocoating is slightly enhanced above 600 nm.

Figure 2A shows the  $E_{abs}$  of CS, PS-CS and R-CS particles in the SOA<sub>clean</sub> scenario. The structures of CS and PS-CS particles show no significant difference, and thereby their  $E_{abs}$  for CS and PS-CS<sub>thin</sub> should be same (Fig. 2A). For the three thicknesses of R-CS particles, an enhanced trend of light absorption is observed above 600 nm. The result shows that entire BC particle exhibits stronger light absorption in the larger wavelength when BC core is located in organic coating. Figure 2C illustrates that the average  $E_{abs}$  of R-CS particles with three different thickness at short wavelengths is lower than them of CS and PS-CS structures. The comparison further confirms our above consumption that the BC redistribution reduces its light absorption at short wavelengths.

#### Optical properties of BC coated by light-absorbing SOA

The above section explored the optical properties of the four mixing structures coated by  $SOA_{clean}$ . When we consider SOA as light-absorbing secondary BrC ( $SOA_{BrC}$ ), how does the  $SOA_{BrC}$  change the optical properties of BC?

The presence of  $\rm SOA_{BrC}$  that strongly absorbs near-ultraviolet light results in higher AAE values for PS-CS and R-CS particles (Fig. 1B). Moreover, the AAE increases significantly as the increased thickness of SOA\_{BrC}. The AAE values of CS, PS-CS, and R-CS structures are 1.3, 1.5  $\pm$  0.2, and 3.7  $\pm$  1.0, respectively. This increased AAE suggests that more BrC leads to a greater AAE.

Figure 1C in above section shows the variation of light absorption across the visible spectrum, controlled by the lensing effect at different BC positions. When SOA is light-absorbing BrC, its light-absorbing contribution contains the lensing/shielding effect and the intrinsic light absorption of BrC itself. To focus on how the BC position affects light absorption, it is necessary to eliminate the intrinsic light absorption of SOA<sub>BrC</sub>. For this purpose, we define  $\Delta C_{abs}$  as the difference between the  $C_{abs}$  of PS-CS and R-CS particles and their corresponding particles without BC core ( $\Delta C_{abs}$  in Fig. S1). In other words,  $\Delta C_{abs}$  represents the absorption cross-section attributed solely to the lensing/shielding effect while the intrinsic light absorption of BrC was removed. By comparing the  $\Delta C_{abs}$  of the SOA<sub>BrC</sub> scenario with the  $C_{abs}$  of the SOA<sub>clean</sub> scenario, we can better understand the specific impact of the shielding effect of SOA<sub>BrC</sub>.

For PS-CS particles, the light absorption decreases by 1.8% at 350 nm due to the  $SOA_{BrC}$ , suggesting the shielding effect of BrC coating. We noticed that the shielding effect of  $SOA_{BrC}$  on PS-CS particle is almost negligible at wavelengths greater than 400 nm. This result is consistent with the findings of Lack et al.<sup>30</sup>, who observed that the optical behavior of thin  $SOA_{BrC}$  were more like  $SOA_{clean}$  as the wavelength increases. For R-CS particles, the shielding effect of BrC is more efficient at wavelengths below 500 nm, with the largest decline of 49.8% occurring at 350 nm. The result is similar to 50% at 400 nm reported by Lack et al.<sup>30</sup>.

Figure 2B, D shows that the light absorption enhancement of BrC coating highly depends on wavelength. For wavelength at 350 nm, the R-CS<sub>thick</sub> model exhibits a  $E_{abs}$  peak at 42.0, which exceeds the range of 3.0–5.0 from PS-CS particles and 2.9 from CS particles. The thick BrC coating undoubtedly becomes the main source of light absorption of R-CS



Fig. 2 | Absorption enhancement ( $E_{abs}$ ) of BC particle coated by different types of SOA. The  $E_{abs}$  of BC particle coated by SOA<sub>clean</sub> (A), SOA<sub>BrC</sub> (B), average  $E_{abs}$  of BC particle coated by SOA<sub>clean</sub> (C) and SOA<sub>BrC</sub> (D). The average  $E_{abs}$  is calculated

across three different thicknesses of both PS-CS and R-CS particles. The circles from small to large indicate the thickness of SOA from thin, moderate to thick, respectively.

particles at 350 nm. With the increase of wavelength, the light absorption of R-CS particles is reduced by 90% at 600 nm, with the most significant reduction between 350 nm and 450 nm (74% reduction) (Fig. 2D). Following the wavelength >600 nm, there is negligible contribution from BrC coating thickness to light absorption of individual particles, and the E<sub>abs</sub> of CS, PS-CS and R-CS particles are all close to  $2.7 \pm 0.7$  (Fig. 2B).

# Light absorption of BC, BrC and lensing/shielding effect in LLPS particles

The sections above examine the impact of SOA thickness, BC position, and  $SOA_{BrC}$  coating on light absorption of entire BC particles during the LLPS. However, AAE and  $\Delta C_{abs}/C_{abs}$  are both influenced by multiple light-absorbing components within each particle. To clarify the contribution of each component, we adopted the calculation method described in Section "Optical absorption of aged BC particles". This method distinguishes the intrinsic light absorption of BC core and  $SOA_{BrC}$  themselves, as well as the lensing or shielding effects of sulfate and  $SOA_{clean}/SOA_{BrC}$ .

For SOA<sub>clean</sub> scenario, there are lensing effects of sulfate and SOA<sub>clean</sub> and BC core (Fig. 3A). Because SOA<sub>clean</sub> and sulfate are non-light-absorbing materials, the light-absorbing contribution of CS and PS-CS structures are highly similar. Therefore, CS and PS-CS structures both exhibit a higher proportion of lensing effect (red bar) at wavelength below 600 nm, at 63.8% and 64.5%, respectively (Fig. 3A). It should be noted that lensing effects are significantly reduced at wavelength above 600 nm, with 57.1% and 56.9% of CS and PS-CS, respectively (Fig. 3A). In conclusion, the phase separation does not significantly alter the lensing effect of LLPS particles in the SOA<sub>clean</sub> scenario.

However, when BC redistributes, it has an obvious decrease on the light absorption of LLPS particles. Compared with CS and PS-CS models, light absorption of R-CS<sub>thin</sub> model is reduced by 48.6% and 47.5%, respectively (Table S3). The reason may be related to the sudden drop of lensing effect caused by BC redistributing to the thin SOA<sub>clean</sub> coating (Table S4). Figure 3A demonstrates that the R-CS<sub>thin</sub> particles are the only structure predominantly influenced by BC core, the average contributions of BC core exceeding 50% across 350–700 nm. Unlike the other structures, the R-CS<sub>thin</sub> particles exhibit distinct light absorption characteristics that the contribution of lensing effect is unstable, reaching a minimum of 19.8% at 350 nm and a maximum of 57.4% at 550 nm (Fig. 3A). As the SOA<sub>clean</sub> coatings become thicker, the lensing effect of  $R-CS_{moderate}$  and  $R-CS_{thick}$  model contributes more than 64.2% like as that of CS and PS-CS models. This result indicates that the lensing effect is more influenced by coating thickness than by the BC position, whether it is located at the outer Ocoating or the inner Icore.

Figure 3B displays the contribution of each light-absorbing component in the scenario of  $SOA_{BrC}$ . Due to the absence of  $SOA_{BrC}$ , the contribution of light absorption in the CS structure remains unchanged and is the same as in the  $SOA_{clean}$  scenario. As  $SOA_{BrC}$  appears and gradually thickens, its lightabsorbing contribution in the ultraviolet band becomes significant. At the wavelength of 350 nm, the contribution of  $SOA_{BrC}$  in PS-CS particles increases from 5.2% to 49.5% as the  $SOA_{BrC}$  coating becomes thicker (Fig. 3B). For the R-CS structure, the contribution of  $SOA_{BrC}$  remains even above 96.3% at 350 nm. However, when the wavelength increases, the light absorption of  $SOA_{BrC}$  diminishes, with contributions in PS-CS<sub>thick</sub> and R-CS<sub>thick</sub> particles dropping to less than 0.11% and 4.6% at 700 nm, respectively (Fig. 3B).

Previous studies confirmed the shielding effect of light-absorbing coating in CS structure<sup>27-30</sup>. Our study found that the shielding effect in LLPS particles is more complex. A net shielding effect under the coating of sulfate and SOA<sub>BrC</sub> in the LLPS particles simultaneously required a sufficiently thick BrC coating and near-ultraviolet wavelengths. We found that the net shielding effect occurs only at 350 nm when the thick coating of  $SOA_{BrC}$ induces BC redistribution (i.e., R-CS structures). Figure 1C illustrates that the shielding effect of BrC coating in R-CS can reduce light absorption of BC core by 49.8% at 350 nm. Accounting for the light absorption of BrC itself and BC core, the contribution of BrC shielding effect to R-CS particles is merely  $-3.0\% \pm 1.6\%$ . In other words, the primary light absorption effect of BrC coating in individual particles is to enhance light absorption, while the shielding effect is only a "side effect". This suggests that atmospheric models should incorporate the light absorption of BrC, as well as the enhancement in light absorption caused by the mixing structure of BC and BrC. Moreover, the  $\mathrm{SOA}_{\mathrm{BrC}}$  in R-CS particles with the coating thickness at 69.6 nm, 139.2 nm, and 208.8 nm has similar shielding effects, with  $C_{abs}$  at  $-0.83 e^{-2}$  $\mu$ m<sup>2</sup> (Fig. S2). To further verify the robustness of our conclusions, we conducted sensitivity analyses on both BC core size (considering additional scenarios of 58 nm and 88 nm alongside the originally modeled 116 nm) and the complex refractive index of BrC (introducing a highly light-



**Fig. 3** | **The contributions of light-absorbing components within individual BC particles.** For SOA<sub>clean</sub> scenario (**A**) including BC core and lensing effect; For SOA<sub>BrC</sub> scenario (**B**) including BC core, BrC, lensing effect, and shielding effect.

Individual particles with increasing  $SOA_{clean}$  (**A**) and  $SOA_{BrC}$  (**B**) thickness clockwise. Each segment represents wavelengths from 350–700 nm. " $\blacktriangle$ " in **B** indicates the present of shielding effect (black column below 0).

absorbing BrC coating scenario in addition to the  $\mathrm{SOA}_{\mathrm{BrC}}$  and  $\mathrm{SOA}_{\mathrm{clean}}$  scenarios.

The shielding effect of BrC coating on BC cores of varying sizes

We conducted sensitivity analyses to evaluate the shielding effect of BrC coating on BC cores of varying sizes. The results indicate that as the BC core size decreases, the shielding effect becomes more pronounced at shorter wavelengths, particularly in R-CS<sub>thick</sub> particles (Tables S5 and S6). This is attributed to the relatively thicker BrC coating surrounding smaller BC cores (Fig. S3, using R-CS<sub>thick</sub> particles as an example), which enhances the occurrence of the shielding effect.

However, despite these variations, the overall magnitude of the shielding effect remains relatively stable. The shielding effect exhibits only minor fluctuations, ranging from  $-3.0\% \pm 1.6\%$  for BC<sub>ESD</sub> = 116 nm to  $-1.4\% \pm 1.3\%$  for BC<sub>ESD</sub> = 88 and 58 nm (Tables S5 and S6). These findings reinforce the conclusion that the primary role of BrC coatings in LLPS particles is to enhance light absorption rather than significantly contribute to the shielding effect.

# Impact of light absorption of BrC coating on its shielding effect

To explore the role of BrC coatings with varying complex refractive indices, we introduced a highly light-absorbing SOA scenario. The results indicate that the shielding effect primarily occurs in redistributed (R-CS) particles, consistent with the findings from the weakly light-absorbing SOA (SOA<sub>BrC</sub>) scenario. The maximum shielding effect remains limited to -4.9% at 350 nm and gradually diminishes with increasing wavelength, eventually transitioning into a lensing effect.

Furthermore, highly light-absorbing BrC coatings in LLPS particles consistently dominate light absorption, contributing more than 89.3% at wavelengths below 500 nm. Although minor variations in the refractive index introduce slight differences in the shielding effect at shorter wavelengths, the overall conclusion remains robust: BrC coatings in LLPS particles primarily enhance light absorption rather than significantly contributing to the shielding effect.

Results from Sections "The shielding effect of BrC coating on BC cores of varying sizes" and "Impact of light absorption of BrC coating on its shielding effect" confirm that while these factors may slightly influence the occurrence of the shielding effect, the magnitude of the shielding effect remains stable, reinforcing the conclusion that BrC coatings in LLPS particles primarily enhance light absorption. These findings suggest that the net contribution of the shielding effect may be less significant than previously reported in the core-shell structure of individual particles containing BC, inorganic components, and secondary BrC.

#### Discussion

In this study, we classified four typical structures (e.g., bare BC, core-shell, phase-separated core-shell and redistributed) in LLPS particles to explore their subtle impact on the optical properties of individual BC-containing particles. The size distributions and RIs of BC, sulfate,  $SOA_{clean}$  and  $SOA_{BrC}$  were used to build mixing structures of BC-containing particles and further calculate their optical properties.

Our study shows that the BC position in individual particles significantly influences light absorption of BC. In CS and PS-CS models, the AAE is 1.33–1.39 across the 400–700 nm when BC core is situated within the Icore. The light absorptions of both CS and PS-CS decrease following the increased wavelength. However, AAE exhibits a minimal value at 0.11–0.85 when BC core is embedded within the Ocoating. The variation trend of light absorption of the R-CS structure resembles that of a "bull horn", where  $\rm C_{abs}$  initially decreases and then increases as the wavelength increases. This result suggests that BC distribution blocks short-wave absorption while enhancing longwave absorption. Therefore, BC core within the Icore and Ocoating exhibits higher light absorption below and above 600 nm, respectively.

The variation of BC-containing particle's light absorption arises from lensing effects of sulfate and SOA<sub>clean</sub>, suggesting the lensing effect contributes the majority of their light absorption for CS and PS-CS particles. We also found that transition from the PS-CS to the R-CS<sub>thin</sub> structure leads to significant fluctuations of light absorption with the contribution of lensing effect from 19.8% at 350 nm to 57.4% at 550 nm.

We introduce a scenario of light-absorbing SOA to discuss the impact of BrC coating on light absorption of LLPS particles. The shielding effect decreases light absorption by 1.8% at 350 nm in PS-CS model (Fig. 4). The optical behavior of thin  $SOA_{BrC}$  is more like  $SOA_{clean}$  and the shielding effect become more negligible above 400 nm. Following the increased thickness of  $SOA_{BrC}$ , it becomes the major contribution of light absorption. The highest  $E_{abs}$  of R-CS structure is up to 12 times at wavelength of 350 nm compared with CS structure. Meanwhile, the BrC coating significantly reduces light absorption of BC core by 49.8% at 350 nm in R-CS structure (Fig. 4). Therefore, the interaction between BC and BrC mixtures is more intricate than the previous reports, and the core-shell model alone is

Fig. 4 | A schematic diagram showing the variation of the averaged light absorption enhancement (Eabs) of aged BC particles during LLPS. In the SOA<sub>clean</sub> scenario, LLPS increases the light absorption of CS particle by 1.2%. Conversely, BC redistribution decreases the light absorption of PS-CS particle by 4.2%. Compared to the CS structure, the BrC coating increases the E<sub>abs</sub> of PS-CS and R-CS particles by 8.8% and 223%, respectively, in the SOABrc scenario. Meanwhile, the shielding effect of the BrC coating reduces the light absorption of BC core by 1.8% and 49.8% in PS-CS and R-CS particles at 350 nm, respectively. Whether SOA is BrC or not, PS-CS particle has higher light absorption below 600 nm, while R-CS particle absorbs more radiation above 600 nm.



#### Methods

#### Sample collection and microscopic analyses

Aerosol particle samples were collected from four distinct locations to capture a range of environmental conditions. These included Mount Wudang in central China (32°23'N, 111°02'E), at 862 meters, rural areas in northeastern China—Tongyu, Jilin (44°25'N, 122°52'E), and Yucheng, Shandong (36°57'N, 116°36'E) and a polar site in the Svalbard Arctic Ocean (78°550'N, 11°560'E). Detailed sampling data, meteorological conditions, and other relevant information for each location are documented in Table S1.

Individual particle samples were collected onto copper TEM grids coated with a carbon film using a sampler at a flow rate of 1.0 L min<sup>-1</sup>. These TEM grids were analyzed using a JEM-2100 TEM (by JEOL, Japan) equipped with an energy-dispersive X-ray spectrometry system (EDS, by Oxford Instruments, U.K.). TEM analysis showed morphology and mixing states of individual aerosol particles, while the EDS system provided the details of elemental composition and the proportional weights of these elements.

#### Shape model generation and optical calculation

The LLPS may occur in aged BC particles containing organic/inorganic aerosols under the RH < 90%. This process may result in BC redistribution, which migrates BC toward the organic phase. Zhang et al.<sup>32</sup> found that the ratio of SOA coating thickness to BC core size ( $T_{OD}/D_{BC}$ ) influences the BC redistribution. When  $T_{OD}/D_{BC}$  is 0.24–1.8, most BC cores locate in organic coating (named as Ocoating). Conversely, most BC cores locate in inorganic cores (named as Icore) under the  $T_{OD}/D_{BC} < 0.12$ . Here, we used the  $T_{OD}/D_{BC}$  of 0.01–0.12 and 0.24–1.8 for modeling BC-in-Icore and BC-in-Ocoating particles, respectively.

TEM identified four LLPS structures of individual BC particle (Table 1): bare BC model, basic core-shell model (CS, BC within the Icore without Ocoating), phase-separated core-shell model (PS-CS, BC within the Icore), and redistributed model (R-CS, BC within the Ocoating). Our study categorized three thicknesses (thin, moderate, and thick) of the Ocoating for both the PS-CS ( $T_{OD}/D_{BC} = 0.01, 0.06$ and 0.11, respectively) and R-CS model  $(T_{OD}/D_{BC} = 0.6, 1.2 \text{ and } 1.8,$ respectively). Except the SOA thickness, the diameters of BC core and sulfate core kept constant, set as 116 nm<sup>32</sup> and 432 nm<sup>32</sup>, respectively (the above diameters are all equivalent spherical diameters, ESD). To isolate the effects of LLPS-induced coating properties and BC redistribution on the optical properties of BC particles, we also fixed the fractal dimension of BC to 2.16<sup>35</sup> in all simulations. This approach ensures that the observed optical changes are directly attributable to LLPS effects, without interference from potential morphological changes in the BC core that could independently influence light absorption.

Luo et al.<sup>38</sup> indicated that variations in the imaginary RI of BC across different bands can be negligible. Consequently, this study assigned a constant value of  $0.71^{39}$  to the imaginary RI of BC, while the RI of SOA<sub>BrC</sub> varies at different wavelengths (for more details, see Table S1).

This EMBS model enables the flexible creation of aged BC particles including complex morphologies and mixing structures to efficiently compute their optical properties under the incident light wavelengths ( $\lambda$ ). The DDA model is critical to maintain the condition |m|kd < 0.5, where "m" is the RI and "k" is  $2\pi/\lambda$ . To ensure accuracy within DDA, the dipole size used in this study is maintained well below the size of a monomer. Further details on this methodology are available in Wang et al.<sup>11</sup>.

#### Optical absorption of aged BC particles

When SOA is not light-absorbing and acts as scattering material (hereinafter called SOA<sub>clean</sub>), the  $E_{abs}$  is calculated as:

$$E_{abs\_all} = \frac{C_{abs\_BC+lens}}{C_{abs\_BC}} \tag{1}$$

where  $E_{abs\_all}$  is the sum of all light-absorbing components of individual particle including BC core, lensing effect of Icore and SOA<sub>clean</sub>.  $C_{abs\_BC}$  is absorption cross section for fresh BC core without any coating.  $C_{abs\_lens}$  is light absorption of lensing effect.

The contributions of BC and lensing effect of Icore and SOA<sub>clean</sub> are as follow:

$$f_{abs\_BC} = \frac{C_{abs\_BC}}{C_{abs\_BC+lens}}$$
(2)

$$f_{abs\_lens} = \frac{C_{abs\_lens}}{C_{abs\_BC+lens}}$$
(3)

For the scenario of  $SOA_{BrC}$ , there are two different versions of  $E_{abs}$  which refer to Lack et al.<sup>40</sup> (Fig. S1 provides a visual representation of formula 4 and 5):

$$E_{abs\_all} = \frac{C_{abs\_BC+lens/shield+SOA_{BrC}}}{C_{abs\_BC}}$$
(4)

$$E_{abs\_NoSOA_{BrC}} = \frac{C_{abs\_BC+lens/shield+SOA_{BrC}} - C_{abs\_SOA_{BrC}}}{C_{abs\_BC}}$$
(5)

In these equations, where  $E_{abs\_all}$  is the sum of all light-absorbing components of individual particle including BC core, lensing or shielding effect of Icore and SOA<sub>BrC</sub> and the intrinsic absorption of SOA<sub>BrC</sub>. It's worth noting that the lensing and shielding effects discussed in our study refer to the combined influence of sulfate and SOA, resulting in net enhancement or attenuation of light absorption.  $E_{abs\_NOSOA (BrC)}$  means the whole individual particle except the intrinsic absorption of SOA<sub>BrC</sub>. C<sub>abs\\_BC</sub> + lens/shield + SOA (BrC) denotes the absorption cross-section of BC core coated with sulfate and SOA<sub>BrC</sub>. C<sub>abs\\_SOA (BrC)</sub> is the light absorption of PS-CS and R-CS structures without BC core, which represents the intrinsic absorption of SOA<sub>BrC</sub>.

To identify the light absorption contribution of each component in the individual particle, the calculation of absorption cross-section and corresponding fraction as follow:

$$C_{abs\_lens/shield + SOA_{ReC}} = (E_{abs\_all} - 1) \times C_{abs\_BC}$$
(6)

Formula (6) means the absorption cross-section of sulfate and  $\rm SOA_{BrC}$ , including the net lensing or shielding effect and intrinsic absorption of  $\rm SOA_{BrC}$ .

$$C_{abs\_lens/Shield} = (E_{abs\_noSOA_{BrC}} - 1) \times C_{abs\_BC}$$
(7)

This equation means the net lensing/shielding effect of sulfate and  $\mathrm{SOA}_{\mathrm{BrC}}$ 

$$f_{abs\_BC} = \frac{C_{abs\_BC}}{C_{abs\_all}}$$
(8)

$$f_{abs\_ens/shield} = \frac{C_{abs\_ens/shield}}{C_{abs\_all}}$$
(9)

$$f_{abs\_SOA_{BiC}} = 1 - f_{abs\_BC} - f_{abs\_lens/shield}$$
(10)

These equations mean the fraction of absorption due to BC, net lensing/shielding effect, and intrinsic absorption of  $SOA_{BrC}$ , respectively.

#### Table 1 | Morphological parameters and schematic representation of different particles with the LLPS

Structures	SOA thickness (nm)	T <sub>OD</sub> /D <sub>BC</sub>	Particle diameter (nm)	BC location	Schematic diagram
BC	None	-	116	Icore	-
CS	None	-	432	Icore	and the second s
PS-CS <sub>thin</sub>	1.2	0.01	434.3	Icore	
PS-CS <sub>moderate</sub>	7.0	0.06	445.9	Icore	
PS-CS <sub>thick</sub>	12.8	0.11	457.5	Icore	
R-CS <sub>thin</sub>	69.6	0.6	571.2	Ocoating	
R-CS <sub>moderate</sub>	139.2	1.2	710.4	Ocoating	
R-CS <sub>thick</sub>	208.8	1.8	849.6	Ocoating	9989 9999

#### Sensitivity analysis of BrC coating on BC cores of varying sizes

Observations indicate that BC particles can reach diameters as large as 300 nm, with some studies even reporting coarse BC particles exceeding 1 µm<sup>41,42</sup>. However, such large particles are typically removed efficiently during long-range transport through dry and wet deposition. In contrast, LLPS primarily occurs in humid environments with abundant organic and inorganic components, such as background sites where aerosols have undergone atmospheric aging. Smaller BC particles, due to their higher surface area-to-volume ratio, exhibit a greater tendency to interact with organic coatings. Field measurements of LLPS phenomenon further confirm that BC cores with diameters below 240 nm are more likely to redistribute from the inorganic core to the organic coating<sup>32</sup>, with a dominant BC core size of 116 nm observed at rural sites<sup>32</sup>.

Based on these observations, this study assumes a BC core diameter of 116 nm to align with real-world conditions and accurately assess the influence of secondary organic coatings within the LLPS particle. To further investigate the effect of BC core sizes on optical properties, additional sensitivity analyses were conducted, considering BC core sizes of 58 nm (50% of 116 nm) and 88 nm (~75% of 116 nm) in addition to the originally modeled 116 nm.

#### Sensitivity analysis of the shielding effect of BrC coating with varying complex refractive indices

To assess the impact of BrC coatings with different light-absorbing properties, we introduced a new scenario of highly light-absorbing SOA, in addition to the two scenarios from the original study—weakly light-absorbing SOA (SOA<sub>BrC</sub>) and non-light-absorbing SOA (SOA<sub>clean</sub>)— forming three distinct scenarios. By varying the complex refractive index parameters, we systematically investigated the shielding effect of BrC coatings on BC particle.

Table S2 summarizes the complex refractive indices of SOA across different wavelengths, where the "higher absorption" scenario corresponds to the newly introduced highly light-absorbing SOA scenario.

Given that secondary BrC is generally weaker in light absorption than BC and considering other sensitivity analyses on LLPS microphysical parameters (e.g., BC position and SOA coating thickness), the highly light-absorbing SOA scenario was ultimately excluded. For the light absorption of BrC coating, only the weakly light-absorbing (SOA<sub>BrC</sub>) and non-light-absorbing (SOA<sub>clean</sub>) scenarios were retained. This decision is further supported by the observation that the shielding effect trends and magnitudes remained similar between the two lightabsorbing SOA scenarios, reinforcing the conclusion that BrC coatings in LLPS particles mainly enhance light absorption rather than acting as a significant shielding shell.

#### Data availability

The data for figures are available on figshare at https://doi.org/10.6084/m9. figshare.27013879.v1. For EMBS, refer to https://doi.org/10.1029/ 2021JD034620. All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Information. Received: 28 September 2024; Accepted: 1 March 2025; Published online: 13 March 2025

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Article

W.L. and Z.Z. conceived the study, led the overall scientific questions, and wrote the manuscript. Z.Z. conducted the optical calculations. Z.Z. and W.L. contributed the data analysis. Y.W., X.C., L.X., Z.Z., J.C., S.Z., D.L. and W.L. reviewed and commented on the paper.

### **Competing interests**

The authors declare no competing interests.

# Additional information

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