Nonlinear Enhancement of Radiative Absorption by Black Carbon in Response to Particle Mixing Structure

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Abstract Black carbon (BC) strongly absorbs solar radiation, contributing to global warming. Absorption enhancement of BC particles is difficult to quantify due to an inadequate representation of their complex morphology and mixing structures, as well as interaction with radiation. Here, we apply a 3D method accounting for detailed BC mixing structures to predict the absorption enhancement of individual BC particles ($E_{abs}$) and the total BC particle population ($E_{abs,bulk}$). The diverse range of mixing structures in individual BC particles leads to variable $E_{abs}$ that could hardly be predicted by empirical approximations. We find that the volume proportion of the BC embedded in coating ($F$) determines $E_{abs}$ when the particle to BC core diameter ratio ($D_p/D_c$) is larger than 2.0. Our findings reveal the potential mechanism behind the differences in observed and modeled $E_{abs,bulk}$. The framework builds a bridge connecting the microscopic mixing structure of individual BC particle with $E_{abs,bulk}$.

Plain Language Summary Absorption by black carbon (BC) in the atmosphere strongly affects radiative balance and global climate. The large discrepancies in observed and modeled BC absorption enhancements raise a hot debate. Through applying a new 3D shape model based on electron microscope observations, we propose a new framework that estimates BC absorption enhancement through accounting for mixing structure diversity in individual particles. Our results reveal that the diverse range of mixing structures in individual particles in ambient air leads to complex absorption enhancement that could hardly be predicted by the empirical approximation. The bulk absorption enhancements based on diverse mixing structures provide an explanation for the globally disparate results from laboratory and field observations. The new framework linking microphysical structures to bulk BC optical properties can be used to improve assessment of climate impact.

1. Introduction

Black carbon (BC) aerosol strongly absorbs solar radiation and hence warms the atmosphere (Ding et al., 2016; Ditas et al., 2018; Jacobson, 2001; Pósfai & Buseck, 2010). Global models estimate the effects of BC absorption based on its mass concentration, size distribution, particle morphology, and mixing structures of BC particles (Ramanathan & Carmichael, 2008; Riemer et al., 2019). Experimental evidence showed that the absorption enhancement, induced by mixing of BC with other nonabsorbing secondary aerosols, can be less than 1.05 (Cappa et al., 2012; Healy et al., 2015) or as large as 2.4 (Peng et al., 2016). Furthermore, absorption enhancement obtained using the core–shell Mie theory based on BC coating thickness measured by single particle soot photometer (SP2) or soot particle-aerosol mass spectrometer (SP-AMS) is ~14%–150% larger than the directly measured ones in field campaigns (Cappa et al., 2012; Liu et al., 2017; McMeeking et al., 2014; Shiraiwa et al., 2010). The large uncertainties in estimating or modeling BC absorption enhancement are due to the challenges in accurately accounting for BC particle morphology and mixing structures in models.

A number of BC shape models were developed to calculate optical properties of individual BC particles considering their fractal morphology and mixing structures through numerical modeling methods (e.g., T-matrix method, discrete dipole approximation [DDA], Rayleigh–Debye–Gans; Ishimoto et al., 2019; Liu et al., 2013; Scarnato
et al., 2013; Teng et al., 2019). Most of these models have limited tunable parameters such as coating thickness and structure (Figure S1 in Supporting Information S1, explained in Text S1 in Supporting Information S1; Ackerman & Toon, 1981; Adachi et al., 2010; Adler et al., 2010; He et al., 2016; Ishimoto et al., 2019; Kahnert, 2017; Liu & Mishchenko, 2007; Martins et al., 1998; Scarnato et al., 2013; Worringen et al., 2008; Wu et al., 2018; Zhang, Mao, et al., 2018; Zhang, Zhang, et al., 2018), which posed challenges to accurately represent the irregular coating morphology and mixing structures of ambient BC particles. Furthermore, studies using these models focused on estimating optical properties of individual BC particles, and they did not provide absorption enhancement of the whole BC particle population with varying mixing structures (Ackerman & Toon, 1981; Adachi et al., 2010; Adler et al., 2010; He et al., 2016; Ishimoto et al., 2019; Kahnert, 2017; Liu & Mishchenko, 2007; Martins et al., 1998; Scarnato et al., 2013; Worringen et al., 2008; Wu et al., 2018; Zhang et al., 2018).

Here, we apply a new electron-microscope-to-BC-simulation (EMBS) tool (Wang et al., 2021), based on electron microscope images and a 3D modeling method, to produce shape models for BC optical calculation through DDA. The EMBS can not only flexibly simulate all morphology and mixing structures within individual BC particles based on morphological parameters obtained from the transmission electron microscope (TEM) observations but also apply these morphological characteristics to estimate the absorption enhancement of individual BC particles ($E_{abs}$) and the total BC particle population ($E_{abs, pop}$). It should be noted that the term “mixing state” in previous studies mostly refers whether BC is internally mixed with other aerosols (Jacobson, 2001; Liu et al., 2017; Wang et al., 2017), while it sometimes refers to the extent of BC embedded in coating in some other studies (Adachi et al., 2010; China et al., 2013; Li et al., 2016), which is consistent with the term “mixing structure” in this study. The mixing structure here describes how BC mixes with coating in individual particles, including the embedded fraction and coating thickness. BC normally means the carbonaceous materials that absorb light, while soot or ns-soot is generally fractal-like aggregates observed using electron microscope (Bond et al., 2013; Buseck et al., 2014). In this study, the term “BC” is equivalent to “ns-soot” or “soot” in the atmosphere, referring to the aerosols containing carbonaceous fractal-like aggregates.

2. Materials and Methods
2.1. Morphology Analysis of Individual BC Particles
Aerosol samples were collected at three sampling sites in China: an urban site in Beijing (39°58′N, 116°22′E), a suburban site in Xianghe (39°48′N, 116°57′E), and a mountain site on Mt. Tai (36°15′N, 117°6′E). Copper TEM grids coated with carbon film were used to collect aerosol samples. The copper TEM grids were analyzed by a JEOL JEM-2100 TEM equipped with an energy-dispersive X-ray spectrometer (EDS). The high-resolution TEM images of the aerosol particles are obtained for each copper grid, and we chose all the 1,180 BC particles in the 42 grids to analyze their morphology, mixing structure, and chemical composition. The fractal dimension ($D_f$) of BC particles reflects the compactness and represents as the exponent in the scaling law (Köylü et al., 1995):

$$ N = k_g \left( \frac{2R_g}{d_p} \right)^d $$

(1)

where $N$ is the total number of monomers (i.e., individual BC sphere) in the BC aggregate, $k_g$ is the fractal prefactor, $R_g$ is the radius of gyration of the BC aggregate, and $d_p$ is the diameter of the monomer.

2.2. Mixing Structure Analysis and Shape Model Generation
The TEM images display the morphology and mixing structures of BC particles. The volume-equivalent-diameter (EVD) ratio of a BC-containing particle to the BC aggregate ($D_f/D_e$) and the embedded fraction ($F$) were calculated based on TEM analysis to estimate coating amount and mixing structures of BC particles. The circle-equivalent-diameter (ECD) obtained from the TEM images can be transformed to the EVD as

$$ \text{EVD} = r \times \text{ECD} $$

(2)

where $r$ is the correlation factor of 0.78, which was referred to the $r$ of the similar sampling sites (i.e., urban and mountain sites) in the North China Plain from atomic force microscopy analysis (Chen et al., 2017). In addition,
the $D_p/D_c$ can be transformed to the mass ratio of the coating to core ($R_{coat\rightarrow BC}$) for comparing with the results with other studies:

$$R_{coat\rightarrow BC} = \frac{\rho_{coating}}{\rho_{BC}} \left(\frac{D_c}{D_p}\right)^3 - 1 \right)$$

where $\rho_{coating}$ is the mass density of the coating material at 1.37 g cm$^{-3}$ (assuming the coating contains equal amounts of inorganics, hydrocarbon-like organic aerosol [HOA], and oxygenated organic aerosol [OOA]; Cappa et al., 2012) and $\rho_{BC}$ is the mass density of the BC aggregate at 1.8 g cm$^{-3}$ (Bond & Bergstrom, 2006). The embedded fraction ($F$) refers to the volume ratio of BC aggregate inside the coating and the whole BC aggregate, which is in the range of 0–1. The $F = 0$ represents fresh (no coating) BC and $F = 1$ represents entirely embedded BC. $F$ is defined as

$$F = \frac{V_{BC_{inside}}}{V_{BC}} = \frac{D_p^3}{D_c^{3_{inside}}} = \frac{(r \times ECD_{BC})^3}{(r \times ECD_{BC\ _inside})^3} = \frac{ECD_{BC}\ ^3}{ECD_{BC\ _inside}^3}$$

where $V_{BC\ _inside}$ is the volume of the BC aggregate inside the coating, $V_{BC}$ is the volume of the whole BC aggregate, $D_c$ is the EVD of BC aggregated inside the coating, $ECD_{BC}$ is the circle-equivalent-diameter of the BC aggregate, and $ECD_{BC\ _inside}$ is the circle-equivalent-diameter of the BC aggregate inside the coating. The $ECD_{BC}$ and $ECD_{BC\ _inside}$ were obtained from the TEM images.

The BC particle shape models with specified $D_p, k, N, d_p$, core size ($D_c$), $D_p/D_c$, and $F$ from electron microscopy analysis were generated and their optical properties were calculated using the EMBS coupling with DDA (Draine & Flatau, 1994; Wang et al., 2021). More detailed description about optical calculation using the EMBS and DDA can be found in the Supporting Information.

### 2.3. Absorption Enhancement by the Total BC Particle Population

The EMBS established by Wang et al. (2021) was utilized to provide optical calculation of individual BC particles. In this study, we applied the EMBS in three field observations through a novel framework predicting the $E_{abs\ _bulk}$ based on individual BC particle analysis, which can be compared with field measurements and applied in further remote sensing retrieval and climate modeling. The modeled $E_{abs\ _bulk}$ was calculated based on the morphological parameters obtained from the TEM observations. The $E_{abs\ _bulk}$ of BC particles with different morphology, BC core size ($D_c$: 50, 250, 450, 650, and 850 nm), $D_p/D_c$, and $F$ was calculated using the EMBS, and the $E_{abs\ _bulk}$ was calculated based on the $E_{abs\ _bulk}$ accounting for different bins of $D_c, D_p/D_c$, and $F$. The $E_{abs\ _bulk}$ at the urban, suburban, and mountain sites at each $D_p/D_c$ (i.e., $R_{coat\rightarrow BC}$) was calculated by

$$E_{abs\ _bulk} = \sum \left( \sum (E_{abs\_i,j} \times F_{c,i}) \times F_{N_{j,i}} \right)$$

where $F_{c,i}$ is the mass fraction of BC particles at different BC core size and $F_{N_{j,i}}$ is the number fraction of the BC particles at different $F$ (Tables S1–S3 in Supporting Information S1). More details for aerosol sampling, individual particle analysis, shape model generation, and optical prediction are explained in the Supporting Information text.

### 3. Results

#### 3.1. Morphology and Mixing Structures of Individual BC Particles

BC particles in the atmosphere can either be “bare” (i.e., no discernable coating, as in Figure 1a) or internally mixed (i.e., mixed with other aerosols, as in Figures 1b and 1c). The internally mixed BC particles display complex mixing structures with other aerosol components and are further classified into partly coated (Figure 1b, partly covered by coating) and embedded (Figure 1c, entirely covered by coating) categories based on their mixing structures. The mixing structures in individual BC particles in the TEM images are quantified by coating parameters, including $D_p/D_c$ and the fraction of BC embedded in coating ($F$, hereafter termed “embedded fraction”) in individual particles. $D_p/D_c$ refers to EVD ratio of a BC-containing particle to its BC aggregate core. The
$D_p/D_c$ of internally mixed BC particles at the urban, suburban, and mountain sites ranges between 1 and 12 but is primarily between 1.2 and 2.8 (Figure S2a in Supporting Information S1). And $F$ is defined as the volume ratio of BC aggregate inside the coating and the whole BC aggregate in an individual particle, which ranges from 0 to 1. Average $F$ of the BC particles at the mountain site is larger than that at the urban and suburban sites (Figure S2b in Supporting Information S1). Furthermore, more BC particles are presented as fully embedded particles ($F = 1$) in the more aged air mass (e.g., over the mountain, Figure S2b in Supporting Information S1). Fractal dimensions ($D_f$) of BC particles are widely used to represent their morphology and aging in the air (China et al., 2013; Wang et al., 2017). When bare BC particles age in the air, they become more compact and thus have a higher $D_f$. Figures 1g–1i show that the $D_f$ of the bare, partly coated, and embedded BC particles is approximately 1.76, 1.85, and 1.91, respectively. Here, we used RADIUS software to manually measure 1,180 individual BC particles in TEM images and obtained their $D_p/D_c$, $F$, and fractal parameters ($D_f$ and $k_g$), which are further applied in constructing 3D BC shape models by the EMBS. The EMBS provides an interface to visually create 3D shape models of any shapes and mixing structures ($D_p/D_c$ and $F$), and the 3D shape models (e.g., Figures 1d–1f) can be exported as DDA input files and used for calculating the $E_{abs}$ of individual BC particles. Finally, $E_{abs, bulk}$ can be

![Figure 1](image-url)
calculated through assigning the particles into different BC core size, $D_p/D_c$ and $F$ bins. More details about $E_{abs}$ and $E_{abs,bulk}$ calculation based on the EMBS are presented in Section 2.

3.2. Absorption Enhancement of Individual BC Particles

Internally mixed ambient BC particles often show irregular-shaped coatings and complex mixing structures (Figures 1b and 1c and 2a–2p; Adachi et al., 2010; Ueda et al., 2018; Wang et al., 2021). Irregular-shaped coatings of different volumes can cover small to large part of the BC aggregate (Figures 2a–2p), which forms various $D_p/D_c$ and $F$ and eventually affects their optical properties. The $F$ values of BC particles are variable due to different aging processes such as coagulation, condensation, and heterogeneous reaction processes in the atmosphere. Simulations revealed a large variability of BC optical and radiative variables due to the variation of mixing state influenced by condensation and coagulation processes (Fierce et al., 2020; Matsui, 2016). Based on the various $D_p/D_c$ and $F$ values from the observation, we constructed the complex mixing structures and irregular-shaped coating rather than simplifying the coating to be one sphere as in previous studies (Kahnert, 2017; Zeng et al., 2019; Zhang et al., 2018). $E_{abs}$ of individual BC particles at different $D_p/D_c$ and $F$ values is calculated based on the new shape models (Figure S3 and Table S5 in Supporting Information S1) by the EMBS. Figure 2q shows that when the $D_p/D_c$ increases from 1.5 to 2.7, $E_{abs}$ is ~1 at $F = 0.1$, but the $E_{abs}$ increases sharply from 1.39 to 2.31 if $F = 1.00$. The $E_{abs}$ increment is higher at larger $F$ because the absorption of more monomers in the BC aggregate is enhanced by the coating at larger $F$ than at smaller $F$. These results show that $E_{abs}$ increases with $D_p/D_c$ at a fixed $F$, consistent with the general understanding that the $E_{abs}$ of BC depends on the coating thickness (Shiraiwa et al., 2010; Zhang et al., 2008; Zhang et al., 2018). Wang et al. (2021) found that the $E_{abs}$ of BC particles increased slightly with $D_p/D_c$ if $F = 0.25$, while the $E_{abs}$ increased significantly if $F = 1$. The variations are consistent with our results shown in Figure 2q.

Figure 2q shows the $E_{abs}$ of BC particles with the same coating amount ($D_p/D_c$) but different $F$ values. $E_{abs}$ increases slowly from 1.12 to 1.39 with $F$ from 0.10 to 1.00 at $D_p/D_c = 1.5$, while the $E_{abs}$ increases rapidly from 1.13 to 2.10 with $F$ from 0.10 to 1.00 at $D_p/D_c = 2.3$. The results suggest that the $E_{abs}$ of BC particles with the same coating amount may vary significantly as the embedded fraction $F$ varies due to different atmospheric processes. Figure S3a in Supporting Information S1 further shows that $E_{abs}$ increases by 14%–22% with increasing $F$ when $D_p/D_c < 2.0$, while it rises by 32%–51% if $D_p/D_c > 2.0$ (Table S6 in Supporting Information S1). The larger
Figure 3. Modeled bulk absorption enhancement ($E_{\text{abs, bulk}}$) at different $R_{\text{coat-BC}}$ (the mass ratio of the coating to core) in comparison to literature values. $E_{\text{abs, bulk}}$ at 550 nm modeled by the electron-microscope-to-BC-simulation (EMBS) at $F = 0.10$ and $F = 1.00$ are represented by the brown and rose red lines and filled circles, respectively. $E_{\text{abs, bulk}}$ at 550 nm modeled by the EMBS based on real observations at the urban, suburban, and mountain sites are shown by green, orange, and blue filled circles and curves, respectively. $E_{\text{abs, bulk}}$ calculated by the core–shell model is shown by the gray curve. Observed $E_{\text{abs, bulk}}$ based on photoacoustic spectrometer is from ambient studies by Cappa et al. (2012) (at 532 nm), Liu et al. (2015) (at 870 nm), Healy et al. (2015) (at 871 nm), and Peng et al. (2016) (at 532 nm) and from biomass burning by McMeeking et al. (2014) (at 871 nm). Note that the $E_{\text{abs}}$ differences at 550 and 781 nm are mostly within 10% (Figure S8 in Supporting Information S1) based on our own calculations. The $E_{\text{abs, bulk}}$ differences induced by incident wavelength are much smaller than that from coating thickness (i.e., $R_{\text{coat-BC}}$). Therefore, $E_{\text{abs, bulk}}$ of nonabsorbing coating versus $R_{\text{coat-BC}}$ can be compared under different wavelengths, which has been pointed out in previous studies (Cappa et al., 2019; Chakrabarty & Heinson, 2018).

As $R_{\text{coat-BC}}$ increases from $\sim 1.1$ to $\sim 2.0$ when $R_{\text{coat-BC}}$ increases from $\sim 0.9$ to $\sim 10.4$. This confirms that the coating thickness influences the bulk BC absorption enhancement. $E_{\text{abs, bulk}}$ at the mountain site is much higher than that at the urban and suburban sites, which likely results from the much higher $F$ at the mountaintop site (Figure S2b in Supporting Information S1) due to both the complete aging during long-range transport and the high relative humidity (RH $\sim 64$%; the general deliquesce point of coating aerosols is RH = $60\%–90\%$) for liquid phase formation (Yuan et al., 2019; Zeng et al., 2019). Moreover, $E_{\text{abs, bulk}}$ at the urban and suburban sites have a similar variation from $\sim 1.1$ to $\sim 1.3$ at $R_{\text{coat-BC}} < 3$, which is comparable with the measured results of BC collected in London (2015) (yellow triangles in Figure 3). McMeeking et al. (2014) found stable small $E_{\text{abs, bulk}}$ (mostly $\sim 1$) at $R_{\text{coat-BC}} < 10$ (purple stars in Figure 3) for freshly emitted BC from biomass burning, which is close to our results at $F = 0.10$; but the $E_{\text{abs, bulk}}$ rises steeply at $R_{\text{coat-BC}} > 10$. The negligible increment of $E_{\text{abs, bulk}}$ with increasing coating thickness at $R_{\text{coat-BC}} < 10$ is likely attributable to the small embedded coated fraction in individual BC particles, which is similar with our new model at $F = 0.10$. The substantial increment of $E_{\text{abs, bulk}}$ with increasing coating thickness at $R_{\text{coat-BC}} > 10$ may result from both larger embedded fraction and increasing coating thickness in individual BC particles during aging processes, which can be explained by our new model at $F = 1.00$. Thus, our new model explains that the negligible and substantial elevation in bulk absorption enhancement from the coating thickness and embedded fraction in individual BC particles. Moreover, $E_{\text{abs, bulk}}$ at $R_{\text{coat-BC}} > 10$ for the biomass burning BC is even larger than our modeled results at $F = 1.00$, but this may attribute to the absorption by high brown carbon (McMeeking et al., 2014) and/or the differences in BC size distribution due to different emission sources.

$E_{\text{abs}}$ increment for thicker coating results from the more intensive “lensing effect” by thick coating. These results indicate that the impact on absorption enhancement by embedded fraction $F$ in individual BC particles is significantly enhanced particularly when $D_c/D_e > 2.0$. Omitting the embedded fraction may result in large bias in optical prediction of individual BC particles with thick coating and hence lead to bias in optical prediction of BC particle population. Therefore, it is essential to consider the embedded fraction in the optical prediction, especially for BC particles with thick coating.

When $F = 1.00$, $E_{\text{abs}}$ estimated from a core–shell model is larger than the new shape models from the EMBS methods (hereafter termed “new model”) at $D_c/D_e < 2.0$ but much smaller at $D_c/D_e \geq 2.0$ (Figure S4a in Supporting Information S1). However, when $F = 0.50$, $E_{\text{abs}}$ estimated from a core–shell model is much larger than our new model at $D_c/D_e = 1.5–2.1$ and 2.5 but much smaller at $D_c/D_e = 2.3$ and 2.7 (Figure S4a in Supporting Information S1). The differences in modeled $E_{\text{abs}}$ at $F = 1.00$ between the new model and core–shell model may result from the different locations of the BC core and the simplification of morphology of coating and fractal BC core in the core–shell model (Adachi et al., 2010; Fuller et al., 1999). The results suggest that the relationship between $E_{\text{abs}}$ estimated from core–shell model and our new model varies nonlinearly with $D_c/D_e$ and $F$.  

3.3. Predicting Absorption Enhancement by the Total BC Particle Population

Based on the $E_{\text{abs}}$ of individual BC particles (Figure S5 in Supporting Information S1), calculated at different BC core size (Figure S6 in Supporting Information S1), fractal parameters ($D_c$ and $\xi$ in Figures 1g–ii), $D_c/D_e$ (Figure S2a in Supporting Information S1), and $F$ (Figure S2b in Supporting Information S1) values from the TEM images at the urban, suburban, and mountain sites, $E_{\text{abs, bulk}}$ of the total BC particle population at different $R_{\text{coat-BC}}$ values were calculated. Figure 3 presents the variations of modeled $E_{\text{abs, bulk}}$ for $F = 0.10$ and $F = 1.00$, the modeled $E_{\text{abs, bulk}}$ at the three sites, and the measured $E_{\text{abs, bulk}}$ from previous studies (Cappa et al., 2012; Healy et al., 2015; Liu et al., 2015; McMeeking et al., 2014). $E_{\text{abs, bulk}}$ at the urban and suburban sites increases from $\sim 1.1$ to $\sim 1.6$, while that at the mountain site increases from $\sim 1.1$ to $\sim 2.0$ when $R_{\text{coat-BC}}$ increases from $\sim 0.9$ to $\sim 10.4$. This confirms that the coating thickness influences the bulk BC absorption enhancement. $E_{\text{abs, bulk}}$ at the mountain site is much higher than that at the urban and suburban sites, which likely results from the much higher $F$ at the mountaintop site (Figure S2b in Supporting Information S1) due to both the complete aging during long-range transport and the high relative humidity (RH $\sim 64\%$; the general deliquesce point of coating aerosols is RH = $60\%–90\%$) for liquid phase formation (Yuan et al., 2019; Zeng et al., 2019). Moreover, $E_{\text{abs, bulk}}$ at the urban and suburban sites have a similar variation from $\sim 1.1$ to $\sim 1.3$ at $R_{\text{coat-BC}} < 3$, which is comparable with the measured results of BC collected in London (2015) (yellow triangles in Figure 3). McMeeking et al. (2014) found stable small $E_{\text{abs, bulk}}$ (mostly $\sim 1$) at $R_{\text{coat-BC}} < 10$ (purple stars in Figure 3) for freshly emitted BC from biomass burning, which is close to our results at $F = 0.10$; but the $E_{\text{abs, bulk}}$ rises steeply at $R_{\text{coat-BC}} > 10$. The negligible increment of $E_{\text{abs, bulk}}$ with increasing coating thickness at $R_{\text{coat-BC}} < 10$ is likely attributable to the small embedded coated fraction in individual BC particles, which is similar with our new model at $F = 0.10$. The substantial increment of $E_{\text{abs, bulk}}$ with increasing coating thickness at $R_{\text{coat-BC}} > 10$ may result from both larger embedded fraction and increasing coating thickness in individual BC particles during aging processes, which can be explained by our new model at $F = 1.00$. Thus, our new model explains that the negligible and substantial elevation in bulk absorption enhancement from the coating thickness and embedded fraction in individual BC particles. Moreover, $E_{\text{abs, bulk}}$ at $R_{\text{coat-BC}} > 10$ for the biomass burning BC is even larger than our modeled results at $F = 1.00$, but this may attribute to the absorption by high brown carbon (McMeeking et al., 2014) and/or the differences in BC size distribution due to different emission sources.
Previous studies reported large differences in bulk absorption enhancement among different field observations and the modeling based on the core–shell theory. For example, the observed $E_{\text{abs, bulk}}$ is very small (~1.07) at $R_{\text{coat-rBC}} \sim 7$ in California (Cappa et al., 2012) and Fontana (Cappa et al., 2019), whereas the $E_{\text{abs, bulk}}$ is much larger (~2.2) at similar $R_{\text{coat-rBC}}$ (~6) for highly aged BC in Beijing (Peng et al., 2016; Figures S7d and S7e in Supporting Information S1). Studies in Gulf of Guinea and inland (Denjean et al., 2020) showed a similar enhancement as in Beijing (Peng et al., 2016; Figures S7d and S7e in Supporting Information S1). On the other hand, the modeled $E_{\text{abs, bulk}}$ based on the core–shell theory using the coating thickness estimated by SP2 or SP-AMS is ~1.8, which is largely different from the results from the observed $E_{\text{abs, bulk}}$ in California and Fontana but close to the measured $E_{\text{abs, bulk}}$ in Beijing and Gulf of Guinea and inland (Cappa et al., 2012, 2019; Denjean et al., 2020; Peng et al., 2016; Figures S7c and S7e in Supporting Information S1). The inconsistencies in these results may be due to the differences in $F$ values in BC particle population. Figure 3 shows that the low $E_{\text{abs, bulk}}$ observed in California (light green triangles) and Toronto (dark red asterisks) is close to the modeled $E_{\text{abs, bulk}}$ (~1) from the EMBS at $F = 0.10$ (Cappa et al., 2012; Healy et al., 2015). The small $E_{\text{abs, bulk}}$ from the EMBS at $F = 0.10$ is caused by the small $E_{\text{abs}}$ (~1) of individual particles due to the small embedded fraction (Figure 2q). Similarly, based on shape models of BC attached to cubic, plate-like, and spherical particles, Adachi and Buseck (2013) estimated that the $E_{\text{abs, bulk}}$ is 1.04 when the BC aggregate is attached to the surface of other particles through coagulation. The results suggest that the low $E_{\text{abs, bulk}}$ is likely attributable to the dominance of BC particles with low $F$ in BC particle population, as is shown in Scenario-1 in Figure S7a in Supporting Information S1.

The embedded fraction in individual BC particles may also be influenced by RH in the atmosphere. When RH is low, the BC particles are more likely to be slightly coated by other aerosols, which leads to smaller $F$. The study by Cappa et al. (2012) was conducted under low RH (~55%), low nonrefractory PM1 (~3–6 μg m$^{-3}$), and potentially not completely aged (up to 20 hr of aging) condition (Cappa et al., 2013), which likely resulted in small embedded fraction in individual particles and small $E_{\text{abs, bulk}}$. The higher $E_{\text{abs, bulk}}$ (~2.2) from aged BC (Figure S7e in Supporting Information S1) is comparable to that from core–shell model, suggesting that the large embedded fraction in most particles leads to higher $E_{\text{abs, bulk}}$ (Scenario-2 in Figure S7b in Supporting Information S1). Figure 3 shows that the variation of $E_{\text{abs, bulk}}$ in Beijing from Peng et al. (2016) is similar to our predicted results at the mountain site but is larger than our predicted results at the urban Beijing site. The larger $E_{\text{abs, bulk}}$ in Beijing from Peng et al. (2016) is attributable to the rapid aging of BC particles due to substantial inorganic species produced by aqueous chemistry during the haze period, which may efficiently enhance the embedded fraction of BC particles and hence increase the growth rate of $E_{\text{abs, bulk}}$. In contrast, the cleaner condition (the PM$_{2.5}$ data can be found in Liu et al. [2021]) and lower RH (Table S7 in Supporting Information S1) at the urban Beijing site in this study are not conducive to coating formation and increase of embedded fraction, which results in lower $E_{\text{abs, bulk}}$. In summary, the above discussions suggest that the large difference in the observed $E_{\text{abs, bulk}}$ in different field observations and modeling works is likely associated with the mixing structures.

Recently, several improved core–shell models were proposed to predict the bulk absorption enhancement. For example, Liu et al. (2017) reproduced $E_{\text{abs, bulk}}$ of 1.0–1.4 through a hybrid model that empirically assumes $E_{\text{abs}}$ of individual BC is linearly related to the results of core–shell model. Fierce et al. (2020) resolved the apparent discrepancy in $E_{\text{abs, bulk}}$ predictions and observations by accounting for per-particle heterogeneity in composition using a linear correlation with core–shell approximation. However, the linear approximation based on core–shell model may not be suitable for BC particles from different emission sources and diverse atmospheric aging processes. Our results show that the core–shell model overestimates $E_{\text{abs}}$ of most BC particles at $F < 1.00$, but it underestimates the $E_{\text{abs}}$ of the BC particles at $F = 1.00$ and $D_T / D_1 > 2.0$ (Figure S4 in Supporting Information S1). Thus, the empirical approximations based on the core–shell model still suffer large uncertainties in bulk absorption enhancement by BC mixing state because they oversimplified the various coating morphology and mixing structures in individual BC particles in the atmosphere. If we assume that all the BC particles are fully embedded in the coating ($F = 1.00$), the $E_{\text{abs, bulk}}$ continually increases from 1.25 to ~2.25 due to the high $E_{\text{abs}}$ in individual particles (Figure 2q), which is much larger than the partially coated BC particles ($F = 0.10$; Figure 3). Therefore, the embedded fraction in individual BC particles should be considered in modeling bulk absorption enhancement, in addition to the coating thickness.
Conclusions

The results from the EMBS show that the embedded fraction in individual particles strongly influences absorption enhancement of individual BC particles when $D_{\text{abs}}/D_p > 2.0$. Moreover, the EMBS methods can be applied to estimate $E_{\text{abs, bulk}}$ of BC particles based on particle-resolved morphology and mixing structures. The embedded fraction and coating thickness reveal the mechanism that could lead to significant differences in individual BC particles and hence in bulk absorption enhancement. The optical properties of individual BC particles with the detailed morphology and mixing structures should be integrated into climate models in the future to improve the quantification of climate effects of BC particles. It should be noted that the crystallization of liquid coating (e.g., ammonium sulfate) during particle collection might induce the potential bias in embedded fraction of BC particles. Further efforts are needed to acquire more accurate mixing structures of the ambient BC particles. In addition, the coating is assumed to be nonabsorbing in this study, but some absorbing coating, such as brown carbon, should be also studied in future absorption enhancement to account for the particle composition heterogeneity.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Processed data are available from the link: https://doi.org/10.6084/m9.figshare.14333222.

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