In-situ growth of CNTs in silica powder by polymer pyrolysis chemical vapor deposition and their separation resistances

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ABSTRACT
This study investigated the in-situ growth of carbon nanotubes (CNTs) in silica (SiO₂) powder by polymer pyrolysis chemical vapor deposition with a polyethylene glycol (PEG) carbon source and cobalt nitrate catalyst. The mass ratio of PEG:citric acid:cobalt nitrate was determined to control the microstructures of the in-situ CNTs. Results indicated that with an increase in the mass ratio of PEG:citric acid:cobalt nitrate, the in-situ generated CNTs content in the SiO₂ powder increased, the CNTs diameters (approximately 40 nm) did not significantly change, and the CNTs lengths decreased from 400–800 nm to 200–400 nm. Additionally, the in-situ CNTs that were anchored on the surfaces of SiO₂ particles presented fewer defects and a high degree of graphitization. However, when the mass ratio of PEG:citric acid:cobalt nitrate exceeded the critical value, excessive amounts of amorphous carbon grown in situ on SiO₂ particles were obtained. The suspension experiments showed that unlike the CNTs/SiO₂ powders prepared by a combination of surfactant and ultrasonic methods with commercial CNTs, in-situ CNTs grown in SiO₂ powders exhibited improved separation resistance in water. This would favor the uniform dispersion of CNTs within the matrix, improving the performance of nanocarbon-modified cement-based composites.

1. Introduction
One-dimensional (1D) nanocarbon-modified cement-based composites (NMCs), which possess good mechanical properties and satisfactory multifunctionalities, are among the most promising candidates for civil engineering applications [1–8]. However, due to their hydrophobic characteristics and large specific surface area, nanocarbons have a high tendency to cluster during composite preparation. This results in poor dispersion of nanocarbons within the cementitious matrix, thus weakening the interfacial bonds between the nanocarbons and matrix and degrading the performance of the NMCs [9,10].

Many methods exist to overcome these issues, including physical methods such as ultrasonication and ball milling, chemical methods such as the use of dispersants and chemical surface treatments, and combinations of physical and chemical methods [11–17]. Despite the highly promising results obtained using these methods, some issues still persist in the fabrication of NMCs using these methods, such as the deterioration of the microstructure and functionality of the nanocarbons, incompatibility with cement [11,18,19], influence on cement hydration and formation of conductive networks in the matrix [2,6,20]. Therefore, it is imperative to develop simple and high-efficiency methods to improve the dispersion and interfacial bonding of nanocarbons in cementitious matrices.

In recent decades, the in-situ growth of CNTs/CNFs on cement/mineral/silica fume particles via the conventional chemical vapor deposition (CVD) route has been proposed to improve the dispersion of nanocarbons in NMCs [21–26]. The experimental results indicated that these methods offer advantages in maintaining the structural integrity of CNTs and improving interfacial bonding between CNTs and the matrix, and are among the most promising methods for preparing NMCs. Unfortunately, the in-situ formation of CNTs by CVD typically requires the use of inflammable and explosive gases (e.g. CH₄ and H₂), which increase the associated risk factors. Additionally, CNTs usually grow in situ on the surfaces of the particles that accumulate during conventional CVD, resulting in their inhomogeneous dispersion in the products.

Consequently, we proposed the synthesis of in-situ nanocarbon composites with combustion synthesis and polymer pyrolysis CVD (PP-CVD) using carbonates and polymers as raw materials, respectively. Specifically, unlike conventional CVD, gases such as CO and CH₄, which are required for the in-situ formation of nanocarbons, are supplied by the pyrolysis of...
the reactants. In a previous study, we synthesized in-situ 2D nanocarbon/calcium aluminate composite (NCAC) via a combustion method using calcium carbonate (CaCO₃) as a carbon source, and found that the prepared nanocarbon had strengthened interfacial bonds and satisfactory separation resistance in water. Simultaneously, nanocarbons were homogeneously in-situ grown in the products [27]. However, combustion synthesis usually requires the use of metallic powders, which are not favorable when trying to reduce production costs. Additionally, the process of combustion synthesis is difficult to control.

Silica powder is usually present in cement-based composites, and has been demonstrated to significantly improve the dispersion of nanocarbons in these materials [28–30]. Hence, in this study, CNTs were in-situ grown in SiO₂ powders via polymer pyrolysis CVD (PP-CVD) using polyethylene glycol (PEG) as the carbon source and cobalt nitrate as the catalyst precursor. The mass ratio of PEG:citric acid:cobalt nitrate was determined to control the microstructures of the in-situ grown CNTs. The separation resistance of the CNTs in-situ grown on the SiO₂ particles was evaluated.

2. Experimental

The SiO₂ powder used in this study had an average particle diameter of 32 μm. PEG (MW1000), citric acid monohydrate (C₆H₈O₇·H₂O, CA), and cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, Co₃) were purchased from Sinopharm Chemical Reagent (Shanghai) Co. Ltd., and used as raw materials without further treatment.

The in-situ growth of CNTs on SiO₂ particles via PP-CVD consisted of three steps. First, PEG, CA, and Co(NO₃)₂·6H₂O were weighed according to the mass ratios listed in Table 1, to which 10 mL ethyl alcohol was added and stirred using a magnetic stirrer for 1 h to obtain the PEG-CA-Co₃ precursor solution (denoted as PEG-CA-Co₃). Second, 10 g of SiO₂ powder was added to the as-prepared precursor solution and stirred for 2 h. The resulting suspensions were dried at 70°C for 10 h to remove the residual solvent and obtain SiO₂ powders coated with the PEG-CA-Co₃ precursor. Finally, the PEG-CA-Co₃ precursor-coated SiO₂ powders were placed in a closed steel reactor and heated to 230°C with a soaking time of 2 h at a rate of 15°C/min in an electric SiC heating element furnace, followed by further heating to 650°C with a soaking time of 1 h.

The morphologies of the CNTs in-situ grown on the SiO₂ particles were observed by field-emission scanning electron microscopy (FESEM, SU6600, Japan) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20, USA). The graphitization degree and content of the in-situ nanocarbons were characterized via Raman spectroscopy (Renishaw, England) using a 532 nm excitation laser with a spectral resolution of 2 cm⁻¹, and thermogravimetric analysis (TGA, NETZSCH STA409, Germany) from room temperature to 800°C at 10°C C/min under ambient atmosphere.

The separation resistance of the CNTs in-situ grown in the SiO₂ powders was evaluated using the suspension method, as described in previous reports [31–33]. The synthesized CNTs/SiO₂ composite powders (10 g) and deionized water (100 mL) were mixed in a beaker and ultrasonicated for 15 min. The resulting suspension was set aside for 30 min, and a photograph of the suspension was captured and labeled as “in-situ CNTs/SiO₂.” The floating materials were separated from the in-situ CNTs/SiO₂ suspension and dried in a vacuum oven at 80°C for 12 h. The floating ratio (FR) was calculated according to Eq. (1). A lower FR corresponded to a higher separation resistance. For comparison, the separation resistance of the CNTs/SiO₂ composite powders (prepared by combining the surfactant and ultrasonic methods with commercial CNTs) was also tested.

\[
\text{FR}(\%) = \frac{\text{FW}}{\text{OW}} \times 100\% \quad (1)
\]

where FR (%) is the floating ratio, FW (g) is the weight of the floating CNTs, and OW (g) is the weight of the original CNTs in the composite.

3. Results and discussion

3.1. Characterization of in-situ CNTs/SiO₂ composite powders

In contrast to the as-received SiO₂ powders, the synthesized composite powders were black. Raman spectroscopy is considered an effective and convenient technology to characterize various carbon materials, and was used to characterize the products. The results are shown in Figure 1. The D band (at approximately 1350 cm⁻¹) and G band (at approximately 1580 cm⁻¹) are present in the Raman spectra of the synthesized composite powders, and represent the defects and crystallinity of the carbon materials, respectively. In contrast to that of the PEG1.5 sample, the Raman spectra of the PEG0.25 and PEG0.75 samples show a 2D band at approximately 2700 cm⁻¹, which can be used to evaluate the number of layers.
in few-layer graphene [34]. Moreover, the D and G bands in the PEG0.25 and PEG0.75 spectra were sharper than those in the PEG1.5 spectrum.

Typically, the $I_D/I_G$ ratio in the Raman spectrum indicates the graphitization degree of carbon materials, where lower ratios correspond to higher graphitic ordering [35]. The $I_D/I_G$ values for the PEG0.25, PEG0.75, and PEG1.5 samples were calculated and are listed in Table 2. The $I_D/I_G$ values of the PEG0.25 and PEG0.75 samples were 0.42 and 0.47, respectively, which were lower than that of PEG1.5. Thus, the carbon materials in-situ generated in the PEG0.25 and PEG0.75 samples had a high graphitization degree. Additionally, the TGA curves shown in Figure 2 indicate that the contents of the carbon materials generated in situ in the PEG0.25 and PEG0.75 are approximately 1.01 and 1.61 wt.%, respectively, lower than that generated in the PEG1.5 sample (2.33 wt.%).

The morphologies of the as-received SiO$_2$ powders and synthesized composites were observed by FESEM, and the results are shown in Figure 3.

**Table 2.** $I_D/I_G$ ratios and contents of CNTs generated in situ in SiO$_2$ powders.

| Samples   | Peak position (cm$^{-1}$) | Ratio of $I_D/I_G$ | Content (wt.%) |
|-----------|--------------------------|-------------------|----------------|
| PEG0.25   | 1354 1587                | 0.42              | 1.01           |
| PEG0.75   | 1360 1585                | 0.47              | 1.61           |
| PEG1.50   | 1363 1590                | 0.89              | 2.33           |

![Figure 1. Raman spectrums of the synthesized in-situ CNTs/SiO$_2$ composites.](image1)

![Figure 2. TGA curves of the synthesized in-situ CNTs/SiO$_2$ composites.](image2)
shown in Figure 3(a), the as-received SiO\textsubscript{2} powders are mainly composed of irregular particles with smooth surfaces. The FESEM images (Figure 3(b,c)) of the PEG0.25 sample show numerous in-situ grown CNTs with diameters of 30–40 nm and lengths of 400–800 nm, which are anchored on the surfaces of the SiO\textsubscript{2} particles. When the PEG:CA:Co\textsubscript{x} mass ratio was increased to 0.75:2.5:0.75, the density of the CNTs in-situ grown on the SiO\textsubscript{2} particles increased significantly, and the lengths slightly decreased (200–400 nm; Figure 3(d,e)). However, when the PEG:CA:Co\textsubscript{x} mass ratio was further increased to 1.5:2.5:0.75, no CNTs were grown in situ on SiO\textsubscript{2} particles (Figure 3(f,g)). A certain amount of amorphous carbon was generated on the SiO\textsubscript{2} particles.

To better examine the microstructures of the in-situ CNTs grown in the SiO\textsubscript{2} powders, the PEG0.75 sample was further examined using HRTEM, and the results are shown in Figure 4. As shown in Figure 4(a), the CNTs are multiwalled, with an outer diameter of approximately 40 nm. Additionally, the Co nanoparticles, which were intended to catalyze the in-situ growth of the CNTs, are encapsulated at the end of the CNTs. This indicates that the in-situ growth of CNTs on SiO\textsubscript{2}...
particles by PP-CVD is governed by the tip-growth mechanism [36]. The HRTEM image shown in Figure 4 (b) reveals that the CNTs grown in situ exhibit clear graphitic layers with an interplanar spacing of 0.339 nm, corresponding to the (002) plane of graphite [36–38]. These results indicate that the in-situ CNTs grown on the SiO₂ particles had a high degree of graphitization, which is consistent with the Raman spectroscopy results.

During the in-situ growth of CNTs in SiO₂ powders by PP-CVD, PEG was decomposed into H₂, CH₄, CO, and CO₂ gases at elevated temperatures [37]. The CoOₓ
nanoparticles, which were generated by the combustion reaction between Co(NO$_3$)$_3$ and CA, were reduced to Co nanoparticles by H$_2$ and CO [38], which played key roles in the in-situ growth of CNTs in the products [39**]. CH$_4$ and CO$_2$ served as carbon sources for the in-situ growth of CNTs [37,40]. The pressure of the carbon source gases within the closed reactor increased with the PEG:CA:Co$_x$ mass ratios, resulting in an increased growth rate of the CNTs. Consequently, the content of in-situ grown CNTs in the synthesized composites increased with the PEG:CA:Co$_x$ mass ratios. However, when the pressure of the carbon source gases within the closed reactor was too high, owing to the superabundance of PEG in the precursor, the generation rate of the activated carbon atoms exceeded their diffusion rate in the Co nanoparticles. This resulted in excessive carbon atoms occupying the active sites of the Co nanoparticles, which minimized the activities of the catalyst particles [40,41]. Thus, as the PEG:CA:Co$_x$ mass ratio increased to 1.5:2.5:0.75, an excessive amount of amorphous carbon in-situ generated in the SiO$_2$ powders was obtained.

### 3.2. Separation resistances of in-situ CNTs/SiO$_2$ composite powders

The separation resistances of the synthesized in-situ CNTs/SiO$_2$ and CNTs/SiO$_2$ composite powders were evaluated using the suspension method, and the results are shown in Figure 5. As shown in Figure 5(a), many black materials floated on the CNTs/SiO$_2$ suspension after being set for 30 min, whereas this phenomenon was not readily observed in the in-situ CNTs/SiO$_2$ suspension. The FR values of the two suspensions are shown in Figure 5(b). The FR of the in-situ CNTs/SiO$_2$ suspension (approximately 8.5 wt.%) was much lower than that of the CNTs/SiO$_2$ suspension (52.5 wt.%). Thus, the CNTs/SiO$_2$ composite powder synthesized

![Figure 5](image-url)

**Figure 5.** (a) The photos of the in-situ CNTs/SiO$_2$ and CNTs/SiO$_2$ suspensions after being ultrasonic vibrated; (b) The floating ratios of the in-situ CNTs/SiO$_2$ and CNTs/SiO$_2$ suspensions.
in situ via PP-CVD showed satisfactory separation resistance, which can be attributed to the enhancement in interfacial bonding between the in-situ grown CNTs and the matrix. This would be favorable for improving the dispersion of CNTs in cement-based materials.

4. Conclusions

CNTs were in-situ grown in SiO2 powders via PP-CVD with PEG as the carbon source and cobalt nitrate as the catalyst. The CNTs in-situ generated in the products had few defects and a high degree of graphitization. As the mass ratio of PEG:CA:Co2 increased, the content of the in-situ grown CNTs increased significantly, and their lengths decreased. However, when the mass ratio exceeded the critical value, amorphous carbon was generated on the SiO2 particles, because the excess carbon atoms occupied the active sites of the Co nanoparticles. Compared to CNT/SiO2 powder, the in-situ CNT/SiO2 composite powders showed satisfactory separation resistance in an aqueous solution because of the enhancement in interfacial bonding between the in-situ grown CNTs and the matrix. This would be favorable for the uniform dispersion of CNTs in cement-based composites.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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