

# Co-effects of Graphene Oxide and Silica Fume on the Rheological Properties of Cement Paste



D. Lu, Z. Sheng, B. Yan, and Z. Jiang

**Abstract** Polycarboxylate superplasticizer is typically used to prepare a high-quality graphene oxide (GO) solution before mixing with cement grains. However, even if GO is well dispersed in water, they tend to re-agglomerate in the alkaline cement hydration environment, thus seriously decreasing the workability of the fresh mixture. In this study, we propose a more targeted method by synthesizing GO-coated silica fume (SF) to promote the utilization of GO in cement-based materials. Specifically, the surface of pristine SF was modified to convert their zeta potential (modified SF: MSF), then GO-coated SF (i.e., MSF@GO) was prepared via electrostatic adsorption of GO onto the MSF surface. The experimental results revealed that adding 5MSF@GO hybrid (0.04% GO and 5% MSF, by weight of binder) significantly reduced yield stress and plastic viscosity by 51.5% and 26.2%, respectively, relative to the 0.04% GO-modified sample. These findings indicated that application of GO-coated SF is an effective and environmentally friendly way to develop sustainable cementitious composites.

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**Keywords** Cement composites · Graphene oxide · Rheological property · Silica fume · Surface modification

## 1 Introduction

Cement-based materials are the most extensively used construction materials because of their low cost, high compressive strength, and durability [1, 2], with an estimated yearly consumption of >30 billion tonnes [3]. However, their brittle nature limits broad application in some structures [4]. Additionally, the cement/concrete industry is energy intensive with a substantial environmental footprint [5]. According to previous studies [5, 6], enhancing the microstructure of cement-based materials and improving their mechanical strengths/durability is considered to be a candidate way to alleviate carbon emissions. Calcium–silicate–hydrate (C–S–H) gel, the principal hydrate of cement grains, is composed of nanocrystalline with an atomic structure similar to that of tobermorite and/or jennyite (i.e., it is a nanoscale material) [7]. Advancements in nanomaterials and nanotechnology have been providing great opportunities to enhance the structure of cement composites at the nanoscale, eventually improving the macroscale properties [7, 8].

As a typical two-dimensional nanomaterial, graphene oxide (GO) has been considered a favorable additive for improving the mechanical strengths and durability of cement-based materials [5, 9]. However, GO tends to agglomerate in an alkaline hydration environment when cement grains dissolve in water [10], which dramatically deteriorates the workability of fresh mixtures. Note that, the fresh properties of mixtures greatly affect the mechanical and durability properties of the hardened composites.

Polycarboxylate superplasticizer (SP) is generally used both for preparing high-quality GO solution and for improving the fresh properties of the cement pastes [10]. However, obtaining a high-quality GO solution before mixing with cement does not directly result in well-dispersed GO in the alkaline cement matrix. It has been demonstrated [9, 11] that using silica fume (SF) can predisperse GO in the cement matrix. These studies claim that the electrostatic repulsion between negatively charged SF and GO is primarily responsible for the improved GO dispersion. Nevertheless, the electrostatic repulsion theory may not apply to such a system because of the remarkably larger lateral size of GO than that of SF [11]. Inspired by GO-coated sand, which can reduce the migration resistance in water and improve the adsorption ability in water treatment applications [12], we developed GO-coated SF via electrostatic adsorption of GO onto the surface of the modified SF (MSF), aiming to better utilize GO in cementitious composites and exert the co-effects of the two materials. Especially, this work focused on investigating the properties of fresh cement pastes incorporating GO-coated SF, aiming to promote the application of GO in environmentally friendly high-performance cement composites.

## 2 Methods

### 2.1 Materials

Cement (P·O 42.5) and SF were used to prepare cement paste. GO was synthesized by modified Hummers' method, leading to a specific surface area (SSA) of ~2600 m<sup>2</sup>/g. The chemical bonds in the GO used in this study mainly contained C–O, C = O, C = C, and O–H. The XPS data revealed that the C/O was ~1.97.

### 2.2 Preparation of GO-Coated SF and Cement Paste

To improve the compatibility of GO and the cement matrix, the concept of GO-coated SF was proposed, enabling the co-effects of GO and SF in the cement composite. Specifically, MSF particles were obtained by treating the surface of SF with Ca(OH)<sub>2</sub> solution. To eliminate potential chemical reactions on the SF surface, the modification process was optimized according to previous experience [5], where the SF was added to the Ca(OH)<sub>2</sub> aqueous solution at a weight ratio of 1:10. After that, the SF/MSF was mixed with the GO solution and stirred for 10 min to synthesize SF-GO or GO-coated SF. All pastes were fabricated by mechanically stirring for 4 min. Finally, the fresh pastes were used for rheological properties tests.

### 2.3 Testing Methods

The micromorphology was observed using a ZEISS electron microprobe. The surface functionality of particles was assessed via a Nano ZS zeta potential analyzer. SmartLab XRD with an incident beam of Cu-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) for a  $2\theta$  scanning range of 15–65° was used to examine the crystalline phase analyses of the powder samples. A high-resolution FEI-TEM was used to compare the morphology of SF-GO and GO-coated SF. A Brookfield RST-SST rheometer equipped with a rotating vane (VT20-10) was used to perform the rheological tests. During testing, the shear rate increased from 5 to 150 s<sup>-1</sup> in 60 s and a corresponding decrease in shear rate from 150 to 5 s<sup>-1</sup> in the following 60 s. The yield stress and plastic viscosity can be obtained as follows:

$$\tau = \tau_0 + \mu\gamma + c\gamma^2 \quad (1)$$

where  $\tau$  is the shear stress (Pa),  $\gamma$  is the shear rate (1/s),  $\mu$  is the plastic viscosity (Pa·s),  $\tau_0$  is the yield stress (Pa), and  $c$  is the second-order coefficient (Pa·s<sup>2</sup>).

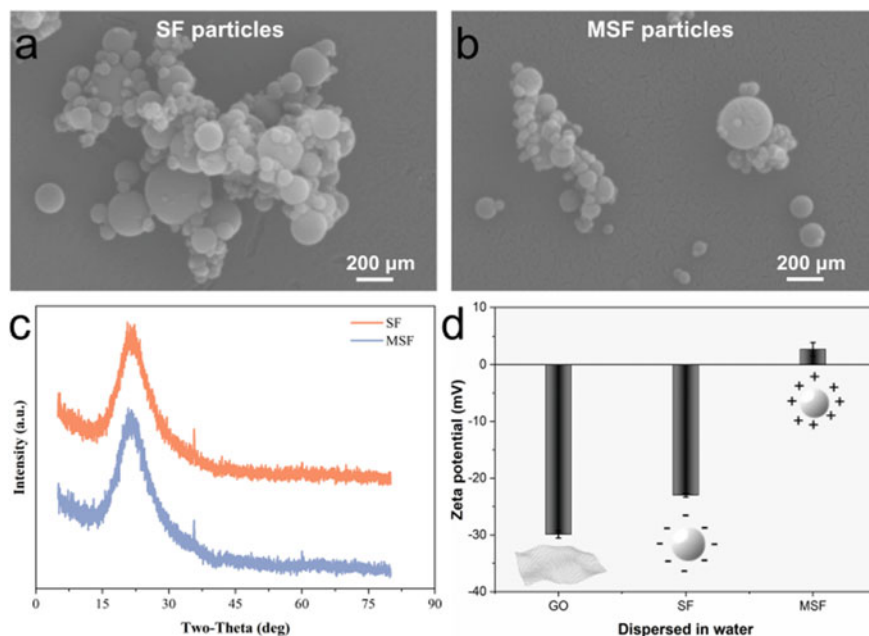
### 3 Results and Discussion

#### 3.1 Evaluation of the Surface Properties of MSF Particles and the MSF@GO

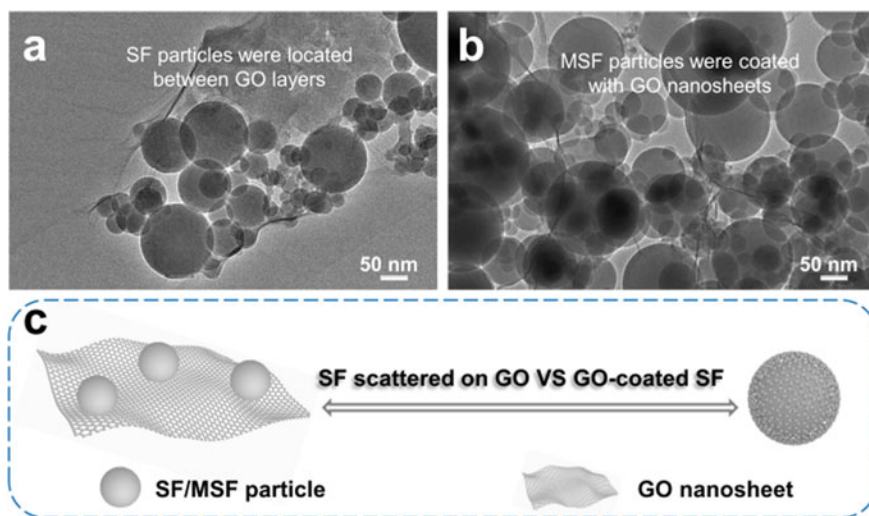
Considering SF particles have the potential to react with  $\text{Ca}(\text{OH})_2$  solution, as such the modification process was optimized, aiming to ensure that any chemical reaction on the SF surface could be discounted.

As presented in Fig. 1a, b, SF and MSF both exhibited a spherical shape with a size ranging from 50 to 300 nm. The XRD patterns of the SF and MSF were almost indistinguishable, without the broad peaks of C-S-H gel found in MSF samples (Fig. 1c). As suggested in Fig. 2d, the zeta potential of the SF ( $-23$  mV) converted to  $\approx +3$  mV (MSF), thanks to some calcium ions grafted onto the SF surface. These findings all support that MSF maintained the surface morphology and crystalline phase after treatment, its surface only achieving ion exchange.

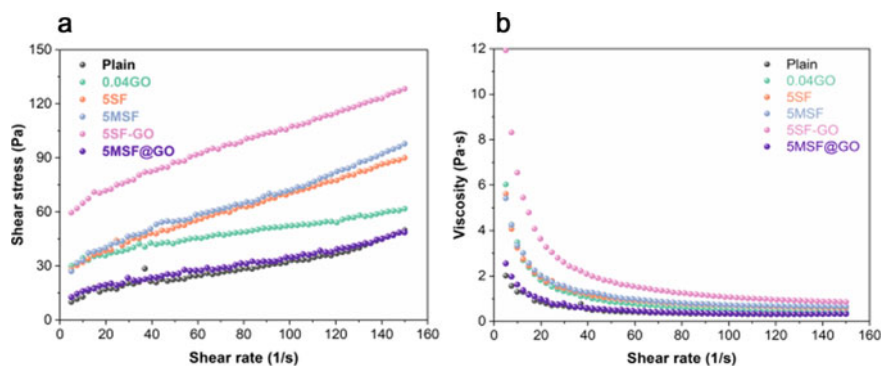
As indicated in Fig. 2, a thin layer of GO was found uniformly and tightly adsorbed onto the surface of the MSF (Fig. 3b). In contrast, several SF particles were merely interspersed between GO layers (Fig. 3a). Such a strong MSF@GO interaction showed great potential to exert their co-effects in cement-based materials.



**Fig. 1** Properties of the silica fume (SF) particles before and after modification: scanning electron microscopy images of **a** SF, **b** modified SF (MSF); **c** X-ray diffraction patterns; and **d** zeta potential



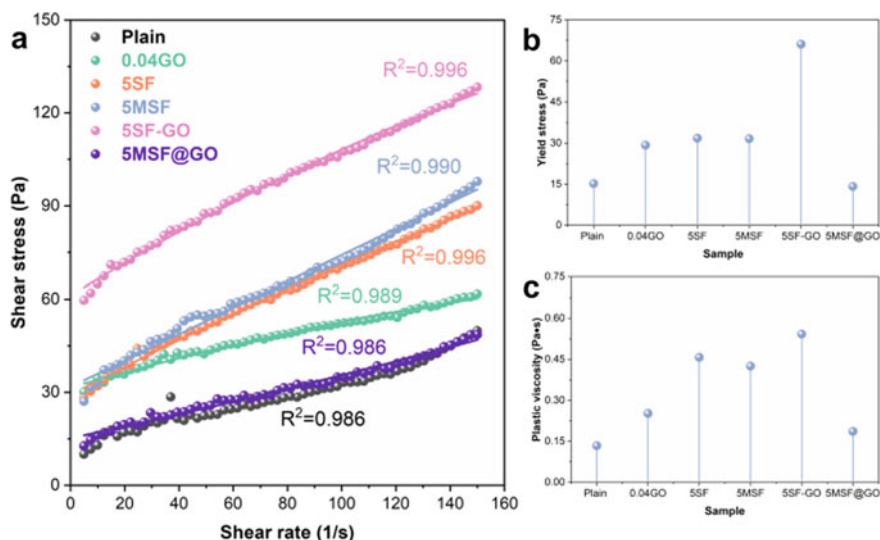
**Fig. 2** Morphology of **a** SF-GO and **b** MSF@GO; **c** schematic diagram of SF particles located between GO layers (SF-GO) and GO-coated SF (MSF@GO). GO, graphene oxide; MSF, modified SF; SF, silica fume



**Fig. 3** Rheological parameters of the paste: **a** shear stress–shear rate curves and **b** viscosity–shear rate curves. GO, graphene oxide; MSF, modified SF; SF, silica fume

### 3.2 Rheological Properties

The shear stress–shear rate curves shifted upwards after admixing 0.04 wt% GO, as compared with plain paste (Fig. 3a). Simultaneously, the viscosity of the 0.04 wt% GO-modified paste also increased at both high and low shear rates (Fig. 3b). Specifically, the yield stress and plastic viscosity of the pastes were calculated based on an improved Bingham's model: adding 0.04 wt% GO to the paste increased the yield stress and plastic viscosity by 92.5% (Fig. 3b) and 88.1% (Fig. 3c), respectively.



**Fig. 4** a Linear regression of shear stress–shear rate curves; calculated b yield stress and c plastic viscosity. GO, graphene oxide; MSF, modified SF; SF, silica fume

Adding SF or MSF decreased the yield stress and plastic viscosity of the pastes (Fig. 4b, c). The mixture of 5SF-GO exhibited the highest shear stress–rate curve (Fig. 3), with the highest yield stress (66.1 Pa) and plastic viscosity (0.54 Pa·s), which implied that this formulation of cement composite has poor workability and is not suitable for practical applications. Additionally, the yield stress and plastic viscosity of the 5MSF@GO mixture decreased by 51.5% and 26.2%, respectively, relative to the 0.04 wt% GO-modified sample (Fig. 4). The MSF@GO hybrid adsorbed GO onto the MSF, thereby making the spherical particles easily migrate. In addition, the negatively charged GO coated onto the surface of the MSF, which provided electrostatic repulsion among particles, enabled better dispersion of GO (and MSF) and released entrapped water to turn into free water.

## 4 Conclusions

In this study we developed a high-performance cement composite incorporating GO-coated SF. The surface properties of GO-coated SF, the rheological properties, and compressive strength of composites were studied.

The surface of pristine SF particles was modified to convert their zeta potential; while the surface morphology and chemical composition remained unchanged, the SF surface merely achieved ion exchange. The positively charged MSF allowed negatively charged GO to adsorb on its surface via electrostatic adsorption. The

strong bonding showed great potential for exerting a cooperative improvement effect in cement composites.

Different from the traditional direct introduction of GO or SF into cement paste, which seriously increased the yield stress and plastic viscosity of the mixtures. Adding 0.04 wt% GO together with 5 wt% MSF decreased the yield stress and plastic viscosity by 51.5% and 26.2%, respectively. The improved fresh properties provide guarantees for the transportation and construction of the cement composites.

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