Supplementary Information

Optimization of the spray-drying process with response surface methodology (RSM) for preparing high-quality graphene oxide slurry

Contents

Discussion S1. Analysis of the graphene oxide powder (GOP)

Powder yield (Y_1)

The GOP was weighed after the storage in a humidity chamber over 48 h, defined as m_{wet}. The dry mass of the GOP (m_{dry}) was estimated by using Eq. S1, in which the humidity of the wet powder (H) was obtained with Eq. S2. Then the powder yield (Y_1) was calculated as Y_1=m_{dry}/m_{feed}, where m_{feed} is the mass of GO introduced in the feed solution and it is 2 g in this study. Each sample was tested 3 times.

$$m_{dry} = m_{wet} \frac{1}{1+H} \quad \text{(S1)}$$

$$H = 0.622 \frac{\varphi P_s}{P - P_s} \quad \text{(S2)}$$

where φ is the relative humility (φ=70%), P_s is the saturated vapor pressure of water (P_s=3.168 kPa, T=25 °C), and P is the standard atmosphere (P=101.325 kPa).

Particle size (Y_2)

The particle size distribution of the GOP was measured by using a dynamic light scattering instrument (S3500, Microtrac Inc. USA). D_{50} was used to represent the particle size (Y_2), which is directly related to the crumpling degree of the obtained GOP.

Re-dispersibility (Y_3)

The re-dispersibility was measured by the following procedure. A certain amount of GOP (about 50 mg) was first weighed, recorded as m_0, and then added into 100 mL (V) deionized water. After 2 h ultrasonication, the GOP dispersion was centrifuged at 4000 rpm for 15 min to remove undispersed powder. Finally, the supernatant was diluted 5 times for UV test and the specific mass concentration of the supernatant (C_s) was obtained by fitting the absorbance to the standard GO curve (Figure S1). The re-dispersibility of the GOP was calculated with Eq. S3.

Each sample was tested 3 times.

$$Y_3 = \frac{5C_s V}{m_0} \quad \text{(S3)}$$

Adsorption capacity (Y_4)

To test the adsorption ability of the GOP, methylene blue (MB) was used as an example for the dye removal experiment. A certain amount of GOP (about 10 mg) was first weighted, recorded as m_1, and then added into 100 mL (V), 25 mg·L^{-1} MB solution (C_0). The mixture was shaken for 8 h in a shaker to reach the adsorption equilibrium, followed by a filtration. The filtrate was used for the UV test to determine the equilibrium concentration (C_e). The adsorption capacity of GOP (Y_4) was calculated with Eq. S4. Each sample was tested 3 times.

$$Y_4 = \frac{(C_0 - C_e)V}{m_1} \quad \text{(S4)}$$

Discussion S2. Calculation of the droplet size

The droplet size used here is the Sauter mean diameter, which is widely used to describe the droplet size in an atomization process. Poozesh *et al.* studied the atomization process of the bi-fluid nozzle and proposed an empirical formula as follows[1]:

$$\frac{D_d}{d_L} = 0.106 \cdot We_g^{-0.188} \cdot GLR^{-0.45} \cdot \left(1 + 1.5 \cdot Oh\right) \quad \text{(S5)}$$

where D_d is the droplet size and d_L is the liquid orifice diameter (7 mm). The measured D_d is only related to Weber number (We_g), gas to liquid mass flow ratio (GLR), and Ohnesorge number (Oh). These dimensionless parameters can be described as:

$$\mathrm{We}_g = \frac{\upsilon_g{}^2 \rho_g d_L}{\sigma} = \frac{\left(\dfrac{4Q_a}{\pi\left(d^2 - d_L^2\right)}\right)^2 \rho_g d_L}{\sigma} = \frac{16Q_a^2 \rho_g d_L}{\pi^2 \sigma \left(d^2 - d_L^2\right)^2} \quad \text{(S6)}$$

$$GLR = \frac{m_g}{m_L} = \frac{Q_a \rho_g}{Q_L \rho_L} \quad (S7)$$

$$Oh = \frac{We^{0.5}}{Re} = \frac{\mu}{\sqrt{\rho_L \sigma d_L}} \quad (S8)$$

where Q_a is the nozzle airflow rate, ρ_g is the gas density (1.251 kg·m^{-3}), σ is the liquid surface tension (0.075 N·m^{-1}), d is the outer diameter of the nozzle (1.3 mm), Q_L is the liquid feed rate, ρ_L is the liquid density (1000 kg·m^{-3}), and μ is the liquid viscosity (1 cp). According to Eq. S6, S7 and S8, We_g, GLR, and Oh can be calculated respectively and then substituted into Eq. S5 to obtain the corresponding droplet size.

Table S1. Single-factor experimental results with various nozzle airflow rates (atomization pressure=0.6 MPa, liquid feed rate =9.0 mL·min^{-1}).

Nozzle airflow rate (L·h^{-1})	Droplet size (μm)	Powder yield (%)	Particle size (μm)	Re-dispersibility (%)	Adsorption capacity (mg·g^{-1})
283	32.91	41.63	13.05	92.81	248.8
439	22.90	68.80	10.34	82.50	238.3
667	16.21	63.36	6.42	37.77	224.3
895	12.72	55.55	4.52	17.35	200.8
1051	11.14	43.27	3.45	4.35	173.6

Table S2. Single-factor experimental results with various atomization pressures (nozzle airflow rate=439 L·h^{-1}, liquid feed rate=9.0 mL·min^{-1}).

Atomization pressure (MPa)	Droplet size (μm)	Powder yield (%)	Particle size (μm)	Re-dispersibility (%)	Adsorption capacity (mg·g^{-1})
0.4	27.26	60.79	12.20	87.81	240.0
0.5	25.31	68.71	11.52	83.85	238.8
0.6	22.90	68.80	10.34	82.50	238.3
0.7	20.64	66.91	9.75	79.99	231.1
0.8	17.62	56.39	8.43	54.01	226.1

Table S3. Single-factor experimental results with various liquid feed rates (nozzle airflow rate=439 L·h^{-1}, atomization pressure=0.6 MPa).

Liquid feed rate (mL·min^{-1})	Droplet size (μm)	Powder yield (%)	Particle size (μm)	Re-dispersibility (%)	Adsorption capacity (mg·g^{-1})
3.0	16.77	60.79	12.20	73.32	231.1
4.5	20.12	68.71	11.52	80.00	232.1
6.0	22.90	68.80	10.34	82.50	238.3
7.5	25.32	66.91	10.84	89.80	240.8
9.0	27.49	56.39	8.43	97.37	244.6

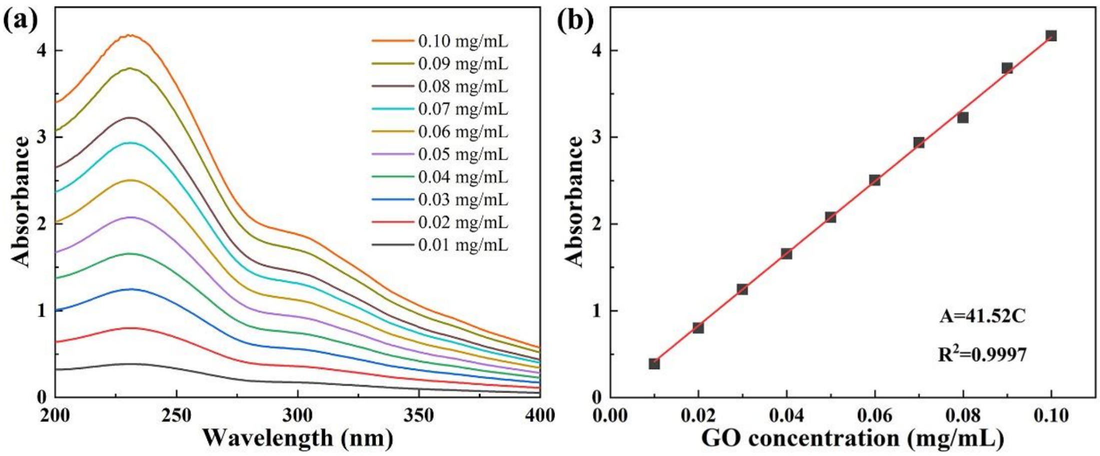

Figure S1. (a) UV-visible spectra of GO dispersion. (b) Fitted standard GO curve.

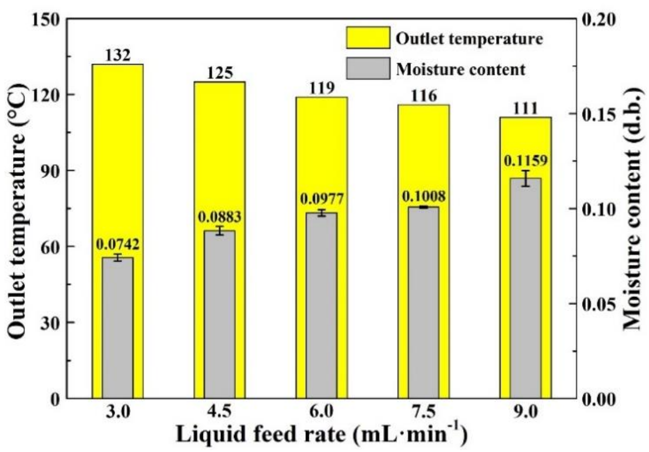

Figure S2. Effects of Q_L on the outlet temperature and the moisture content of GOP.

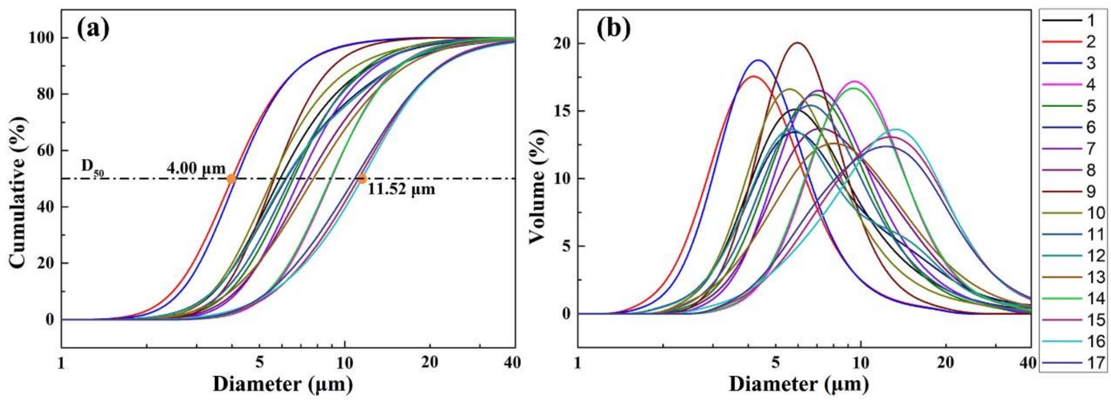

Figure S3. Particle size distributions of GOPs at all the experimental conditions.

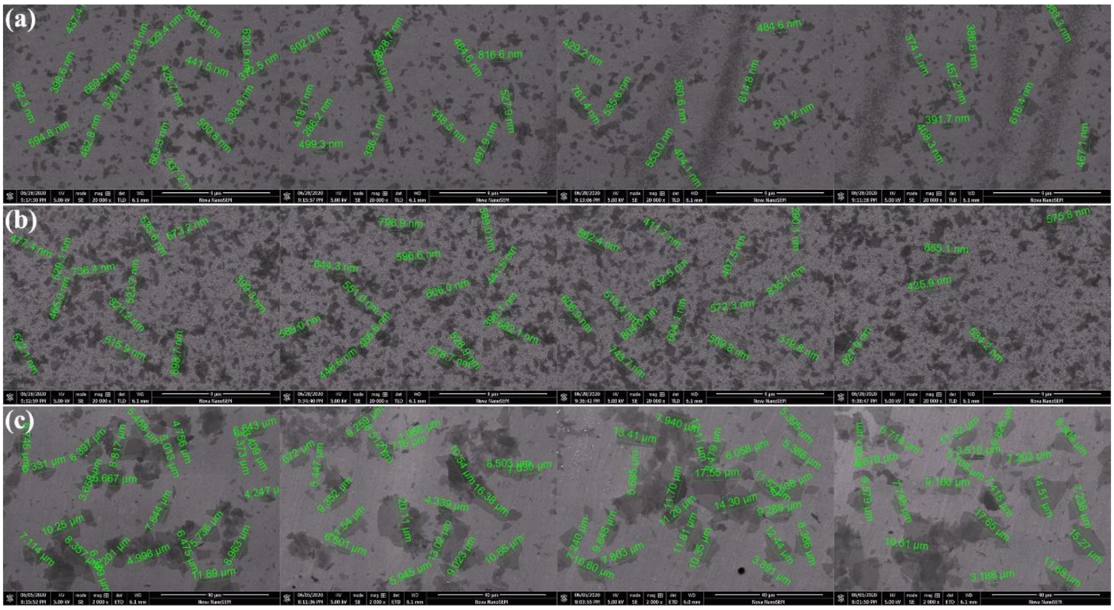

Figure. S4. SEM images of exfoliated (a) GOP, (b) pristine GO, and (c) graphite oxide for size statistics.

Reference

1. Poozesh, S.; Setiawan, N.; Akafuah, N.K.; Saito, K.; Marsac, P.J. Assessment of predictive models for characterizing the atomization process in a spray dryer's bi-fluid nozzle. *Chem. Eng. Sci.* **2018**, *180*, 42–51.