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# Simultaneous measurement of internal and external properties of nanoparticles in flame based on thermophoresis

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### ABSTRACT

The mechanism of nanoparticles processed in flame aerosol reactors involves vapor to solid reaction, nucleation, coalescence, agglomeration, diffusion and other processes. Determination of internal (e.g., particle size distribution (PSD), aggregate fractal dimension (AFD), and particle volume fraction (PVF)) and external (e.g., temperature and flow velocity) properties of nanoparticles through numerical simulations or experimental measurements is critical to understanding the underlying particle dynamics, which still remains a major challenge. Multiple key internal and external properties of nanoparticles in flame were measured and characterized simultaneously in this study by a simple and novel dual time-interval thermophoretic sampling (DTTS) method. A tailor-made fine-wire thermocouple was first used to measure flame temperature, with a sufficiently short residence time to reduce the effects of radiation losses and nanoparticles deposition as possible and thereby the thermocouple response met the first-order dynamic equation where only heat convection was considered. Two TEM grids were used for nanoparticle sampling at a position and were exposed to flame for two different time intervals. As the amount of particles deposited on the probe surface by the thermophoretic force is a function of gas temperature, flow velocity, PVF and the probe exposure time in the flame, we proposed an integrative solution for these multiple parameters using the two samples by accounting for the effects of the unsteady temperature gradient of the probe. The effects of flow velocity on convection heat transfer of flame and TEM grids were considered by analyzing the visible microscopic state of thermophoretic-deposited particles. A co-flow diffusion CH<sub>4</sub> flame for TiO<sub>2</sub> nanoparticle synthesis by feeding TiCl<sub>4</sub> vapor was measured via the DTTS method. The experimental measurements of flame temperature, flow velocity and PVF at the different flame heights agree well with the simulation results by coupled computational fluid dynamics with population balance modeling (CFD-PBM).

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## 1. Introduction

Flame synthesis of nanoparticles is routinely used to make a variety of commercial materials, including TiO<sub>2</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, amounting to millions of tons annually. They are used industrially as pigments, opacities, catalysts, and for other functions [1,2]. Flame synthesis is a complex process, as all characteristics of the product particles are determined within a few milliseconds and can be influenced by many process variables [3]. Consequently, it is not surprising to find a large number of early research studies focusing on all sorts of tricks and devices to control product characteristics or to facilitate design and operation of flame reactors [4,5]. At present, a clear understanding of flame synthesis of nanoparticles remains a major challenge even though a variety of

scientific communities have studied it closely [3]. The complex chemistry and particle dynamic processes that include combustion, flow and particle evolution need to be explored more deeply by measurement and diagnostic techniques. The concentration distribution and temperature history of reactants (including fuel, oxidants, precursors and particulates) have been shown to be the most important parameters that determine the characteristics of the product particles [6]. In flame reactors, the temperature history is influenced primarily by the flame temperature and gas flow. Therefore, flame temperature, flow velocity, particle concentration (i.e., particle volume fraction (PVF)) and particle internal characteristics (typically particle size distribution (PSD)) must be measured simultaneously.

Flame temperatures as a function of height are typically measured with a fine-wire thermocouple [7]. The measured temperatures are then corrected for radiation loss according to Collis and Williams [8]. It is worth noting that thermocouple measurement

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temperature. K

residence time of TEM grid in flame, s

temperature of thermocouple junction, K

geometric average volume of aggregate, m<sup>3</sup>

total volume of deposited particles in a FSEM image, m<sup>3</sup> projected maximum width of *i*-th aggregate (normal to

particle thermophoresis velocity, m/s

actual flame temperature, K surrounding temperature, K

temperature of TEM grid, K gas flow velocity, m/s

particle volume, m<sup>3</sup>

maximum length), m

position, distance, m

molar mass of the component *i* 

## Nomenclature

а	particle surface area, m <sup>2</sup>	Т
A <sub>ai</sub>	projected area of <i>i</i> -th aggregate, m <sup>2</sup>	t <sub>e</sub>
a <sub>g</sub>	gas thermal diffusivity, m <sup>2</sup> /s	$T_{g}$
Åi	total area of FSEM image, $m^2$	T <sub>sur</sub>
A <sub>ni</sub>	projected area of a primary particle within <i>i</i> -th aggre-	$T_{th}$
<i>p</i> .	gate. m <sup>2</sup>	$T_w$
С	mole concentration of gas, mol/m <sup>3</sup>	u <sub>o</sub>
Cσ	specific heat capacity of gas. I/(kg K)	ит
C <sub>th</sub>	specific heat capacity of thermocouple junction mate-	v
- ui	rial. I/(kg K)	$v_{a}$
Cuu	specific heat capacity of TEM grid material. I/(kg K)	V <sub>n</sub>
D	diameter of thermocouple junction, m	Wai
d	diameter of lead wire m	•• 11
d <sub>a a</sub>	geometric mean volume-equivalent diameter of aggre-	W:
æu,g	gate m	x
De	mass-fractal dimension	л
D <sub>f</sub>	scaling exponent based on projected area	Cues
d	geometric mean diameter of primary particle m	Gree
d.	primary particle diameter within i-th aggregate m	$\alpha_{mon}$
$D_m$	primary particle diameter within <i>i</i> -th aggregate, in particle thermonhoretic diffusivity $m^2/s$	$\alpha_n$
DT F	activation energy kl/mol	β
L <sub>S</sub> f	narticle volume fraction	c
J v h	convective heat transfer coefficient $W/(m^2 K)$	8
n Þ	turbulent kinetic energy $m^2/s^2$	$\Delta I$
K L	Poltzmann constant 1 22065 $\times 10^{-23}$ L/V	3
K <sub>B</sub>	$\frac{1}{3} \int \frac{1}{3} \int \frac{1}$	$\varepsilon_p$
Kf L	nacial prefactor	$\varepsilon_{th}$
K[ Kn	Vielacioi Knudsen number, dimensionless	$\mathcal{E}_W$
	neciested maximum length of <i>i</i> th aggregate m	θ
L <sub>ai</sub>	projected maximum length of <i>i</i> -th aggregate, in molecular weight of TiO $_{-70.965} \times 10^{-3} \text{ kg/mol}$	$\vartheta_T$
IVI <sub>p</sub>	1101000000000000000000000000000000000	$\lambda_g$
TL N	number density function of particle, $\#/(\Pi^2 \Pi^2)$	$\lambda_{th}$
N <sub>i</sub>	number of primary particles within the <i>i</i> -th aggregate	
NU	Nusselt number, dimensionless	vg
Pr	Prandtl number, dimensionless	$v_i$
<b>q</b> <sub>Cond</sub>	conduction neat flux, W/m <sup>2</sup>	$ ho_{g}$
$q_{Conv}$	convection heat flux, w/m <sup>2</sup>	$ ho_p$
$q_{Rad}$	radiation neat flux, W/m <sup>2</sup>	$ ho_{th}$
r	reaction rate, $mol/(m^2 s)$	$ ho_w$
ĸ	gas constant, 8.314 J/(mol K)	$\sigma$
ке	Reynolds number, dimensionless	τ
SA	specific surface area, m <sup>2</sup> /g	$ au_s$
ť	time, s	

ek symbols momentum accommodation coefficient normal absorptivity agglomeration rate coefficient (agglomeration kernel),  $m^{3} s^{-1}$ thickness of TEM grid, m temperature error, K dissipation rate of turbulent kinetic energy, m<sup>2</sup>/s<sup>3</sup> emissivity of TiO<sub>2</sub> particle emissivity of thermocouple junction emissivity of TEM grid dimensionless temperature dimensionless particle deposition flux gas thermal conductivity coefficient, W/(mK) thermal conductivity coefficient of junction material, W/(m K)gas kinematic viscosity, m<sup>2</sup>/s stoichiometric coefficient of component *i* gas density, kg/m<sup>3</sup> density of TiO<sub>2</sub> particle, kg/m<sup>3</sup> density of thermocouple junction material, kg/m<sup>3</sup> density of TEM grid material, kg/m<sup>3</sup> Stefan-Boltzmann constant,  $5.67 \times 10^{-8}$  W/(m<sup>2</sup> K<sup>4</sup>) time constant, s characteristic sintering time, s

in the presence of the precursor results in the deposition of particles on the wire by thermophoresis and diffusion, which changes the emissivity of the wire and may deteriorate the measurement accuracy. Laser-induced fluorescence (LIF), which has been used in gas phase combustion, was successfully used for flame temperature measurement in dilute particle-laden low pressure flames [9]. Fourier transform infrared (FTIR) spectroscopy is also particularly attractive, as it concurrently provides information on the flame temperature, gas composition and particle concentration during flame synthesis [10]. However, LIF thermometry is hard to carry out and lacks accuracy [11], and FTIR can suffer from isolating the signal region in addition to accuracy [12,13], both of which require novel approaches and further development.

There is not currently an available measurement solution for flow velocity in flame synthesis because most flow velocity measurements depend on micron-sized tracer particles, such as particle image velocimetry (PIV) [14] and laser Doppler velocimetry (LDV) [15]. As is known, the introduction of tracer particles to flame aerosol reactors has deleterious effects on nanoparticle synthesis and the measurement of other parameters, such as PVF. The flow velocity distribution is therefore generally obtained by numerical simulation, especially for some measurement-difficult object. Many efficient models and algorithms have been developed and applied [16–18]. The accuracy of numerical simulation strongly depends on the models and algorithms used.

The experimental detection and quantitative measurement of particles with sizes below 10 nm are still intractable. Most notably, the characteristic fingerprints of very small particles from molecular spectroscopy are generally not available [19]. A laser-based diagnostic for nanoparticles has recently been developed called laser-induced incandescence (LII) [20]. Complex instruments and data processing algorithms must be used and developed. A few commercial instruments, such as scanning mobility particle sizers (SMPS), are available for measurement of PVF and PSD, based on evaluating their concentration in the gas by sampling analysis [21].

To individually characterize fine particles using electron microscopy (EM) methods, the particles must be collected on special substrates, such as TEM grids, for subsequent detailed analysis by techniques including transmission electron microscopy (TEM), scanning electron microscopy (SEM). Methods of collecting particles onto substrates for microscopy include those employing inertial impaction, gravitational settling, vapor deposition, and electrostatic precipitation [22]. An alternative to these methods is a method based on thermophoretic deposition, which is also the most common and easily realized way of collecting particles out of a flowing gas, introduced by George et al. [23] and further improved by Dobbins et al. [24] for measuring the size and morphology of flame-generated soot. Köylü et al. [25] put forward the thermophoretic sampling particle diagnostic (TSPD) method based on the theory of particle deposition rate by Eisner and Rosner [26], which can be used to determine not only particle/aggregate size and microstructure but also absolute soot volume fraction. However, the TSPD technique is subject to the following assumptions and restrictions [25]: (1) The gas flow velocity is known, being approximately 1 m/s; (2) The probe exposure time (23-65 ms) is chosen to have less than 15% total particle coverage of the TEM grids; (3) The probe wall temperature is constant at 350 K. In fact, there is spatial correlation of gas flow velocity even in a steady flame, with exact numbers not known in advance, and the wall temperature of the probe changes over the exposure time in the flame due to heat transfer.

To summarize, there are many options for measuring the external and internal properties of nanoparticles in flame, but due to functional limitations, they are typically functionally onefold, are hard to carry out and lack accuracy. A comprehensive and practical measurement method is highly required. As thermophoretic sampling can obtain information on particle volume fraction, particle size distribution and particle microstructure, we extended the TSPD method to develop a novel but simple method for simultaneous measurements of flame temperature, flow velocity, PVF, and PSD in flame. The relationship between thermophoretic sampling and flow field was considered. A fine-wire thermocouple, which can reduce disturbance to flame as possible, was used to measure the flame temperature, and nanoparticles in the same position were sampled by two TEM grids, which were exposed to flame for two different time intervals. Based on SEM images of these samples, PSD was obtained by grouping the nanoparticles by size and counting particle numbers within each size section using the image processing software ImageJ. PVF and flow velocity were further calculated using an integrative solution based on the two samples with different probe residence times, considering that the flame temperature, flow velocity, PVF and the probe residence time in the flame are interrelated. This multi-parameter measurement method is called dual time-interval sampling (DTTS) at a single point method. The DTTS was examined in a co-flow diffusion CH<sub>4</sub> flame for TiO<sub>2</sub> nanoparticle synthesis by feeding TiCl<sub>4</sub> vapor. The experimental measurements of flame temperature, flow velocity and PVF at different flame heights were compared with simulation results by coupled computational fluid dynamics (CFD) with population balance modeling (quadrature method of moments (QMOM) method and population balance-Monte Carlo method (PBMC)). It was found that the thermophoretic sampling technique can be used to reasonably determine not only particle/aggregate size and microstructure (i.e., aggregate fractal dimension (AFD)) but also absolute PVF, flow velocity and PSD in flame.

# 2. Experimental

#### 2.1. Apparatus

The laboratory apparatus for the synthesis of  $TiO_2$ , shown in Fig. 1, consists of a flame reactor, vaporizer of precursor  $TiCl_4$ , thermophoretic sampling probe, thermocouple and other equipment. In our work, a co-flow diffusion burner was designed (shown in Fig. 1c), in which four concentric tubes were aerated with  $TiCl_4$  (vapor) and  $N_2$  ( $N_2$  was dilute gas and carrier gas),  $CH_4$ +Ar (Ar was used to dilute  $CH_4$  to eliminate the generation of soot in the

combustion process), O<sub>2</sub> (oxidizer), and N<sub>2</sub> (sheath gas), from the outside to the center. The precursor TiCl<sub>4</sub> was vaporized in a constant temperature and pressure container (vaporizer) and was then carried into the flame reactor by N<sub>2</sub>. The chemical reactions involved in the flame were  $CH_4 + 2O_2 \rightarrow 2H_2O(g) + CO_2$  and  $TiCl_4$  $(g) + O_2 \rightarrow TiO_2 + 2Cl_2$ . The CH<sub>4</sub> combustion flame leads to a stable temperature field that provides the energy needed for the nanoparticle synthesis process, including the oxidation of the TiCl<sub>4</sub> and the dynamic evolution of particles. The oxidation of TiCl<sub>4</sub> is a rapid reaction process, in which TiCl<sub>4</sub> is first transformed into gaseous TiO<sub>2</sub> molecular clusters [27]. At the high supersaturation pressure, a series of dynamic events including collision between primary particles, sintering and surface reaction leads to the formation of polymorphic aggregates. As the underlying mechanisms involved in this process were still unknown, detailed and quantitative measurements of multiple parameters in the flame (i.e., flame temperature, flow velocity, PVF and PSD) were essential to study the effect and range scale of the kinetic events involved.

#### 2.2. Flame temperature measurement

The flame temperature profiles were measured by a B-type (Pt/ Rh 70%/30% – Pt/Rh 94%/6%, by weight) fine-wire thermocouple that was insulated with an alumina sheath tube (ID 0.8 mm, OD 3 mm). The last centimeter of the two lead wires up to the welded junction was uncoated. The junction diameter is 0.7 mm, and the lead wire diameter is 0.3 mm. The temperature profiles along the axial line of flame at several specified measuring points (T1, T2, ..., T11, see Fig. 1d) were then obtained. Generally, the flame temperature can be estimated from the junction temperature by equating the heat transfer that consists of three aspects: (1) the convection heat transfer from the flame into the junction; (2) the radiative heat transfer by the junction to its surroundings through an optically thin flame; and (3) the conduction heat transfer along the lead wires. The unsteady energy equation for the thermocouple junction takes the form [28]

$$\rho_{\rm th} c_{\rm th} \frac{\pi D^2}{4} \frac{\partial T_{\rm th}}{\partial t} = N u \lambda_g \pi (T_{\rm g} - T_{\rm th}) - \pi D \sigma \varepsilon_{\rm th} \left( T_{\rm th}^4 - T_{\rm sur}^4 \right)$$
  
+ 
$$\lambda_{\rm th} \frac{\pi d^2}{4} \frac{\partial^2 T_{\rm th}}{\partial x^2}$$
(1)

where  $T_{th}$  is the temperature of the junction,  $T_g$  is the actual flame temperature, and  $T_{sur}$  is the surrounding temperature;  $\lambda_g$  and  $\lambda_{th}$ are the thermal conductivity coefficients of the gas and the junction material, respectively;  $\rho_{th}$  and  $c_{th}$  are the density and specific heat capacity of the junction material, respectively; d and D are the diameters of the lead wire and junction, respectively;  $\varepsilon_{th}$  is the emissivity of the junction, as provided by Hindasageri et al. [29], whereas the emissivity of the surroundings is approximately equal to 1; and  $\sigma$  is the Stefan–Boltzmann constant. The non-dimensional convective heat transfer coefficient, the Nusselt number *Nu*, can be expressed as [30]:

$$Nu = \frac{hD}{\lambda_g} = \left[2 + 0.6 \left(c_g \rho_g v_g / \lambda_g\right)^{0.33} \left(u_g D / v_g\right)^{0.5}\right]$$
(2)

where  $c_g$ ,  $v_g$ , and  $\rho_g$  are the specific heat capacity, kinematic viscosity and density of gas in flame, respectively, and  $u_g$  is the gas flow velocity.

The response of a temperature sensor known as a thermocouple may be modeled as a first-order system. When the thermocouple is subjected to a rapid temperature change, it will take some time to respond. If the dominant mechanism of heat exchange is convection (neglecting conduction and radiation), as it is for a thermocouple in a fluid, then this energy balance is



Fig. 1. Schematic of experimental equipment: (a) thermophoresis sampler; (b) thermocouple; (c) flame reactor; (d) measuring points of flame.

$$h\pi D^2 (T_g - T_{th}) = \rho_{th} c_{th} \frac{\pi D^3}{6} \frac{dT_{th}}{dt}$$
(3)

The solution to Eq. (3) with the initial temperature  $T_0$  (293.15 K) at time t = 0 is then [31]

$$T_{\rm th}(t) = T_0 + (T_{\rm g} - T_0)(1 - \exp\left(-t/\tau\right))$$
(4)

namely first-order response equation of thermocouple, where the time constant is  $\tau = \rho_{th} c_{th} D/6h$ , *t* is the residence time of the thermocouple in the flame, and  $T_{th}(t)$  is the response temperature at *t*. The rate at which the response approaches the final temperature is determined by the time constant. Typically, when  $t = \tau$ ,  $T_{th}$  can reach 63.2% of  $T_g$ ; when  $t = 5\tau$ ,  $T_{th}$  has reached 99.3% of  $T_g$ . However, the radiation losses of the thermocouple junction increases sharply with the junction temperature increasing, which cause the thermocouple deviating from the first-order response and the final temperature of the junction being much less than the flame temperature. When using regular thermocouples like thin R-type thermocouples with a relatively smaller time constant presented in [32,33], the radiative heat transfer out of the thermocouple junction causes larger deviations between the flame temperature and the recorded junction temperature due to junction rapid temperature rise in a short time, and therefore cannot be neglected. Generally, radiation correction was conducted to reduce the large measurement errors as much as possible under high temperature, and typically required multiple empirical formulas with uncertainties that were difficult to quantify [34-37]. It was observed that the initial phase of the thermocouple met the first-order response very well due to weak radiation at low temperature in our experiment. The flame temperature could be predicted by fitting the initial response data to determine  $T_g$  and  $\tau$  in Eq. (4). Consequently, a potential way to obtain the flame temperature without radiation correction was presented, which can be achieved by reducing the residence time (i.e., response time) of the thermocouple in the flame. Therefore, the residence time was set to be much less than that of traditional methods. For traditional methods, the residence time of the thermocouple was generally required to exceed five times as much as time constant for reaching thermal steady state. In this measurement process, the thermocouple was rapidly swept into the prespecified measuring position in the flame by a three-axis translation stage (the translational speed was approximately 0.5 m/s), before being removed after a few seconds. This rapid thermocouple insertion method had been used extensively by other experimenters to measure temperatures in soot-containing flames, and the thermocouple's output data were averaged between 1 and 3 transient response times [32,33,38]. In this study, the temperature signal response was recorded by a computer with a sampling frequency of 50 Hz. The goal was that the interaction between the thermocouple and the flame met the first-order response equation in a sufficiently short time so that the radiation losses of the thermocouple, at a lower temperature, were negligible. The measurement errors introduced by conduction losses through the lead wires and the additional thermal resistance caused by particle deposition on the junction surface can also be minimized due to the low temperature of the junction and the short residence time. The finite difference technique [39] can be applied to solve Eq. (1), and one of the results is the difference between the true gas temperature and the thermocouple temperature at steady state

$$\Delta T(\partial T_{\rm th}/\partial t = 0) = T_{\rm g} - T_{\rm th}$$
<sup>(5)</sup>

While the junction is at unsteady state,  $t = \tau$ , the variables of heat flux by convection, radiation and conduction are  $q_{Conv}$ ,  $q_{Rad}$  and  $q_{Cond}$ , respectively, and the three factors of heat transfer are compared by the following two indexes:

$$\gamma_{\rm Rad}(t=\tau) = \frac{q_{\rm Rad}}{q_{\rm Conv}} \times 100\%$$
(6)

$$\gamma_{\text{Cond}}(t=\tau) = \frac{q_{\text{Cond}}}{q_{\text{Conv}}} \times 100\%$$
(7)

Table 1 shows the temperature errors  $\Delta T$  at steady state and the relative amounts among the three types of heat flux at  $t = \tau$ . Radiation varies with the fourth power of temperature, so a sharp increase in radiation losses from the thermocouple to the environment is observed with increases in gas temperature. At the high temperatures typically encountered in flame environments, the temperature error resulting from these losses can be hundreds of degrees. It is found that the effects of radiation and conduction are very weak when *t* is equal to  $\tau$ , which can be neglected, so that the interaction between the thermocouple and the flame meets the first-order response equation when heat transfer is only through convection.

In this work, the residence time t was reasonably close to the time constant  $\tau$ . Based on the collected thermocouple's data  $(t, T_{th}), \tau$  and  $T_g$  can be obtained by an exponential curve fit according to Eq. (4). For this technique, the results need not be corrected for heat losses at the junction through radiation and conduction.

To validate the method of temperature measurement, we first implemented temperature measurements in a benchmark sooting flame that was generated with ethylene and air flow rates of 0.194 slm and 284 slm respectively in a Gülder burner (the experimental apparatus of sooting flame was provided by Dr. Chun Lou in our laboratory). The temperature at six heights (10, 20, ..., 60 mm) along the center axis of flame was compared with previously published results from some noninvasive measurement (i.e., coherent anti-Stokes Raman scattering (CARS) spectra [40], flame image [41] and CCD spectra [42]), as shown in Fig. 2, the result was fairly satisfactory on the trend of temperature and agreed well with three noninvasive measurements within relative error of less than 6%. Error bars on thermocouple data indicate the precision of the thermocouple temperature measurement was within  $\pm 30-50$  K. It is noted here that the aim of this work is to provide an easy and cheap measurement method for flame temperature and nanoparticles in flame. Compared to some well-established optical techniques, it is at disadvantage of measurement accuracy, however at advantages of cost and convenience. The measurement error should be acceptable.

# 2.3. Thermophoretic sampling for particle volume fraction and flow velocity

The thermophoretic sampler was composed of a double acting high-speed pneumatic cylinder (Festo, DSNU), a programmable logic controller (PLC), a self-closing tweezers, TEM grids and other auxiliaries, as shown in Fig. 1a. The pneumatic rod end of the double acting cylinder was connected with the self-closing tweezers, carrying the TEM grid to the specified sampling points (S1, S2, ..., S6, see Fig. 1d) for a specific sampling time. The three-dimensional translational platform is able to ensure the accurate location of the sampling points, and the PLC determines the residence time (sampling time,  $t_e$ ) of the TEM grids. The TEM grid was made of molybdenum (density 10.2 g/cm<sup>3</sup> at room-temperature, specific heat capacity 242.8 J/(kg K)), which can withstand

**Table 1** The temperature errors at unsteady state and a quantitative comparison of heat flux at  $t = \tau$ .

$T_g$ (K)	600	800	1000	1200	1400	1600	1800	
$\Delta T \left( \partial T_{th} / \partial t = 0 \right) (\mathbf{K})$	7.1	15.8	32.3	61.7	116.2	174.4	230.9	
$\gamma_{Rad} (t = \tau) (\%)$	0.42	0.85	1.24	1.88	2.74	3.63	4.65	
$\gamma_{Cond} (t = \tau) (\%)$	0.51	0.58	0.72	0.90	1.18	1.43	1.84	



**Fig. 2.** Comparison of the temperature at the center axis of the Gülder sooting flame (the residence time of the thermocouple was 1.0 s, and five independent tests were conducted for each point and error bars were presented) with the results in Refs. [40–42].

high temperatures, and 200 meshes with a diameter of 3 mm and a thickness of 20 µm were employed in the work. Once the TEM grids were moved to the sampling point, nearby nanoparticles will deposit on the surface due to the thermophoretic force. After this sampling process, the central zone of the TEM grid with an area less than 0.01 mm<sup>2</sup> was observed by SEM to characterize these nanoparticles in terms of aggregate size distribution, fractal dimension, particle volume fraction, and other properties. In this work, the TEM grid was rapidly inserted into the pre-specified sampling position in the flame by the high-speed pneumatic cylinder (the piston velocity up to 6 m/s). The timer function of the PLC was used to determine the residence time at the sampling position. The grid traveled through other particle containing regions in the flame before reaching the sampling position, with the travel distance approximately 0.01 m. Thereby, the travel time (approximately 1.7 ms) was limited to smaller than 10% of the residence time to minimize the unavoidable contamination during the travel [33], also ensuring particle deposited on the grid was a representative of the sampling location. Furthermore, the residence times of TEM grid were controlled using the PLC so that aggregates covered no more than 15% of the TEM grid in order to avoid overlapping aggregates on the grid.

Thermophoresis drives particle migration from the high-temperature side to the low-temperature side under the temperature gradient in the gas-particle system. The local particle thermophoresis velocity  $u_T$  is related to the thermophoresis diffusivity  $D_T$ , gas temperature  $T_g$  and temperature gradient  $\nabla T$  [25]:

$$u_{\rm T} = D_{\rm T} \left( -\frac{\nabla T_{\rm g}}{T_{\rm g}} \right) \tag{8}$$

In the free molecular regime for a single spherical nanoparticle [25]:

$$D_{\rm T} = \frac{3}{4} \left( 1 + \frac{\pi}{8} \alpha_{\rm mom} \right)^{-1} v_{\rm g} \tag{9}$$

with  $\alpha_{mom}$  being the momentum accommodation coefficient (1 is used here). Ronser et al. [43] had proved that this theory can be applied to agglomerates. Eisner and Rosner [26] showed that thermophoresis is the main mechanism affecting particle deposition on a cold surface in a flame. It was found that the deposition was affected not only by the flame temperature but also by the temperature history on the wall surface. The volume fraction of particles is calculated as [25]:

$$f_{\rm v} = \frac{2xV_{\rm p}}{D_{\rm T}Nu_{\rm x}A_{\rm i}t_{\rm e}} \left[1 - \left(\frac{T_{\rm w}}{T_{\rm g}}\right)^2\right]^{-1} \tag{10}$$

in which x is the vertical position on the sampling probe measured from the lower edge; x = 1.5 mm in this work. The Nusselt number is  $Nu_x = 0.332 Pr^{1/3} Re_x^{1/2} = xh_x/\lambda_g, T_w$  is the surface temperature of the TEM grids,  $A_i$  is the size of the observing area,  $V_p$  is the total volume of particles in this area ( $V_p$  will be concretely described in the next section), and  $t_e$  is the residence time of the TEM grid. Köylü et al. [25] measured the particle volume fraction, assuming that the flow velocity of the gas  $u_g$  was 1 m/s, the residence time  $t_e$ was 23–66 ms, and  $T_w$  was maintained at 350 K. As known, the flow velocities in the concentric tubes were actually different from one other because of thermal expansion and buoyancy in flame. The jet radial velocity was also different because of the shear flow between layers. On the other side, although the gas flow velocity and particle concentration are stable in the flow boundary layer of the TEM grid surface, the surface temperature of the TEM grid continues to increase, leading to an unstable thermal boundary layer. As the wall temperature increases, both the temperature gradient of the layer and the thermophoretic deposition rate decrease accordingly. Therefore, employing only one TEM grid sampling will lead to a large uncertainty in the measurement of the particle volume fraction. It is also impossible to measure flow velocity.

In this work, two TEM grid samplings at the same point with two different residence times ( $t_{e1}$  and  $t_{e2}$ ) were conducted to simultaneously measure particle volume fraction and flow velocity. The DTTS method is based on the assumptions that the flame is stable, which means that the particle volume fraction  $f_v$ , gas temperature  $T_g$ , and flow velocity  $u_g$  are constant at the sampling point and that the thermophoretic deposition is related to  $u_g$ ,  $T_g$ ,  $f_v$  and  $t_e$ . According to Eq. (10), two deposition states observed by FSEM (field-emission electron microscope) will follow:

$$f_{v} = \frac{2xV_{p1}}{D_{T}Nu_{x}A_{i1}t_{e1}} \left[1 - \left(\frac{T_{w1}}{T_{g}}\right)^{2}\right]^{-1}$$
$$= \frac{2xV_{p2}}{D_{T}Nu_{x}A_{i2}t_{e2}} \left[1 - \left(\frac{T_{w2}}{T_{g}}\right)^{2}\right]^{-1}$$
(11)

The final temperature of the TEM grid at the end of the sampling should be constrained to not be too high, generally far lower than the TiO<sub>2</sub> sintering temperature (790 °C), to avoid significant changes in the morphology, size and state of the nanoparticles deposited on the TEM grid. Maintaining an appropriate surface temperature of the TEM grid will also maintain a sufficient temperature gradient for the thermophoretic deposition of nanoparticles. The surface temperature of the TEM grid is generally affected by the residence time and heat transfer. In this work, to reduce radiation heat transfer from the flame to the thermophoresis probe, a special type of molybdenum TEM grid was adopted based on the radiation characteristics of a TiO<sub>2</sub> particle-laden flame and the selective absorption properties of a molybdenum TEM grid. The flame emission spectra were acquired using a CCD spectrometer and a blackbody furnace [44]. The continuous spectra of a flame in the wavelength range of  $0.6 \,\mu\text{m}$  to  $1.2 \,\mu\text{m}$  can be detected, and the radiation intensity increases with the wavelength. As is known, the absorption spectrum of a Mo TEM grid is mainly in the wavelength range of 0.4–0.8 µm [45]. Therefore, the Mo TEM grid absorbs only weak flame radiation of a narrow wavelength range. We calculated the normal absorptivities to be  $\alpha_n = 0.05$  at 200 °C and  $\alpha_n = 0.06$  at 500 °C [46]. The effect of flame radiation on the heat transfer of the Mo TEM grid was estimated.

Similar to the earlier mentioned energy equation of the thermocouple, the analytical expressions of the heat balance for the TEM grid is given in Eq. (12), in which only convection and radiation are considered whereas conduction is very weak and can be ignored due to high thermal contact resistance between TEM grid and self-closing tweezers. The TEM grid temperature  $T_w$  was computed, and the result indicates that the effect of radiation on the heat transfer between the Mo TEM grid and the flame did not exceed 8%. The radiation effect is therefore slight and can be reasonably ignored.

$$\tau_{x} \frac{dT_{w}}{dt} = \left(T_{g} - T_{w}\right) + \frac{4\tau_{x}\varepsilon_{w}\sigma}{\rho_{w}c_{w}\delta} \left(\varepsilon_{p}T_{p}^{4} - T_{w}^{4}\right)$$
(12)

where  $\tau_x$  is the time constant of the TEM grid;  $\lambda_g$  is the thermal conductivity coefficient of the gas;  $\rho_w$  and  $c_w$  are the density and specific heat capacity of the TEM grid material, respectively;  $\delta$  is the thickness of the TEM grid; and  $\varepsilon_w$  and  $\varepsilon_p$  are the emissivities of the TEM grid and the TiO<sub>2</sub> particles, respectively.

The surface temperatures of the TEM grids with residence time  $t_{e1}$  and  $t_{e2}$  were calculated as:

$$\begin{cases} T_{w1} = T_0 + (T_g - T_0)(1 - e^{-t_{e1}/\tau_x}) \\ T_{w2} = T_0 + (T_g - T_0)(1 - e^{-t_{e2}/\tau_x}) \end{cases}$$
(13)

The time constant  $\tau_x$  of the temperature response at the center of the TEM grid was calculated, ignoring the radiation heat transfer:

$$\tau_x = \frac{\rho_w c_w \delta}{2h_x} \tag{14}$$

where the convection heat transfer coefficient  $h_x$  at the center of the TEM grids was calculated as [25]:

$$h_x = 0.332\lambda_g P r^{1/3} R e_x^{1/2} / x \tag{15}$$

The Prandtl number is  $Pr = v_g/a_g$ , with  $a_g$  being the gas thermal diffusivity; the local Reynolds number is  $Re_x = u_g x/v_f$ ; the kinematic viscosity  $v_f$  is calculated as [25]:  $v_f = 1.29 \times 10^{-9} T_f^{1.65}$ ; and the average film temperature is defined by  $T_f = (T_g + T_w)/2$ .

The particle deposition quantity on the TEM grid surface was derived from Eq. (10):

$$V_{\rm p}(t) = f_{\rm v} A_{\rm i} t \frac{D_{\rm T} N u_{\rm x}}{2 x} \left[ 1 - \left(\frac{T_{\rm w}}{T_{\rm g}}\right)^2 \right]$$
(16)

The particle deposition flux is:

The deposition flux ratio of two samplings within  $t_{e1}$  and  $t_{e2}$  is:

$$\vartheta_{\rm T} = \frac{\langle V_{\rm p2} \rangle}{\langle V_{\rm p1} \rangle} = \frac{2 e^{-t_{\rm e2}/\tau_{\rm x}} - (1 - T_0/T_{\rm g}) e^{-2t_{\rm e2}/\tau_{\rm x}}}{2 e^{-t_{\rm e1}/\tau_{\rm x}} - (1 - T_0/T_{\rm g}) e^{-2t_{\rm e1}/\tau_{\rm x}}}$$
(18)

where  $\langle V_{p1} \rangle$  and  $\langle V_{p2} \rangle$  were derived from FSEM-image processing, flame temperature  $T_g$  was measured by the thermocouple. The time constant  $\tau_x$  of the TEM grid was obtained by solving Eq. (18), then was used to calculate the temperature of the TEM grid  $T_w$  by Eq. (13). The flow velocity  $u_g$  could then be calculated by combining Eqs. (14) and (15):

$$u_{\rm g} = v_{\rm f} x \left( \frac{\rho_{\rm w} c_{\rm w} \delta}{0.664 \lambda_{\rm g} P r^{1/3} \tau_{\rm x}} \right)^2 \tag{19}$$

With the particle deposition quantity  $V_p$  from FSEM-image processing, the flame temperature  $T_g$ , the TEM grid wall temperature  $T_w$  and the gas velocity  $u_g$ , the particle volume fraction  $f_v$  can be determined by Eq. (10).

# 2.4. Thermophoretic sampling for aggregate size distribution and fractal-like property

Thermophoretic sampling can also measure the properties of each type of morphology as a particle evolves from translucent precursor particles to mature aggregates in flame. Notice that an extremely small zone in the center of the TEM grids was analyzed under the electron microscope. Based on the TEM/SEM images (in this work, samples are characterized using a FSEM (FEI Sirion 200)) of these samples, key parameters of the aggregate were obtained using ImageJ image processing software, including primary particle diameter ( $d_{pi}$ ), projection area ( $A_{ai}$ ), projected maximum length ( $L_{ai}$ ) and projected maximum width normal to maximum length ( $W_{ai}$ ) of every aggregate. These aggregates are self-similar or scale-invariant over a given size range, and the similar patterns often called fractal-like [47]. The number of primary particles within the *i*-th aggregate is

$$N_i = k_\alpha \left( A_{\rm ai} / A_{\rm pi} \right)^\alpha \tag{20}$$

where  $k_{\alpha} = 1.15$ ,  $\alpha = 1.09$  [48], and the spherical primary particle cross-sectional area  $A_{pi} = \pi d_{pi}^2/4$ . Aggregates exhibit complex geometry that fortunately can be characterized as mass fractals; that is, the number of primary particles per aggregate,  $N_i$ , scales with the radius of gyration  $R_{gi}$ , as follow:

$$N_i = k_f \left( R_{\rm gi} / d_{\rm pi} \right)^{D_{\rm f}} \tag{21}$$

where  $k_f$  is the fractal prefactor and  $D_f$  is the mass-fractal dimension. The mass-fractal dimension can be obtained directly from the projected data of aggregates when the overlapping is not dominant [49]. Typically,  $N_i$  was plotted as a function of the geometric mean projected aggregate size  $(L_{ai}W_{ai})^{1/2}$  [48]:

$$N_{i} = k_{\rm f} \left[ (L_{\rm ai} W_{\rm ai})^{1/2} / d_{\rm pi} \right]^{D_{\rm f}}$$
(22)

where  $k_L$  is a constant prefactor and  $D_L$  is a scaling exponent. Based on the projection analysis of aggregates,  $D_L$  could act as surrogate of mass-fractal dimension  $D_f$  [48].

Assuming the monodisperse distribution of primary particles, the total volume of particles deposited on the TEM grids is given by:

$$V_{\rm p} = \sum_{i} N_i \cdot \frac{\pi d_{\rm pi}^3}{6} \tag{23}$$

The PSD can be obtained by analyzing the FSEM images. By counting the number of aggregates within each size bin (discretized by the logarithmic rule) in the FSEM images, the aggregate size frequency  $f_k$  (order number of bins k = 1, 2, ...) and geometric average volume  $\bar{\nu}_a$  can be obtained. The total number concentration of aggregates is calculated from the particle volume fraction:

$$N_{\rm a} = f_{\rm v} / \bar{\nu}_{\rm a} \tag{24}$$

Within the *k*-th bin, the concentration of aggregate is

 $\Delta N_{\rm ak} = f_{\rm v} \cdot f_k / \bar{\nu}_{\rm a} \tag{25}$ 

In this way, the size distribution of aggregates at each sampling point can be obtained.

Once  $d_p$ ,  $A_a$ ,  $L_a$  and  $W_a$  are measured by FSEM images analysis, multiple key parameters of the particles and aggregate (i.e., particle volume fraction, size distribution of primary particles and aggregates, fractal dimension and fractal prefactor) can be obtained. Collecting two samples at a single point with different residence times can not only calculate gas flow velocity but also make the measurement of these other particle parameters more reliable.

# 3. Computational models and numerical methods for comparison

#### 3.1. CFD-PBM models

To compare with the experimental measurements, a coupled CFD-PBM model for flame synthesis processes was employed. The flame model consists of the continuity equation, the Navier–Stokes (N–S) equations for momentum, the k- $\varepsilon$  turbulence equations, the species transport equations based on the eddy dissipation model (EDM) and the radiation transport equation. The reaction rate of methane and oxygen combustion in the diffusion flame was approximated by a single-step reaction with an Arrhenius expression as following [7,50]:

$$r_{\rm CH_4} = A_{\rm s} \exp\left(-\frac{E_{\rm s}}{RT}\right) C^a_{\rm CH_4} C^b_{\rm O_2} \tag{26}$$

where the pre-exponential factor  $A_s = 1 \times 10^{12} \text{ mol}/(\text{m}^3 \text{ s})$ , activation energy  $E_s = 125 \text{ kJ/mol}$ , the exponents a = -0.3 and b = 1.3,  $C_{\text{CH}_4}$  and  $C_{0_2}$  is concentration of CH<sub>4</sub> and  $O_2$ , respectively. EDM assumes that chemical reaction is fast than species transport, since the reaction in the diffusion flame is controlled by the turbulent mixing rates. It consists of two rate expression  $r_1$  and  $r_2$  as follow [50,51]:

$$r_1 = A_{\text{EDM}} \frac{\varepsilon}{k} \min\left(\frac{C_i}{\nu_i}\right) \tag{27}$$

where  $r_1$  accounts for the mixing of the reactants in turbulent eddies,  $C_i$  is concentration of reactant i,  $v_i$  is stoichiometric coefficient of component i, k is turbulent energy and  $\varepsilon$  is its dissipation rate,  $A_{FDM}$  is a numerical constant (in this paper,  $A_{FDM} = 1.0$ ) [50,51].

$$r_{2} = A_{\text{EDM}} B_{\text{EDM}} \frac{\varepsilon}{k} \min\left(\frac{\sum_{p} C_{i} W_{i}}{\sum_{p} v_{i} W_{i}}\right)$$
(28)

where  $r_2$  accounts for the mixing of hot product gases with cold reactant gases when heat transport to the unreacted gases is the limiting factor, *P* is the number of all product components in the reaction,  $W_i$  is molar mass of the component *i*,  $B_{EDM}$  is a numerical constant (in this paper,  $B_{EDM} = 0.5$ ) [50,51]. The rate of combustion is determined by the smaller of the two rates  $r_1$  and  $r_2$ .

Radiation was taken into account by the so-called P-1 model, and a composition-dependent absorption coefficient for  $CO_2$  and H<sub>2</sub>O mixtures was defined using the weighted sum of gray gases model (WSGGM) (Fluent 6.3 User's Guide). The computation was implemented in the commercial CFD software Fluent.

The following bivariate population balance equation (PBE) mathematically formulates the nanoparticle dynamics, including nucleation, agglomeration and sintering [52]:

$$\begin{aligned} \frac{\partial n(\nu,a,t)}{\partial t} &= \left\{ \left( k_{a} + k_{b} C_{0_{2}}^{1/2} \right) C_{\text{TiCl}_{4}} \frac{M_{p}}{\rho_{p} \nu_{0}} \right\}_{\text{nucl}} \\ &+ \left\{ \frac{1}{2} \int_{\nu_{0}}^{\nu} \int_{a_{0}}^{a} \beta(\nu',\nu-\nu';a',a-a';t) n(\nu',a',t) n(\nu-\nu',a-a',t) d\nu' da' \\ -n(\nu,a,t) \int_{\nu_{0}}^{\infty} \int_{a_{0}}^{\infty} \beta(\nu',\nu;a',a;t) n(\nu',a',t) d\nu' da' \\ &- \left\{ \frac{\partial}{\partial a} \left[ \frac{(a-a_{\text{final}})}{\tau_{s}(\nu,a)} n(\nu,a,t) \right] \right\}_{\text{sin}} \end{aligned}$$
(29)

where n(v, a, t) is the number density function at time t such that n(v, a, t)dvda represents the number concentration of particles in the volume range v to v + dv and the surface area range a to a + da. The simulation is for the synthesis process of nanoparticles (TiO<sub>2</sub>) produced by the oxidation reaction of titanium tetrachloride



Fig. 3. The flowchart of the PBMC simulation and the illustration of particle dynamic evolution.

in flame: TiCl<sub>4</sub> (g) + O<sub>2</sub>  $\rightarrow$  TiO<sub>2</sub> + 2Cl<sub>2</sub>. The formation rate of TiO<sub>2</sub> nuclei was given by Nakaso et al. [53]. *C*<sub>02</sub> and *C*<sub>TiCl4</sub> respectively represent the mole concentrations of O<sub>2</sub> and TiCl<sub>4</sub> (mol/m<sup>3</sup>), *k* is the rate of thermal decomposition,  $k_a = 8.26 \times 10^4 \exp(-88.8 \times 10^3/R_g/T)$ ,  $k_b = 1.4 \times 10^5 \exp(-88.8 \times 10^3/R_g/T)$ ,  $M_p$  is the molecular

weight of TiO<sub>2</sub> (79.865×10<sup>-3</sup> kg/mol),  $\rho_p$  is the density of TiO<sub>2</sub> (4230 kg/m<sup>3</sup>), and  $v_0$  is the critical volume of TiO<sub>2</sub> nuclei (0.1438 nm<sup>3</sup>; they are considered as spherical particles).  $\beta(v', v; a', a; t)$  is the agglomeration rate coefficient (i.e., agglomeration kernel) between one particle of state (v', a') and another particle of state (v, a);  $\tau_s(v, a)$  is the characteristic sintering time of one particle of state (v, a), and  $a_{final}$  is the surface area of the sphere after complete coalescence.

In this paper, the Brownian agglomeration kernel in the transition regime (1 < Kn < 50,  $Kn = 2\lambda/d$  with  $\lambda$  the mean free path of the surrounding gas and d the particle diameter) was employed. An approximate kernel valid for the transition regime, which is the harmonic mean of the slip flow kernel  $\beta_{sf}$  and the free molecular kernel  $\beta_{fm}$  [54–56], was used

$$\beta_{\rm tr} = \frac{\beta_{\rm sf} \cdot \beta_{\rm fm}}{\beta_{\rm sf} + \beta_{\rm fm}} \tag{30}$$

$$\beta_{\rm sf} = \frac{2k_{\rm b}T}{3\mu} \left( v_i^{1/D_{\rm f}} + v_j^{1/D_{\rm f}} \right) \left( \frac{C_{\rm ci}}{v_i^{1/D_{\rm f}}} + \frac{C_{\rm cj}}{v_j^{1/D_{\rm f}}} \right)$$
(31)

$$\beta_{\rm fm} = 2^{2-D_{\rm C}} \left(\frac{3}{4\pi}\right)^{1/6} \sqrt{\frac{6k_{\rm B}T}{\rho_{\rm p}}} v_0^{2/3-D_{\rm C}/D_{\rm f}} \left(v_i^{1/D_{\rm f}} + v_j^{1/D_{\rm f}}\right)^{D_{\rm C}} \left(\frac{1}{v_i} + \frac{1}{v_j}\right)^{1/2},$$
  
$$D_{\rm C} = \min\left(2, D_{\rm f}\right) \tag{32}$$

where slip correction coefficient  $C_c = 1.0 + 1.257Kn$  and  $D_f$  is the aggregate mass-fractal dimension.

With respect to sintering, the surface area of the agglomerate towards its final area will change with rate of  $1/\tau_s$ . The characteristic sintering time  $\tau_s$  based on the surface diffusion mechanism [57] was given by:

$$\tau_{\rm s}(d_{\rm p},T) = 7.44 \times 10^{16} d_{\rm p}^4 T \exp\left(\frac{258 \times 10^3}{RT}\right)$$
(33)

where  $d_p$  is the diameter of a primary particle in an agglomerate and R is the gas constant.

# 3.2. QMOM for particle dynamics

Nanoparticle formation and growth were predicted using a quadrature method of moments (QMOM) method [58] to obtain the first-order moment of PSD, namely PVF. Its applications by Marchisio et al. [59] have shown that the method requires a relatively small number of scalar equations to track the moments of population with small errors. The QMOM provides an attractive alternative to the discrete method when aggregation quantities, rather than an exact PSD, are desired. Its advantages are fewer variables (typically only six or eight moments) and a dynamic calculation of the size bins. The mathematical equation for the particle dynamics includes the terms of fluid convection, Brownian diffusion, precursor reaction, nucleation, coagulation and coalescence. The transformed moment equations based on the size distribution are written as [60]:

Table 2			
Operating conditions	for the	measurement	experiment.

Items	Setting
Fuel	CH4 (1.2 NL/min) + Ar (0.6 NL/min)
Oxidant	O <sub>2</sub> (2.4 NL/min)
Carrier gas	N <sub>2</sub> (0.6 NL/min)
Precursor	TiCl <sub>4</sub>
Vaporization temperature	65 °C
Pressure	101 kPa
Vapor partial pressure	$\sim \! 10 \text{ kPa}$



**Fig. 4.** (a) Temperature response curves of the thermocouple (TC) at each measuring position in  $TiO_2$ -laden flame; (b) Temperature response curves of the TC at each measuring position in the flame without  $TiO_2$ ; (c) Measured and calculated flame temperature profiles at the center axis (five independent tests were conducted and error bars were presented).

$$\begin{aligned} &\frac{\partial m_{k}}{\partial t} + \frac{\partial u m_{k}}{\partial x} = \frac{\partial}{\partial x} \left( \Gamma \frac{\partial m_{k}}{\partial x} \right) + k \int_{0}^{\infty} G(\upsilon) n(\upsilon, t) \upsilon^{k-1} \mathrm{d}\upsilon + J(\upsilon_{p0}) \upsilon_{p0}^{k} \\ &+ \frac{1}{2} \int_{0}^{\infty} \int_{0}^{\infty} \left[ (\upsilon + \upsilon')^{k} - \upsilon^{k} - \upsilon'^{k} \right] \beta(\upsilon, \upsilon') n(\upsilon, t) n(\upsilon', t) \mathrm{d}\upsilon \mathrm{d}\upsilon', \quad (k = 0, 1, 2, \ldots) \quad (34) \end{aligned}$$

where *u* is the flow velocity,  $\Gamma$  is the particle diffusivity coefficient, *G* is the nucleus volume growth rate, *J* is the nucleation rate, and the *k*-th moment  $m_k$  is defined by

$$m_k = \int_0^\infty n(\nu) \nu^k \mathrm{d}\nu \tag{35}$$

A direct way to calculate the quadrature approximation is by means of the following assumption

$$m_k \approx \sum_{i=1}^N \omega_i v_i^k \tag{36}$$

where *N* is the order of the quadrature formulation and  $\omega_i$  is the number intensity.

The disadvantages of QMOM are that the number of abscissas may not be adequate to describe the PSD and that solving the Product-Difference algorithm may be time consuming. Furthermore, it is troublesome for QMOM to handle multi-variable and more-dimensional problems. In this study, we also developed the PBMC method to predict the aggregate size distribution and the primary particle size distribution in real processes.

### 3.3. PBMC for particle dynamics

The differentially weighted Monte Carlo (DWMC) method [61-64] directly simulates the dynamic evolution of nanoparticle volume and surface area based on the bivariate PBE (Eq. (29)). The PBMC approach is demonstrated by a one-dimensional model along the centerline of flame in the previous CFD environment. The coupling strategy adopted here is based on the appropriate selection of a time-step within which the coupling between particle behavior and fluid flow is neglected [65,66]. Within an appropriate time-step, it is considered not only that the flow transport and the particle transport are uncoupled to each other but also that the particle transport and the particle dynamics are uncoupled to each other. As mentioned above, the kernels of dynamic events, e.g., the coagulation kernel  $\beta_{ii}(x_k, t)$ , which models the occurrence probability of a coagulation event between any two particles at time t and space position  $x_k$ , is typically dependent on the environmental variables of gas-particle flow. Thus, within a time-step, gasparticle flow fields should first be simulated using CFD models, without consideration of particle dynamics. Using the gas-particle flow fields, spatiotemporally dependent coagulation kernels can be calculated. The PBMC method was then used to capture particle coagulation events in each grid [67].

The basic frame of the PBMC for simultaneous nucleation, agglomeration and sintering is that within a well-designed time step, the three events are uncoupled and can be described separately. First, the waiting time between two successive agglomeration events for a simulation particle ( $\Delta t_{agg}$ ) is calculated, and the time step  $\Delta t$  is constrained to a reasonable time scope to make the uncoupling assumption generally reasonable. Possible agglomeration events, nucleation events and sintering events are then determined in serials [52]. The flowchart of the PBMC simulation is shown in Fig. 3. In this paper, the number of simulation particles was limited to less than 10,000 in order to compromise between computational cost and accuracy. The MC simulations were run



Fig. 5. The dimensionless particle deposition flux at sampling point S4.



**Fig. 6.** Typical FSEM images (with a magnification of 25,000 in original images) of thermophoresis sampling along the flame centerline at six heights above the burner exit. The upper row of images has  $t_{e1} = 50$  ms, while the lower row has  $t_{e2} = 150$  ms.

three times using different seeds from the random number generator. The constant-number scheme [68–70] was introduced to keep the simulation particle number constant in case the nucleation event sharply increases the number of simulation particles, especially in the initial stage. To reduce the computation cost, a fast version of the DWMC method [71,72] was implemented to greatly accelerate the simulation of agglomeration events (the CPU time was reduced from hundreds of hours to approximately one hour), and the sintering and agglomeration were uncoupled based on the finite-rate sintering idea. With respect to sintering, the monodisperse primary particle (MPP) model [73] was adopted to describe the size distribution of primary particles within agglomerates. Hao et al. [52] has demonstrated that the PBMC framework has sufficiently small statistical and systematic error. Using this PBMC simulation, the size distributions of aggregate and primary particles, the specific surface area of particles produced, and the particle volume fraction can be obtained.

# 4. Results and discussion

#### 4.1. Conditions

In this work, we used an enclosed methane/oxygen diffusion flame to produce  $TiO_2$  nanoparticles. Nanoparticles were formed by the oxidation of  $TiCl_4$  vapor fed into a N<sub>2</sub> stream at production rates of 20 g/h. The experimental conditions are summarized in Table 2. Because of the slow bubbling process, in which the carrier gas was dispersed into small bubbles, the  $TiCl_4$  gas was thought to be saturated in the vaporizer. For selected operating conditions, the burner can organize a rational flow field and support a quite stable combustion. The height of the visible flame was approximately 11 cm. The flame temperature profiles were first obtained by a fine-wire thermocouple. The product particle volume fraction, primary particle size, and the structure and size of the aggregates as well as the gas flow velocity were then measured by combining a thermophoresis probe with a FSEM.

# 4.2. Flame temperature

In our case, the residence time of thermocouple was 2 s. The thermocouple was rapidly inserted into the sampling position in the flame by the three-axis translation stage (the translational speed is approximately 0.5 m/s), so the travel time (approximately 0.02 s) was about 1% of the residence time. The signal acquisition frequency of the thermocouple was 50 Hz, recording a data point (T,t) every 0.02 s. By fitting the first-order response equation (Eq. (4)) to these data points, we can obtain the thermocouple temperature response curves, including the flame temperature  $T_g$  and time constant  $\tau$  at every sampling point, as shown in Fig. 4a. There were slight fluctuations in the time constant of these measuring points. This is the result of dissimilar zones in the flame with different heat transfer coefficients. In order to clarify the radiation and particle deposition effect on temperature measurement as well as to compare with temperature simulation without TiO<sub>2</sub> particles, we also measured the temperature of flame without TiO<sub>2</sub> particles in same operating condition, and the temperature response curves was presented in Fig. 4b. Measured and calculated flame temperatures along the center axis were compared in Fig. 4c. As shown in Fig. 4c, the measured temperature of flame without TiO<sub>2</sub> particle was higher than that of TiO<sub>2</sub>-laden flame<sub>2</sub>, whereas the difference was not significant. It was indicated that radiation losses and adjunctive thermal resistance due to particle containing and depositing were negligible. Some deviations between measurement and predictions were observed, especially in the high-temperature section (approximately 15-35 mm) and beyond 65 mm height above the burner (HAB), although they follow consistent trends. The former differences in measured and simulated temperatures may arise from high-temperature enhancing radiation between the thermocouple and the surroundings as well as TiO<sub>2</sub> particles and the surroundings, while the latter may be caused by particle deposition on the thermocouple junction that increases

Table 3			
Statistical results	of FSEM	image	analysis.

	S1 (5 mm)	S2 (15 mm)	S3 (25 mm)	S4 (45 mm)	S5 (65 mm)	S6 (85 mm)
$d_{a,g}$ (nm)	35 ± 6	40 ± 5	$50 \pm 6$	$60 \pm 6$	65 ± 7	75 ± 8
$d_{p,g}$ (nm)	6 ± 3	10 ± 3	13 ± 4	15 ± 5	$16 \pm 4$	16 ± 4
$V_{p1}$ (10 <sup>6</sup> nm <sup>3</sup> )	91.88 ± 15.1	485.6 ± 19.3	385.4 ± 14.7	390.3 ± 24.5	304.1 ± 27.0	260.8 ± 26.6
$V_{p2}$ (10 <sup>6</sup> nm <sup>3</sup> )	247.3 ± 21.1	1286.9 ± 28.5	1063.8 ± 26.2	1047.9 ± 23.9	787.1 ± 24.7	654.4 ± 28.3
$V_{p2}/V_{p1}$	$2.69 \pm 0.26$	$2.65 \pm 0.23$	$2.76 \pm 0.24$	$2.68 \pm 0.25$	$2.59 \pm 0.27$	$2.51 \pm 0.28$

<sup>a</sup>  $d_{ag}$  is the geometric mean volume-equivalent diameter of the aggregate, and  $d_{pg}$  is the geometric mean diameter of the primary particle.



**Fig. 7.** Evolution of particle volume fraction along the flame centerline. Error bars are calculated based on five independent tests. The sensitivity analysis at each HAB is indicated by the cyan shaded area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 8.** Evolution of gas flow velocity along the flame centerline. Error bars are calculated based on five independent tests. The sensitivity analysis at each HAB is indicated by the cyan shaded area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

heat resistance because many loose soft aggregates were formed and had higher thermal resistance in the upper section of the flame. At this point, the residence time can be further reduced to limit the highest temperature of thermocouple and minimize the particle deposition. Additionally, the temperatures predicted by the Fluent simulations typically contain model uncertainties and calculation errors, especially when there is combustion in the flow field (chemical plus sensible).

## 4.3. Particle volume fraction (PVF) and flow velocity

To study the evolution of particle thermophoretic deposition with residence time, five samplings were carried out at sampling point S4 with different residence times, 20 ms, 50 ms, 80 ms, 100 ms, 150 ms, with  $t_{e1} = 20$  ms viewed as the benchmark. The experimental results of the dimensionless particle deposition flux were consistent with the analytical solutions  $(\vartheta_{\rm T} = \frac{\langle V_{p,n} \rangle}{\langle V_{p,i} \rangle} = \frac{2e^{-t_{e,i}/\tau_{\rm X}} - (1-\theta_0)e^{-2t_{e,i}/\tau_{\rm X}}}{2e^{-t_{e,i}/\tau_{\rm X}} - (1-\theta_0)e^{-2t_{e,i}/\tau_{\rm X}}})$  of the five different sampling times, as shown in Fig. 5. This result demonstrates that particle deposition on the TEM grid surface is mainly dominated by convective heat transfer between the TEM grid and flame, whereas the influence of radiation heat transfer is negligible.

In the DTTS method, different residence times in the flame  $t_{e1} = 50 \text{ ms}, t_{e2} = 150 \text{ ms}$  were used. The FSEM images of nanoparticles at different sampling points for two residence times are shown in Fig. 6. The diameter of the primary particles and the total particle volume were then attained from image processing by ImageJ software, as shown in Table 3. In this work, the ratio between the two different residence times  $t_{e2}/t_{e1} = 3$ , but the deposition particle mass rate  $V_{p2}/V_{p1} < 3$ , which demonstrates the nonlinearity of the thermophoresis phenomenon.

Figure 7 shows the local particle volume fraction  $f_v$  at different sampling points obtained from experiment and simulation. For each sampling point, five independent tests were conducted, and error bars are presented. Notice that some uncertainties are associated with the results of the thermophoretic sampling, followed by FSEM image analysis for measuring particle volume fraction, up to ±5% for  $d_p$  and  $N_i$  within 95% confidence interval [33], so the reliability of the experimental results needs to be validated by sensitivity analysis. We set  $V_p$  changing within ±5% and the corresponding ranges of  $f_v$ were calculated according to Eq. (10) over six different sampling points. The result clearly shows an insignificant amount of error (<5%) from FSEM observation and image analysis. It is worth noting that the PBMC simulation data agree better with the experimental results, especially from the middle to the end of the flame centerline, which might be due to that PBMC could track the particle size distribution with broad-spectrum and high-resolution in discrete particle population. It was important that no simulation particle was lost on the evolution of particle population [62].

Gas flow velocity profiles determined by the DTTS along the flame centerline are shown in Fig. 8, which also includes the sensitivity analysis with the relevant flame temperature errors (see Fig. 4c. For the sensitivity analysis, the upper and lower limits of five independent temperature tests in each sampling point were used to calculate the variation range of flow velocity (upper temperatures corresponding to upper flow velocities). As shown in Fig. 8, there is a rather moderate deviation in the gas flow velocity, and the experimental measurement exhibits the same tendency as the CFD simulation, although there is some difference between them. In our experiment, the velocity  $u_g$  is calculated from measured  $T_g$  and  $V_p$ , so the experimental error of  $u_g$  was mainly affected by  $T_g$  and  $V_p$  measurements. It is noted that if



**Fig. 9.** (a) Number of primary particles in an aggregate (*N*) as a function of the dimensionless size  $((LW)^{1/2}/d_p)$  for six sampling points. Each scatter plot represents a measured aggregate. The linear least-square fit to the data is shown, and the slopes of the linear regression lines represent the projected area exponent  $D_L$ . (b) Evolution of  $D_L$  along the flame centerline.

the measured  $T_g$  is lower (higher) than the actual flame temperature or  $V_p$  from FSEM-image processing is lower (higher) than actual particle deposition, the calculated results of  $u_g$  will be higher (lower) than actual performance. This pattern can be found by combining Figs. 4c, 7 and 8. For gas flow velocity measured by DTTS, the results are relatively stable in the laminar region, while there are some fluctuations in the turbulent region during the short sampling time. The results thereby indicate that the DTTS method is able to effectively determine the flow velocity.

#### 4.4. Fractal dimension

Fractal dimension is an indicator of the structural characteristics of a complex aggregate. Following the mass fractal theory, the number of primary particles in an aggregate is a function of the non-dimensional aggregate diameter, as discussed earlier. The number of primary particles N was plotted as a function of the geometric mean projected aggregate size, and the projected area exponent  $D_L$  was directly determined from the linear leastsquare fit to the data illustrated in Fig. 9a. The constant prefactor  $k_L$  and  $D_L$  values were obtained for six sampling locations along the flame centerline.  $D_L$  was estimated as a function of flame height, which first increased and then decreased from the bottom to the top of the flame centerline, and the evolution pattern implies a competition mechanism of particle sintering and collision. In this work, projected area exponent  $D_L$  could act as surrogate of massfractal dimension  $D_f$  used for PBMC simulation later.

# 4.5. Aggregate and primary particle size distributions (ASD and PPSD)

The aggregate and primary particle size distributions at three typical sampling locations along the flame centerline are shown in Fig.10, where  $d_a$  is the volume-equivalent diameter of the aggregate and  $d_n$  is the diameter of the primary particle. Both experimental measurements and simulation results indicate that aggregate mean particle size increases and aggregate number concentration decreases due to the combined effects of collision, sintering, and diffusion. As noted earlier, the PBMC simulation implements the Brownian agglomeration kernel in the transition regime (Eq. (30)) with constant  $D_f = 3$  and a dynamic value of  $D_f$ according to the experimental data from Fig. 9b, respectively. The difference between the predictions by  $D_f = 3$  and using a dynamic  $D_{\rm f}$  for aggregate size distribution indicates that the fractal dimension not only reshapes the aggregates but also has an essential effect on the dynamic evolution of nanoparticles. In addition, using a dynamic  $D_f$  based on measurements provides better agreement with the measurements of the physical particle evolution processes. With respect to the measurement and simulation, the results exhibit some minor differences for ASD, while there are significant differences for PPSD. Notice that detecting the edges of smaller primary particles in FSEM images would lack sufficient resolution, so larger errors are associated with the results of FSEM image analysis for measuring primary particle size. On the other side, with respect to the PPSD within agglomerates, the monodispersed primary particle (MPP) model was adopted to simulate particle sintering. The MPP model assumed that agglomerate consisted of equal-sized primary particles, which is a simplified model to actual aggregates and their primary particles [52,74]. So another possible reason for the discrepancy of the PPSD between PBMC simulation results and experimental measurements may be the monodispersity assumption. Moreover, the models for the Brownian agglomeration kernel in the transition regime, the characteristic sintering time and the rate of TiCl<sub>4</sub> thermal decomposition need more identification [75] (although they were widely used in many



**Fig. 10.** A comparison between measured and simulated (a) aggregate and (b) primary particle size distribution for three typical sampling points (HAB = 5 mm, 45 mm, 85 mm): measured results by DTTS (scatter plot), simulated results by PBMC with constant  $D_f = 3$  (dash line) and dynamic  $D_f$  from this experiment (solid line).



**Fig. 11.** Evolution of  $d_{ag}$ , aggregate number concentration ( $N_a$ ) and specific surface area ( $S_A$ ) along the flame centerline.

references). However, the values of the mean primary particle diameter are in good agreement between the experiment and simulation.

The specific surface area of particles can be estimated by the geometric mean diameter of the primary particle  $d_{p,g}$  from Table 3 as

$$S_{\rm A} = \frac{6}{\rho_{\rm p} d_{\rm p,g}} \tag{37}$$

Moreover, the end product of flame synthesis were collected on a water-cooled glass plate at the end of flame (HAB = 105 mm), and

then  $S_A$  of the product was measured using multipoint nitrogen adsorption at 77 K based on the Brunauer-Emmett-Teller (BET) method in a physisorption apparatus (Micromeritics ASAP-2020).

The geometric mean volume-equivalent diameter of the aggregate  $(d_{a,g})$ , aggregate number concentration  $(N_a)$ , and specific surface area  $(S_A)$  of particles produced in the flame centerline are shown in Fig.11. Reasonable agreement was obtained between the experiment and the PBMC simulation. The variation of  $d_{a,g}$  is not significant in the initial flame region, and there is an enormous increase in particle diameter downstream due to the high particle coagulation rate. Further downstream, the low collision rate and competitive sintering results in a slow increase in particle diameter. In the burner mouth, where monomers are primarily formed from precursor oxidation,  $N_a$  first reaches its maximum and then decreases as the gas particle flow proceeds downstream. In addition to the particle diameter and number concentration, the specific surface area is another key parameter for determining the properties of nanoparticles. The S<sub>A</sub> quickly decreases in the hightemperature region (within HAB = 25 mm) due to predominant sintering, whereas a slight increase and subsequent stability is observed in the region beyond HAB = 25 mm due to the competition or balance between agglomeration and sintering. The specific surface area computed from PBMC far exceeds the values obtained from the FSEM images in the initial stage of flame synthesis (HAB = 5 and 15 mm), and this may be attributed to the assumption that only nucleation event was firstly implemented and dominant to produce large amount of TiO<sub>2</sub> nuclei with tiny volume of  $v_0 = 0.1438 \text{ nm}^3$ . In the high-temperature section (HAB = 25 mm), the temperature of simulation was higher than that of measurement (in Fig. 4c), and thereby the over-prediction sintering then caused a lower surface area. Moreover, the MPP model assumed that agglomerate consisted of equal-sized primary particles, which leaded to the results of higher surface area (typically, at HAB = 65, 85 and 105 mm).

# 5. Conclusions

A better understanding of the evolution of nanoparticles is desired in order to determine more properties of flame-aerosol processes and to improve the production of nanopowders. In this paper, a simple but novel thermophoretic sampling method named dual time-interval sampling (DTTS) at single point was proposed to obtain multiple parameters including flow velocity, particle volume fraction and particle size distribution (for aggregates and primary particles). In contrast to traditional measurement methods, DTTS considers the changeability of gas velocity and the instability of the probe surface temperature due to heat transfer, which provides its superiority in simplicity and convenience over the traditional sampling method. The unknown gas flow velocity can be calculated by double sampling with different time intervals at a single point, coupled with FSEM image analysis. Moreover, we improved the procedure of temperature measurement by fitting thermocouple signal data, to reduce the errors introduced by conduction heat transfer along the wire and the additional thermal resistance caused by particle deposition on the junction surface.

The obtained profiles of flame temperature, gas flow velocity, particle volume fraction, and particle size distribution along the axial line of flame were close to simulation results from CFD-PBM. By FSEM images, we can obtain the size distribution of primary particles within aggregates and also the microstructure of particles (such as fractal dimension). Based on this measurement method, we can obtain sufficient information about the flow field and particle population, which is extremely valuable for researching and understanding the transport and dynamic evolution processes of particles. In general, all of results are in good

agreement between experiment and simulation, and the reliability of the DTTS method has been validated by sensitivity analysis. It should be noted that the CFD-PBMC model does not account for dilution of the flame aerosol due to weak air entrainment in this study. Therefore, it may need further revision or development for air dilution in strong turbulent flame.

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