Submerged arc discharge for producing nanoscale graphene in deionised water

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This work proposed a novel nanomanufacturing approach, in which a submerged arc discharge method was adopted to produce graphene in deionised water. Graphene produced using this approach can be evenly dispersed and suspended in deionised water without the use of a surfactant or stabiliser, and is suitable for storage at room temperature. Ultraviolet–visible spectroscopy was employed to analyse the optical properties of the graphene nanostructure. The Zetasizer system was used to examine the particle size and zeta potential of the graphene nanoparticles, and scanning electron microscopy, energy-dispersive X-ray spectroscopy, and high-resolution transmission electron microscopy were adopted to explore the morphology, size, and dispersion of the particles, using the Raman spectrum, it is observed that there are two characteristic peaks. Without mixing any surfactant or stabiliser in deionised water, the zeta potential of negatively charged graphene nanoparticles was −51.5 mV. The nanoparticles were stably suspended in the deionised water instead of depositing as sediments. The results of this work confirmed that graphene production with submerged arc discharge is a low-cost, fast, and effective manufacturing method.

1. Introduction: Nanoscale graphene is currently the thinnest and hardest nanomaterial worldwide. It is prevalent in various domains (e.g. physics and material science) and applications (e.g. solar cells and antibiotic materials), and its production methods have received substantial attention [1]. Approximately ten methods are feasible for creating nanoscale graphene; these methods are categorised into physical and chemical approaches, and include mechanical exfoliation, epitaxial growth, metal surface growth, graphene oxide reduction, hydrazine reduction, sodium ethoxide decomposition, nanotube cutting, and sonoelectrochemical methods [2, 3]. Chemical methods for producing graphene can involve toxic reagents and damage the environment [4, 5]. In addition, graphene materials produced through the aforementioned methods usually require a stabiliser to prevent the aggregation of nanoparticles; this greatly increases the costs of related experiments and is harmful to the environment and human health.

The experiment of this Letter verified that applying pulse direct-current arc discharge in deionised water is a convenient and fast method for producing nanoscale graphene; moreover, this method is inexpensive and environmentally friendly. In an arc discharge process, the temperature between the two electrodes can reach thousands of degrees Celsius while graphene is etched in the deionised water [6], which causes the carbon-containing steam to condense into graphene nanoparticle suspensions. The produced graphene can be examined using a particle size analyser, such as the Zetasizer system, to determine the zeta potential and particle size distribution [7, 8]. Raman spectroscopy can be adopted to verify the composition of the graphene [9], and finally, electron microscopy can be employed to observe the morphology, particle size, and dispersion. The nanoscale graphene produced in this Letter was verified to exist as stable suspensions in deionised water. Through this experiment graphene can be quickly manufactured, it is expected that in application side, since the improvement of costs and production technologies, the developmental process can speed up gradually in the future.

2. Experiment

2.1. Materials: A block of graphite was cut to 1 mm rods using lathe processing (Fig. 1). The tips of the graphite rods were used as electrodes for electricity discharge in deionised water (pH = 6.5, conductivity = 1.16 μS/cm).

2.2. Experimental: Fig. 2 illustrates the submerged arc discharge method (SADM) system used in this study [10, 11], with a discharge monitoring interface for determining the discharge success rate (Fig. 3). The interface also displays and records data regarding the system hardware and software configuration, the number of successful discharge, and the power consumption rate. Observing the changes in the discharge success rate facilitated adjusting related parameters to improve the production process, thereby identifying the most suitable parameter settings for optimising the production efficiency and quality. The SADM system mainly comprises five parts: (i) two electrodes; (ii) a servo motor for controlling the discharge distance (10–30 μm) and preventing a short circuit; (iii) controls for system parameters, as listed in Table 1; (iv) a glass container for submerging the electrodes in deionised water and collection of nanoscale graphene; and (v) a stirring bar for evenly dispersing the reaction solution. Fig. 4 illustrates the discharge principles of graphene nanomanufacutring.

2.3. Preparation of graphene nanoparticle suspension: The SADM system provided stable pulse voltage to etch graphene in deionised water. To sustain the water medium between the electrodes, this system provided a pulse voltage of approximately 100 V for 10–10 μs, and maintained a discharge voltage of 20–40 V between the electrodes for 3–5 μs. The peak etching current reached 4 A. The proportional-integral and derivative control (PID) parameters were controlled automatically to obtain the optimal conditions for producing graphene nanoparticles.

The control parameters of the system such as working voltage, electrode distance, pulse current, continuous pulse time (on/off time), deionised water temperature and purity, and impurity content, are key factors affecting nanoparticle production. During the process of arc discharge, the surface layer of the graphite evaporated and condensed to form stable suspensions in the deionised water. After the graphene nanoparticle colloid solution was collected, various devices were used to analyse the solution and

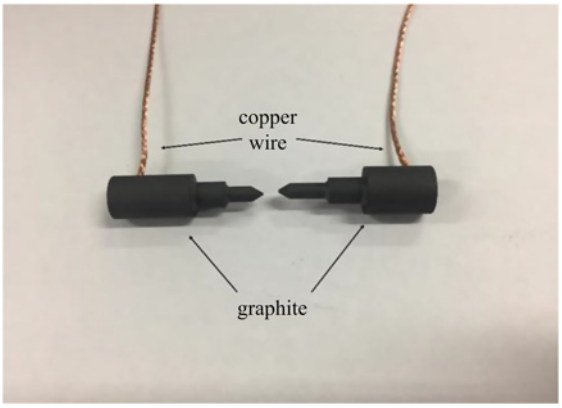

Fig. 1 *Processed graphite rods*

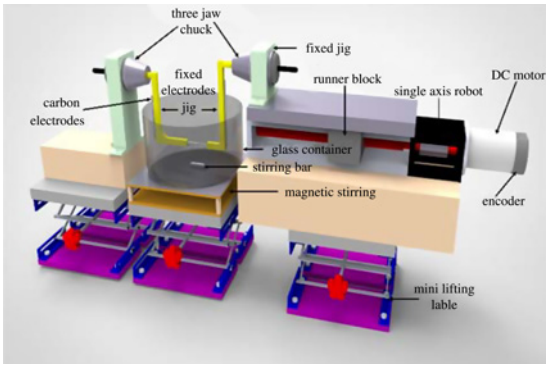

Fig. 2 *Structural representation of m-EDM*

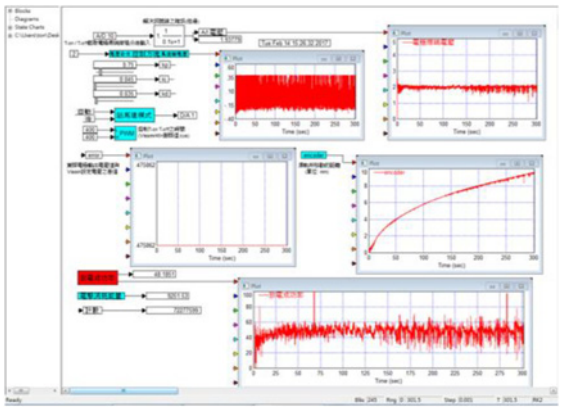

Fig. 3 *Human–machine interface of the microscale discharge processing machine*

Table 1 Parameter of micro-electrical discharge machining (m-EDM) setting and material and testing condition

T_{ON}–T_{OFF}	10–10 µs
PID	$K_p = 0.75$, $K_i = 0.045$, $K_d = 0.035$
diameter of material	anode: 1 mm; cathode: 2 mm
discharge time	5 min
dielectric fluid	deionised water
beaker	200 ml
atmosphere (ATM)	1 atm

determine the particle size distribution, zeta potential, and optical properties. In a 5 min experiment, the consumption per minute of electrodes was about 9.55 (mg/min). After the formation of

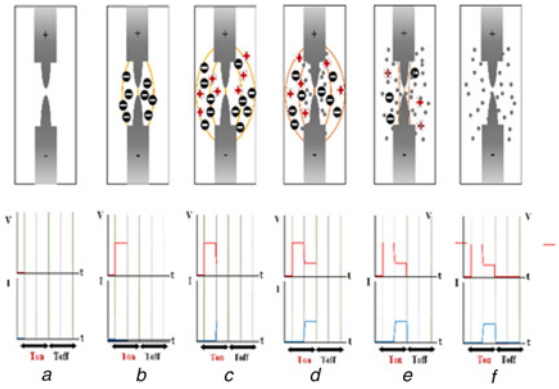

Fig. 4 *Schematic diagram of the discharge principle*

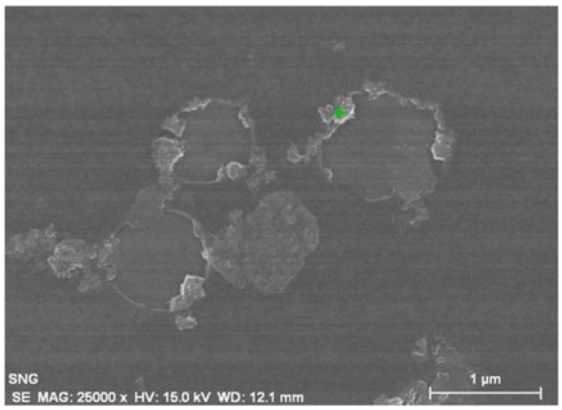

Fig. 5 *SEM image of the graphene nanoparticles*

nano-colloid, precipitate for 2 h. Since graphene can be suspended in deionised water, the supernatant is taken to ensure the purification.

2.4. Surface morphology of graphene nanoparticles: A few drops of the prepared graphene nanoparticle colloid solution were added to the surface of a conductive silicon chip. Conductive carbon glue was used as the adhesive. Scanning electron microscopy (SEM, HITACHI S-4700) was used to observe the surface morphology of the nanoparticles [12]. Energy-dispersive X-ray spectroscopy (EDX) was employed to determine the chemical composition of the graphene nanoparticles. The Zetasizer system (NanoZS90, Malvern) was adopted to estimate the zeta potential, particle size, and particle size distribution. Ultraviolet–visible spectroscopy (UV–Vis, 9423UVA1002E Helios Alpha) was used to analyse the optical properties of the graphene nanostructure [13, 14].

3. Results and discussion: Fig. 5 illustrates the SEM image of the graphene nanoparticles; the particle size distribution is clearly displayed and determined to be within 1 µm. Fig. 6 and Table 2 present the EDX results. Using a conductive silicon chip as the substrate revealed a notable peak at 0.227 keV, which corresponds to the location of C Kα. In addition, the peak of Si was observable at 1.713 keV, confirming the presence of the silicon chip.

The zeta potential of the carbon colloid was approximately −51.5 mV (Fig. 7), showing that negatively charged graphene nanoparticles are less likely to deposit as sediments when the magnitude of zeta potential is greater than −30 mV. In the present experiment, the zeta potential of −51.5 mV indicted that the graphene nanoparticles did not deposit but instead remained

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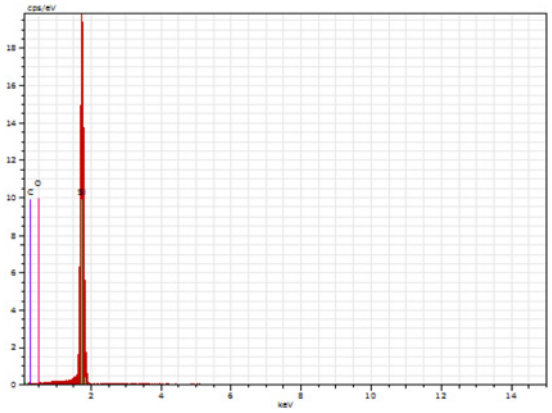

Fig. 6 *Chemical composition of the graphene nanoparticles*

Table 2 EDX application for the analysis of the proportions of elements in graphene

Element	Weight, %	Atomic, %
C	12.15	29.09
Si	64.92	66.48
O	2.47	4.44

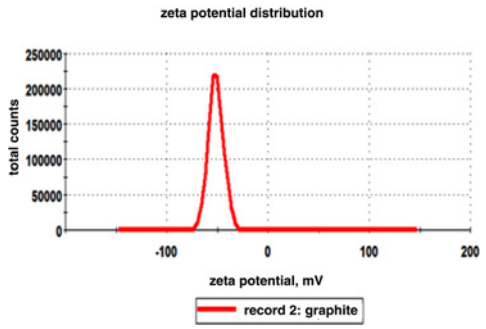

Fig. 7 *Zeta potential*

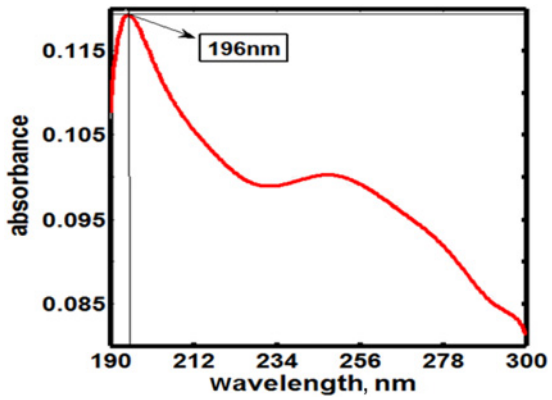

Fig. 8 *UV–Vis absorption spectrum of the aqueous carbon colloid*

suspended. Fig. 8 presents the UV–Vis spectrum of the graphene nanoparticle colloid. The maximum absorbance was determined to occur at ∼196 nm. Finally, using the Raman spectrum (Figs. 9 and 10), it is observed that there are two characteristic peaks (1531 wavenumber cm^{-1} and 2417 wavenumber cm^{-1}) in this figure, which confirms the presence of graphene, there are two

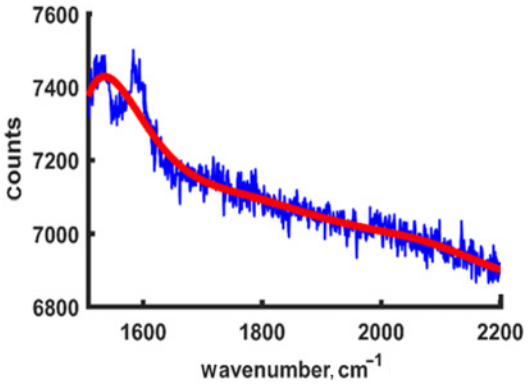

Fig. 9 *Raman spectra of carbon colloids precipitated (1600–2200)*

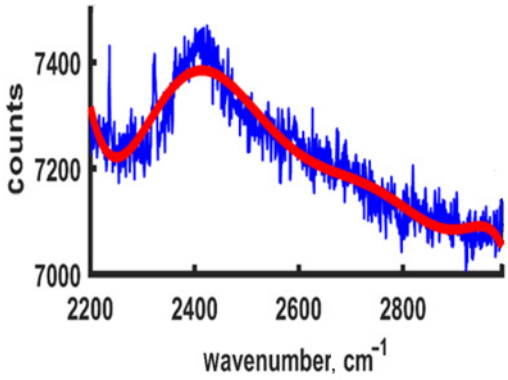

Fig. 10 *Raman spectra of carbon colloids precipitated (2200–2800)*

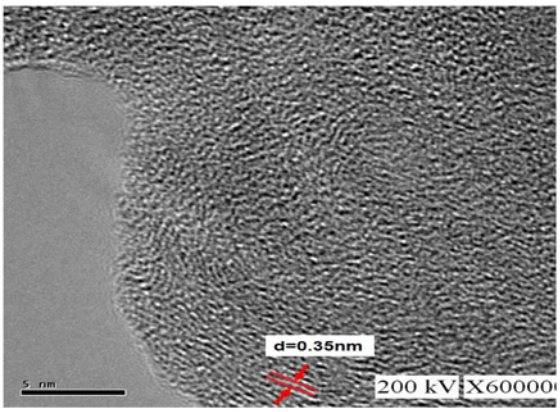

Fig. 11 *Graphene interlayer spacing of 0.35 nm was measured*

burst (2237 wavenumber cm^{-1} and 2323 wavenumber cm^{-1}) that come from the noise generated by the instrument. Observed HRTEM photos which gradually zoom in, the result has been confirmed that graphene interlayer spacing of 0.35 nm was measured (Fig. 11).

During the production of graphene nanoparticles, arc discharge in the deionised water enabled observing the electrohydrolysis of water, through which oxygen ions and hydrogen gas were formed and appeared as small gas bubbles that partially dissolved in the deionised water [15–17]. The produced oxygen ions and gaseous hydrogen then reacted with each other. The inexpensive and simple SADM used in this study enabled producing graphene nanoparticles of similar size, confirming this method as an efficient alternative for producing graphene nanoparticles. In this method, water

serves as an excellent medium that facilitates a stable, effective, and fast mass production scheme. In addition, water acts as a stabiliser and deters the needs of using a surfactant for producing graphene nanoparticles.

4. Conclusion: The initiation of this research is using graphite in the SADM to manufacture graphene. Below are the benefits of our method:

(i) Applying pulse direct-current arc discharge in deionised water is a convenient, inexpensive, effective, fast, and environmentally friendly method for producing graphene nanoparticles. The proposed method is applicable to the mass production of graphene nanoparticles.

(ii) The proposed SADM was confirmed to successfully produce graphene nanoparticles in deionised water.

(iii) Without adding any surfactant or stabiliser, the negatively charged graphene nanoparticles exhibited a zeta potential of −51.5 mV. As this value exceeded −30 mV, the particles did not deposit as sediments, but instead remained as stable suspensions. An extensive period of observation verified no notable sediments formed by the nanoparticles.

(iv) Graphene produced through the proposed method can be stored at room temperature. As the quality of graphene nanoparticle colloids is not affected by temperature, they can be stored for an extensive period.

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