Review Article

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Parameter control and concentration analysis of graphene colloids prepared by electric spark discharge method

<https://doi.org/10.1515/ntrev-2019-0018>

Received Dec 17, 2018; accepted Jul 01, 2019

Abstract: In this study, graphene colloids were prepared using the electric spark discharge method (ESDM) with graphite rods (99.9% purity) in deionized water (DW) at a normal temperature and pressure. Five different types of graphene colloids were prepared using an electrical discharge machine (EDM) with five different pulse cycle switching times ($T_{on}:T_{off}$) = 10:10, 30:30, 50:50, 70:70, and 90:90 μ s. According to the Ultraviolet-visible spectra (UV-Vis) and Zetasizer analysis, the results showed that the 10:10 μ s parameter was the most suitable for the preparation of graphene colloids. UV-Vis was also used to detect the concentration of the graphene colloids; a comparison with a graphene oxide (GO) confirmed that this method could be used to calculate the discharge time needed to produce graphene colloids with different concentrations in the ESDM process.

Keywords: Electric spark discharge method, Graphene colloid, Absorbance, Zeta potential, Concentration

1 Introduction

Graphene is completely different from GO in nature and can be clearly distinguished by chemical bonding. Graphene is a planar film in the form of a hexagonal lattice composed of carbon atoms in the sp^2 orbit domain. Graphene has the characteristics of low resistivity, high thermal conductivity, and high mechanical properties [1–

3]. The bond of GO is similar to graphene; however, the carbon atom layers are destroyed due to oxidation and oxygen atoms are inserted into the gaps between carbon atom layers to form a structure in which the carbon atom layer coexists with the oxygen atom [4]. GO has high hydrophilicity and mechanical properties [5], and it has high dispersion stability in water [6]. Based on these advantages, graphene and GO have numerous applications, including transparent electrodes, supercapacitors, composite materials, and solar cells [7–10]. There are numerous chemical preparation methods for graphene, including chemical vapor deposition [11], chemical exfoliation [12], the Hummers method [13], and the epitaxial growth method [14], of which the Hummers method is the method that can produce GO with different concentrations in large quantities and with properties that are closely related to this study. Although it could be known from the literature [15] that the peaks of the UV-Vis characteristics of GO and graphene are completely different (230 and 262 nm, respectively), from the viewpoint of the chemical bond, the difference between the two is only whether the oxygen atom is inserted into the broken carbon atom layers or not; the orbital domain formed by the carbon itself does not change dramatically. Under such conditions, a GO can be used to detect the concentration of graphene colloids prepared by ESDM.

Previous studies on graphene colloids made with self-developed micro-EDM devices have been published [16]. Limited by the PID parameters of the VisSim program in micro-EDM, $T_{on}:T_{off}$ can only be set to 10:10 μ s, however no research has been done on other $T_{on}:T_{off}$ parameters, and at the same time, the results of nanometer colloids fabricated by micro-EDM and EDM are totally different. In this study, five different $T_{on}:T_{off}$ parameters were used to prepare graphene colloids through EDM, and the quality of the finished products was determined by the results of UV-Vis and Zetasizer analysis. Finally, the best quality finished products were analyzed using Raman and Transmission electron microscope (TEM) analysis. After finding the optimum preparation parameters, it is difficult to control the discharge process of graphene colloids prepared by

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the physical method and it is not easy to obtain graphene colloids with a specific concentration. Therefore, it is a very important topic to develop a new EDM qualitative and quantitative method to prepare graphene colloids with specific concentrations at different discharge times; at the same time, it is also a major research focus for the preparation of nanometer colloids by ESDM. Because ESDM cannot control the concentration of nanometer colloids as meticulously as the chemical method in the process, the new qualitative and quantitative method provides a mechanism for judging the concentration, which can be used to accurately grasp the concentration of nanometer colloids during ESDM preparation.

2 Experimental system and method

2.1 Experimental system

In this experiment, graphene colloids were prepared using an EDM. The principle is to use electric energy to convert heat energy and to melt the lower electrode rapidly without direct contact between the upper and lower electrodes. This method is called ESDM. The schematic diagram of the EDM is shown in Figure 1. The upper and lower electrodes are made of a conductive material, the dielectric fluid is made of insulating DW [17]. The upper electrodes slowly approach the lower electrodes using Pulse Width Modulation (PWM) as a servo control until the electrodes are immersed in the DW. When the distance between the two electrodes is about 30 μm , the electric field intensity on the surface of the electrode will exceed the insulating withstand voltage of the DW, resulting in the insulation being destroyed, a high-temperature arc forming between the two electrodes.

The EDM related parameters include T_{on} : T_{off} , the current segment, and high-low voltage switching. T_{on} : T_{off} was the most important parameter in this study and was set according to the principle of PWM. The current segment potential (IP) consists of seven segments in which the larger the IP value, the higher the discharge current (I_{gap}) between electrodes and the faster the processing speed; however, a lower processing fineness will result in the larger the size of the prepared nanoparticles. EDM is a transistor discharge circuit and the switch of the processing power supply can be controlled. In the process of a continuous discharge, it can be controlled by PWM. The arc discharge process is shown in Figure 2. The voltage and current between the two electrodes in EDM are the V_{gap} and I_{gap} signal values, respectively, and the con-

Figure 1: EDM

Figure 2: Arc discharge process: (a) discharge begins; (b) ionization; (c) melting; (d) discharge cut-off; (e) insulation restored

cept of V_{gap} is the potential difference. When the transistor in the power supply is turned on the DC pulse will be T_{on} ; conversely, when the transistor is open, the discharge cutoff is T_{off} , and T_{on} and T_{off} combine to form a fixed discharge pulse wave period. The time ratio of T_{on} to the wave period is called the duty cycle. In order to find a suitable PWM for preparing nanometer colloids with any metal or conductive electrode, the time setting and duty cycle of T_{on} and T_{off} are very important. The arc discharge process is as follows. At the beginning of the first cycle, when the T_{on} time begins, the V_{gap} rises, and the distance between the two electrodes is 30 μm , the electric field intensity will reach the maximum, the dielectric liquid insulation will gradually be destroyed, and the arc will form after the electrons are generated. Next is ionization, in which the dielectric fluid is completely destroyed and forms a low-resistance channel. When I_{gap} rises, V_{gap}

drops, electrons flow rapidly to the upper electrode (anode), and cations are generated. Arc melting then occurs. Based on the successful stage of discharge, I_{gap} maintains its maximum value. Under the action of repeated ionization, positive and negative ions hit the metal surface and kinetic energy converts into heat energy to generate a discharge arc, which melts the two electrodes. The surfaces of the electrodes peel off metal particles and the T_{on} time ends. Regarding the discharge cutoff, when T_{off} time starts, V_{gap} and I_{gap} drop, the electrode no longer supplies electrons, the ionization disappears, and the metal particles become suspended in the dielectric fluid. Finally, the discharge ends when the first cycle ends, the T_{off} time is over, there is no V_{gap} and I_{gap} , the surface temperature of the electrode is lowered, and the withstand voltage of the dielectric fluid is restored, waiting for the electric discharge machining for the next cycle.

2.2 Electrode material and GO solution

The electrode material was made of a graphite blocks with 99% purity. Through lathe processing, whole graphite blocks were made into graphite rods, which could be used as electrodes. Because the discharge process used point discharge, the discharge end of the electrode required a small surface area (about 1 to 2 mm in diameter); however, as graphite is not ductile and its structure is brittle, graphite rods with diameters of 1 to 2 mm would be difficult to fabricate and easily broken. Therefore, the graphite block was made into graphite rods with a diameter of about 1 cm, and one end of the rod was sharpened to complete the small surface area required for the tip discharge, as shown in Figure 3. In addition, this study used a GO prepared by the Hummers method to dissolve GO in DW at a concentration of 1000 ppm, as shown in Figure 4. The solution of GO was diluted to different ratios for qualitative and quantitative analysis of the concentration.

Figure 3: Graphite rod electrode

Figure 4: GO solution

2.3 Experimental method

In this study, EDM was used to prepare graphene colloids, and the most suitable parameters for preparing graphene colloids were found through different $T_{on}:T_{off}$ parameter settings. In this study, five different $T_{on}:T_{off}$ parameters were used, which were 10:10, 30:30, 50:50, 70:70 and 90:90 μs , respectively. The environmental parameter settings are shown in Table 1. In addition to the five different $T_{on}:T_{off}$ parameters, the current segment was set to the second segment, and at this time, the current value was about 6.4 A. There was no need to turn on the high-low voltage switching button, and the no-load voltage was 140 V. The dielectric fluid was 150 mL DW with a discharge time of five minutes for preparation at normal pressure and temperature. After the five groups of different $T_{on}:T_{off}$ graphene colloids were prepared, in order to compare the advantages and disadvantages of graphene colloids, UV-Vis and a Zetasizer were used for analysis and comparison, and the most suitable preparation parameters were obtained according to the results. Using UV-Vis spectrum (9423UVA1002E Helios Omega) for optical analysis of the ultraviolet section [18], the characteristic peak of graphene was around 260 nm, thus confirming that graphene was indeed formed in the colloids. In addition, the size ratios of concentration could be distinguished by the absorbance; the greater the value, the higher the concentration, thereby indicating a higher discharge success rate. Absorbance has no units, therefore the values were only applicable to the UV-Vis spectrum of the same models. The suspension stability of graphene sheets in the graphene colloids was confirmed using the

Table 1: Environmental parameter settings

Material	Graphite
$T_{on}:T_{off}(\mu s)$	10:10, 30:30, 50:50, 70:70, 90:90
Current segment (IP)	2
Voltage (V)	140
Dielectric fluid	DW
Capacity (mL)	150
Discharge time (min)	5
Temperature ($^{\circ}$)	25

Zetasizer (NanoZS90, Malvern) electrophoretic measurement technique, and the suspension stability was determined according to the zeta potential. When the absolute value of the zeta potential was greater than -30 mV, the sample was considered to have high suspension stability [19]. After the detection of the graphene colloids prepared using five different $T_{on}:T_{off}$ parameters, the data were compared to find the most suitable $T_{on}:T_{off}$ parameters for the preparing graphene colloids, and Raman spectroscopy (Ramboss 500i, DONGWOO) and TEM (HRTEM, JEM2100F) were used for analysis. The Raman analysis detected the D, G and 2D-band of graphene and inferred the number of graphene layers and defect degree [20]. TEM analysis was used to observe the distribution and inter-layer distance of the graphene sheets [21].

Because absorbance is proportional to concentration, the basic qualitative and quantitative analysis of the graphene concentration was conducted using the UV-Vis spectra. The standard solution uses a GO to estimate the concentration of graphene prepared by ESDM. Most UV-Vis spectra studies do not pay attention to the numerical value of absorbance and prefer optic analysis; however, for qualitative and quantitative analysis, this value is an effective and highly reliable reference, and the only condition is that the same model UV-Vis spectroscope must be used. For the standard solution, this study used a GO fabricated using the Hummers method and prepared five different concentrations, including 5, 10, 15, 20 and 25 ppm. After measuring the absorbance, the results could be integrated into a fitted curve (1). In addition, the graphene prepared by ESDM required five different discharge times, including five, 10, 15, 20 and 25 minutes. After preparation, the absorbance was also measured and the results could be also integrated into a fitted curve (2). The feasibility of this qualitative and quantitative analysis method was confirmed by cross-comparison of the two results and actual verification. The practical verification steps were as follows: (a) prepare a GO below 25 ppm and measure the

absorbance; (b) substitute the absorbance into Eq. (1) and (2) to calculate the concentration of the GO and the discharge time required to prepare graphene colloids; (c) prepare graphene colloids based on the calculated discharge time and measure the absorbance; (d) substitute the measured absorbance into Eq. (1) to obtain the concentration of the graphene colloids; and (e) compare the concentration of the graphene colloids with that of the GO.

3 Results and discussion

3.1 UV-Vis and zeta potential detection of different $T_{on}:T_{off}$

In this study, EDM was used to prepare graphene colloids with five different $T_{on}:T_{off}$ parameters, and the discharge time was five minutes. The numerical values of the absorbance and zeta potential are shown in Table 2 and the UV-Vis spectra are shown in Figure 5. The results indicated that the graphene colloids with five different preparation parameters had nearly the same conjugated structure and the characteristic peaks were all at 256 nm. Due to dif-

Table 2: Absorbance and zeta potential of different $T_{on}:T_{off}$

$T_{on}:T_{off}(\mu s)$	Absorbance	Zeta potential (mV)
10:10	0.336	-43.8
30:30	0.404	-35.1
50:50	0.477	-22.3
70:70	0.419	-23.8
90:90	0.405	-24.5

Figure 5: UV-Vis of different $T_{on}:T_{off}$

Figure 6: Zeta potential of different $T_{on}:T_{off}$

ferent preparation parameters, the graphene colloids also had different absorption values. The maximum absorption value could be obtained at 50:50 μs , which indicated that the discharge success rate was higher, and that this parameter could be suitable for preparing graphene colloids. The zeta potential values for the different preparation parameters are shown in Figure 6. The zeta potential at 10:10 μs was -43.8 mV, and the actual test results were as shown in Figure 7. It was also found that the zeta potential at 30:30 μs was -35.1 mV, therefore it could be concluded that graphene colloids prepared at 10:10 and 30:30 μs could obtain high suspension stability. After comparing the UV-Vis spectra and zeta potential, it was known the absorbance of 50:50 μs was the largest while that of 10:10 μs was the smallest, and that the success discharge times of 50:50 μs was better than that of 10:10 μs . However, the obtainment of stable suspended and dispersed graphene colloids remained the most important purpose. As 10:10 μs had the highest zeta potential, it was the most suitable for preparing graphene colloids.

3.2 Graphene colloid analysis (10:10 μs)

Based on the results of the above discussion, the optimum $T_{on}:T_{off}$ parameter for preparing graphene colloids was 10:10 μs . Raman and TEM analysis were used to confirm the results and the quality of the finished products. The Raman detection results are shown in Figure 8. There were three distinct D, G, and 2D-band characteristic peaks, and some layers of graphene could be judged through the intensity of the characteristic peaks from G and 2D. The D-band was the disordered vibration peak of graphene at 1331 cm^{-1} , which was used to represent the structural de-

Figure 7: Zeta potential of 10:10 μs

Figure 8: Raman of graphene

fects of graphene. The G-band was the main characteristic peak of graphene at 1579 cm^{-1} , which was caused by the structural vibration of the sp^2 carbon atom. The 2D-band was a second-order Raman peak of two-phonon resonance at 2700 cm^{-1} , which was used to represent the interlayer stacking mode of carbon atoms in graphene. The TEM images are shown in Figure 9. From Figure 9(a) and (b), it could be clearly seen that the thickness of the graphene sheets was smaller in the shallower areas and larger in the darker areas. Figure 9(c) shows the existence of lattice lines, which represented the interlayer distance of the graphene sheets. The distance was 0.35 nm.

Figure 9: TEM images of the graphene scale bar: (a) 100; (b) 20; (c) 5 nm

3.3 Qualitative and quantitative concentration analysis of graphene colloids

The UV-Vis detection results for the five GO with different concentrations (5, 10, 15, 20 and 25 ppm), are shown in Figure 10(a), which indicates that the GO had an obvious characteristic peak at 232 nm. This represented a typical GO map, in which the higher the concentration, the greater the absorbance will be. The test results could be integrated into a fitted curve (1). Eq. (1) was $y=137.82x^4-292.67x^3+196.14x^2-23.343x+5.6519$, as shown in Figure 10(b). According to Eq. (1), for an unknown concentration of a GO, the same model UV-Vis could be used to

detect the absorbance and then enter the formula to calculate the concentration of the GO.

Next, the discharge time required for the graphene colloids prepared by EDM was calculated using the UV-Vis detection results of the GO. Figure 11(a) are the UV-Vis detection results for graphene colloids prepared at five different discharge times (5, 10, 15, 20 and 25 minutes), showing that the characteristic peak value of graphene was 260 nm, and that the longer the discharge time, the larger the absorbance would be. The detection results could be integrated into a fitted curve (2). Eq. (2) was $y=-23.348x^3+44.558x^2+7.876x-1.5891$, as shown in Figure 11(b). According to Eq. (2), the known absorbance of the GO could be substituted into Eq. (2) to calculate the discharge time required for preparing graphene by EDM. After dis-

Figure 10: Different concentrations of GO (a) UV-Vis; (b) Eq. (1)

Figure 11: Different discharge time of graphene (a) UV-Vis; (b) Eq. (2)

Figure 12: 10 ppm UV-Vis: (a)GO solution; (b)graphene colloids

charge, graphene colloids with the same concentration as that of the GO could then be obtained.

3.4 Graphene colloids concentration analysis and verification

When preparing the unknown concentration GO, its absorbance was detected to be 0.338, as shown in Figure 12 (a). Substituting 0.338 into Eq. (1) revealed that the concentration was 10 ppm. Substituting 0.338 into Eq. (2) revealed that if graphene colloids with the same concentration were to be prepared, the discharge time would take five minutes. After preparation of the graphene colloids was completed, the absorbance was detected to be 0.32, as shown in Figure 12(b). Substituting 0.32 into Eq. (1) revealed

the concentration of the graphene to be 10 ppm. The results showed that this method was indeed suitable for the qualitative and quantitative analysis of graphene colloid concentration. The only restriction was to use a specific UV-Vis spectroscope to obtain the approximate absorbance.

4 Conclusion

This study found the most suitable $T_{on}:T_{off}$ parameters for preparing graphene colloids in EDM and used a GO as the standard solution. Basic qualitative and quantitative analysis of the concentration was carried out by UV-Vis, and no dispersants or strong oxidants were added during the process of study. The findings of this study represent the most environment friendly, fast and optimal method for preparing graphene colloids at present. The contributions of this study were as follows.

1. ESDM can be used to prepare nanometer colloids under normal temperature and pressure and can obtain graphene colloids with high suspension property without adding dispersants or chemicals, which indicates that the process will not be suspicious of environmental pollution and is harmless to the human body.
2. By comparing the UV-Vis with the zeta potential for graphene colloids prepared by ESDM, it was found that when $T_{on}:T_{off}$ was 10:10 μ s the zeta potential was -43.8 mV, which had the best suspension mechanism and was the most suitable for preparing graphene colloids.
3. The Raman spectra could obtain complete D, G and 2D-band characteristics, while the TEM analysis

clearly showed the distribution of the graphene layers. The inter-layer distance of graphene was about 0.35 nm.

4. Different concentrations of GO were used as standard solutions, and qualitative and quantitative analysis of the concentration was carried out through absorbance in UV-Vis. Eq. (1) was used to calculate the concentration, and Eq. (2) was used to calculate the discharge time.
5. The experimental results showed that the absorbance of a GO with an unknown concentration was 0.338 (10 ppm) and the discharge time was five minutes. The absorbance of graphene colloids prepared after five minutes of ESDM discharge was 0.32 (10 ppm).
6. Through the conversion of Eq. (1) and (2), the concentration of nanometer colloids could be controlled in the environment using ESDM. The application of ESDM to nanometer colloid concentrations is an area of future study.

Acknowledgement: The authors would like to thank the Precision Research and Analysis Center, NTUT for technical supporting this research.

Conflict of Interests: The author(s) declare no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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