Fabrication of nano-bismuth colloids in deionized water using an electrical discharge machine

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Abstract
Bismuth (Bi) is used to treat certain diseases, however the Bi powder or colloids used in medicine must be nonpolluting and safe. The use of electrical discharge machines (EDMs) to produce nano-Bi powder is a green process. A nonpolluting and safe nano-Bi colloid can be produced swiftly and easily in deionized water using the electrical spark discharge method, adjusting the discharge pulse width $T_{on}$, $T_{off}$ and the discharge current $I_{p}$ of the EDM. Transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy, the Zetasizer technique, ultraviolet–visible spectroscopy (UV–Vis), and other techniques were used to analyze a nano-Bi colloid prepared under various discharge parameters to optimize the preparation of Bi nanoparticles (Bi-NPs) using EDMs. The results of this study indicated that Bi-NP colloids were successfully prepared using EDM. TEM images revealed that the NPs were smaller than 50 nm with only the Bi element in the colloid. Furthermore, the zeta potential of the nano-Bi colloid exceeded 30 mV, which indicated that the suspension of the colloid was excellent. A UV–Vis absorption peak was observed at approximately 234–237 nm.

Keywords: electrical discharge machine, nano-bismuth colloid, electrical spark discharge method

(Some figures may appear in colour only in the online journal)

1. Introduction

Bismuth (Bi) is a chemical element with the atomic number 83, and is a silvery white cluster in appearance. The chemical properties of Bi are similar to those of arsenic and antimony. Bi is the most diamagnetic metal and has one of the lowest thermal conductivities among metals behind manganese. Bi also has the highest Hall coefficient, which means it has high resistance. When Bi is deposited on the surface of an object in an extremely thin layer, it has the properties of a semiconductor. Bi-containing drugs have been used to treat gastrointestinal diseases [1, 2] such as diarrhea, indigestion, and peptic ulcers of the stomach and duodenum caused by H. pylori [3, 4]. Bi powder or colloids used in medicine must be nonpolluting and safe. Typically, grinding and chemical methods are used to produce metal powder or nanometal compounds [5–9]. An electrical discharge machine (EDM) can be used to produce nanometal compounds [10–14]. A nanometer is a unit of length with the mathematical symbol nm. Generally, particles with a size of less than 100 nm are classified as nanograde, and the products produced are nanoproducts. Scientists have found that at the nanometer scale, materials no longer have regular periodic structural features. Because of the increased proportion of boundaries and reduction in
2. Principles of electrical spark discharge method

The principle of the ESDM is to convert electrical energy into thermal energy, which causes the surface of the anode to melt rapidly. Because the anode and cathode are not in direct contact, no collision occurs between the electrodes. In nanometal preparation using an EDM, an anode and a cathode are placed in a dielectric liquid, and a direct current of 140 V is applied to the upper and lower electrodes. The servo control system controls the distance between them. When the distance between the electrodes is approximately 30 µm, the dielectric strength of the dielectric fluid can be nullified to generate a spark between them. The spark temperature is as high as 5000–6000 K. The high-energy spark concentrated at one point on the surface melts the surface of the electrode, sputters NPs, and dissociates ions [16, 17]. Figure 2 illustrates the processes of preparing a nano-Bi colloid using the ESDM. Figure 2(a) depicts the two metal electrodes being kept at a small distance and both are insulated. Figure 2(b) depicts how when the distance between the two electrodes is small, the electric field gradient exceeds the dielectric voltage of the dielectric fluid; electrons are emitted from the cathode to the anode, and the process of discharge begins. Figure 2(c) depicts the dielectric liquid insulation as completely destroyed, and simultaneously, the electrons rapidly flow toward the anode to form an ion channel and generate a current. Figure 2(d) illustrates that the electrode gap is transformed into thermal energy by kinetic energy to form a discharge spark under repeated ionization. The high temperature melts the two electrodes, and molten metal particles are sprayed from the electrode surfaces. Figure 2(e) illustrates that when the two discharge pulses enter the \( T \) at time state, the ion path swiftly dissipates and the metal particles and some of the ions produced by melting are suspended in the dielectric liquid. Figure 2(f) depicts how when the electrode stops discharging, numerous metal particles are scattered in the dielectric liquid and discharge machining marks are formed on the surface of the electrode, which awaits the next discharge.

In this study, nano-Bi colloids were prepared using ESDM. Deionized water (DIW) was used as the dielectric fluid because it is environmentally friendly and easy to store and analyze. After discharge, the particles and ions of the electrode that melt become suspended in the DIW. This solution is called a nanometal colloid, and the particles in it are less than 100 nm in size. The small particles become suspended in the DIW because of the thermal energy from the external temperature. When the particle size is 1–10 µm, the force between the particles is considerably affected by gravity, and the particles combine into larger particles after mutual

**Figure 1.** Schematic of the nano-Bi colloid system.

**Figure 2.** Process of preparing a nano-Bi colloid using the ESDM (top row) and the waveform of discharge (bottom row).
attraction and collision, causing particle precipitation. When the particle size is less than 0.1 µm, van der Waals and electrostatic repulsive forces affect the suspension of particles considerably [18, 19]. When the repulsive force between NPs is greater than the attractive force, it can maintain a proper equilibrium distance between particles and prevent aggregation and precipitation between them, ensuring the colloid is in a stable state. This phenomenon is called hydrostatic equilibrium [20].

Figure 3 displays the discharge waveform measured using an oscilloscope. Figure 3(a) depicts a large section of the discharge waveform. In the oscilloscope screen window, the upper waveform is the voltage across the discharge electrode, and the electrode current is displayed in the lower window. Figure 3(b) indicates that the melting time of the discharge is 8.6 µS. Figure 3(c) displays the voltage change from a high voltage to 2.4 V when the electrode is melted. Figure 3(d) displays the current when the electrode is melted at 2.88 A. If the ESDM continues to successfully generate the successful discharge waveform depicted in figure 3, a nano-Bi colloid solution can be prepared after a period of time.

2.2. ESDM for producing a nano-Bi colloid

Bi rods (Type B3-2002-R3) with a diameter, length, and typical purity of 3.175 mm, 100 mm and 99.99%, respectively, were used as electrodes for the ESDM to prepare a nano-Bi colloid in DIW. The total preparation time was 2 min, and the current segment $I_p = 1$ (in level). According to studies of ESDM, a duty cycle of 50% PWM (pulse-width modulation) is most conducive to nano-Bi colloid preparation. In this study, we tested for PWM with $T_{on} = 10$ µS. Because of the low melting point of Bi, if the $T_{on}$ time is too long, Bi-NPs become too thick and form a dark black colloid. Therefore, the discharge time was set within 100 µS. Accordingly, cross references were implemented to determine the optimal PWM parameters for preparing Bi-NP colloids, and then the following PWM parameters were set: 50% duty cycle: 10–10, 20–20, 40–40, 80–80, and 100–100 µS; $T_{on} = 10$ µS: 10–10, 10–30, 10–50, 10–100, and 10–300 µS. Next, the size and zeta potential were analyzed. The results indicated that the particles should be smaller than 100 nm, and the zeta potential must exceed the absolute value of 30 mV for satisfactory colloidal suspensibility. This is a promising technology for application in the future [21, 22].

2.3. Experimental and parameter settings

Figure 4 depicts the preparation process of the nano-Bi colloid. The preparation method involved placing the Bi rod in the fixture of the EDM. Then, a moderate quantity of DIW was placed in the beaker. Subsequently, two Bi electrodes were aligned in an appropriate position, and the parameters of the EDM were adjusted, such as current value, $T_{on}$ time, $T_{off}$ time, and preparation time. A burette was used to collect samples for Zetasizer, ultraviolet–visible spectroscopy (UV–Vis), transmission electron microscopy (TEM), and energy-dispersive x-ray (EDX) measurements to evaluate whether the prepared nano-Bi colloid met the target demand. If the desired results were not obtained, then the current value and $T_{on}$ and $T_{off}$ times were adjusted. These steps were repeated until the desired results were achieved.

Table 1 lists the parameter settings. $I_p = 1$ was used to prepare the samples because a low $I_p$ segment is suitable for the particle size required by the nanometer process. A greater number of $I_p$ segments results in faster processing, and larger particles result in an increase in the sample concentration. Furthermore, analyses of lattice, crystal structure, chemical...
Table 1. Parameter settings for nano-Bi colloids.

| Parameter Name                  | Parameters          | Parameter Name                  | Parameters          |
|---------------------------------|---------------------|---------------------------------|---------------------|
| Current setting (I_p)           | 1 (3.04 A)          | Voltage setting (V)             | 140                 |
| Dielectric fluid                | DIW                 | Dielectric fluid volume (ml)    | 200                 |
| Temperature (°C)                | 25                  | Preparation time (min)          | 2                   |
| Ton-Toff (µs) with duty cycle is 50% | 10–10, 20–20, 40–40, 80–80, 100–100 | Ton-Toff (µs) with Ton = 10 µs  | 10–10, 10–30, 10–50, 10–100, 10–300 |

3. Results and discussion

With the duty cycle of 10–100 µs and I_p = 1, the nano-Bi was fabricated and it was contained in a glass bottle as depicted in figure 5. Furthermore, DIW was placed in another glass jar. Laser light was projected on both bottles. The glass bottle containing the DIW did not exhibit the Tyndall effect, whereas that containing the nano-Bi colloid did. The nano-Bi colloid exhibited nanometer characteristics, but the size of the nanometer metal particles was unknown. Furthermore, it was uncertain whether the material was nano-Bi. The size and material of the particles in the nano-Bi colloid were assessed through TEM.

Because TEM is complex, we first used a simple method to confirm whether the prepared nano-Bi colloid had nanometer characteristics. A Zetasizer was used to measure whether the dielectric potential of the metal particle colloid was greater than 30 mV and particle size was smaller than 100 nm. If these two conditions were satisfied, then the metal colloid contained NPs. The use of a Zetasizer can save time and cost.

3.1. Zetasizer results

Tables 2 and 3 list the size and zeta potential of the metal colloid solution measured under the various duty cycle preparation procedures. Table 2 lists the experimental results of the T_on–T_off (10–10, 20–20, 40–40, 80–80, and 100–100 µs–µs time periods) duty cycle at 50%. Table 3 presents the experimental results of changing T_off with a fixed T_on: 10–10, 10–30, 10–50, 10–100, and 10–300 (µs–µs) of 10. The period of T_on set to 10 was fixed because the melting temperature of Bi in metal materials is low (271.5 °C). A large T_on time causes Bi to take longer to melt and may result in large particles. Therefore, T_on was used as a reference to change T_off. A nanometal particle colloid solution can be prepared with a 50% duty cycle or a duty cycle with a T_on of 10.
Table 4. EDX analysis of the weight and proportion of Bi content in the nano-Bi colloid.

| Element | Peak Area | Area Sigma | k factor | Abs Corrn. | Weight % | Weight % Sigma | Atomic % |
|---------|-----------|------------|----------|------------|----------|----------------|----------|
| O       | 20,932    | 250        | 1.810    | 1.000      | 70.27    | 0.73           | 96.86    |
| Bi      | 5713      | 188        | 2.806    | 1.000      | 29.73    | 0.73           | 3.14     |
| Totals  | –         | –          | –        | –          | 100.00   | –              | –        |

Figure 6. TEM image of Bi-NPs: (a) Original image and (b) an enlargement of a particular area of the original.

Figure 7. EDX spectrum of the nano-Bi colloid deposited on the copper carrier.

3.2. TEM results

The optimal zeta potential measurement result (10–30 µs) for TEM observation was selected. The enlarged image in figure 6(b) displays particles smaller than 50 nm.

3.3. EDX results

EDX (JEOL JEM-2100F) was used to investigate the chemical composition of nano-Bi colloids. Figure 7 displays the EDX spectrum of a nano-Bi colloid deposited on a copper (Cu) carrier. The presence of Bi peaked at 1.8, 2.5, and 13.1 keV. The composition strength of the Bi was strong, but in addition to Bi, elements including carbon (C), oxygen (O), Cu, and thorium (Th) were observed. Their presence was attributed to the use of a Bi metal wire and sampling on a Cu mesh during the preparation. The occurrence of Bi, C, O, and Cu is normal, but the presence of Th is unusual. The presence of Th was expected to have originated from the Bi metal wire. Figure 8 displays the EDX analysis of Bi-NPs. Figure 8(a) illustrates the distribution of Bi particles, and figure 8(b) depicts the distribution of O. Table 4 lists the weight value and ratio of Bi content in the Bi-NP colloid.

3.4. UV–Vis results

Figure 9 displays the results of UV–Vis examination of the nano-Bi colloid prepared using an EDM. Three curves are observed in the figure. UV–Vis absorption peaks of the nano-Bi colloid are observed at 234 and 237 nm. If the particles were small, then the absorption peak occurred at 234 nm, and if the particles were relatively large, the absorption peak occurred at 237 nm.

4. Conclusions

In this study, a nano-Bi colloid was successfully prepared using an EDM with the electrical spark discharge method (ESDM). The Zetasizer, UV–Vis, TEM, and EDX test results...
confirmed the colloid to be nano-Bi. The conclusions of this study are as follows:

a. A nano-Bi colloid was successfully prepared using the ESDM. This is the first time a nano-Bi colloid has been prepared using this method. The method is nonpolluting, and the prepared nano-Bi colloid is suitable for medical use.

b. The results of the Zetasizer and TEM analyses revealed that the nano-Bi particles prepared by ESDM NPs were suspended in the colloid.

c. Bi-NP absorption peaks in UV–Vis occurred at 234–237 nm: The pure nano-Bi colloid prepared using the ESDM exhibited an absorption peak in the UV–Vis spectrum, which is a characteristic of nano-Bi.

d. Regarding the parameter setting of the 50% duty cycle of \( T_{\text{on}} - T_{\text{off}} \), 10–10 \( \mu \text{s} \) had the smallest size (48.18 nm) and a good zeta potential of 51.1 mV. Under the parameter of \( T_{\text{on}} = 10 \mu \text{s} \), \( T_{\text{off}} = 10 \mu \text{s} \) yielded the optimal nano-Bi colloid. With the parameter of \( T_{\text{on}} - T_{\text{off}} = 10–10 \mu \text{s} \), the nano-Bi colloid had the smallest particle size; by contrast, \( T_{\text{on}} - T_{\text{off}} = 10–300 \mu \text{s} \) had a particle size of 81.51 nm.

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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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