Properties of carbon onions produced by an arc discharge in water

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A simple method to fabricate high-quality nanoparticles including spherical carbon onions and elongated fullerene-like nanoparticles similar to nanotubes in large quantities without the use of vacuum equipment is reported. The nanoparticles are obtained in the form of floating powder on the water surface following an arc discharge between two graphite electrodes submerged in water. High-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy images confirm the presence of spherical carbon onions with diameters ranging from 4 to 36 nm. The specific surface area of the floating powder was found to be very large, 984.3 m^2/g, indicating that the material is promising for gas storage. From the surface area measurements, the mean particle diameter was calculated to be 3.7 nm. This value is close to the lower limit of the carbon onions observed in HRTEM. However, closer HRTEM observations also reveal that some carbon onions are not well crystallized. The large specific surface area can be attributed to the ''surface roughness'' induced by the defective nature of the carbon onion shells. To explain the formation mechanism of the carbon onions, a model of arc discharge in water with two quenching zones is proposed: (1) the presence of ion current conducive for elongated nanoparticles growth and (2) the absence of ion current for isotropic growth of carbon onions. Based on this model, we propose that the physical characteristics of the product can be controlled. © *2002 American Institute of Physics.*
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I. INTRODUCTION

Carbon nanomaterials have received a great deal of attention since the discovery of the C_{60} fullerene molecule[1] and the carbon nanotube.[2] C_{60} research in the early 1990s was enabled by the capability to produce to large quantities (a few milligrams) of the material using the high pressure arc discharge method first demonstrated by Krastchmer *et al.*[3] The ability to readily generate high purity carbon nanotubes has also led to a rapid expansion in exploration of its properties. Carbon nanotubes are being considered for a wide range of electronic and mechanical applications because of their extraordinary properties. However, for applications such as fuel cell electrodes and nanocomposite structural materials, large quantities (kilograms) of the material are desired. Presently, several industrial and governmental projects are underway to mass produce several kilograms of single and multiwalled carbon nanotubes in a cost-effective manner.[4] In addition to carbon nanotubes, spherical carbon onions are interesting because they are expected to have superior lubrication properties. Nevertheless, onions can only be produced in minute quantities by electron beam irradiation of amorphous carbon using a transmission electron microscope at 700 °C,[5,6] annealing nanodiamonds at 1100–1500 °C,[7] implantation of 120 keV carbon ions in sil-

ver or copper,[8] radio frequency plasma enhanced chemical vapor deposition[9] and shock wave treatment of carbon soot.[10] Recently, we have reported an economical method to produce carbon onions in bulk quantities using an arc in water.[11]

The widely used methods to fabricate carbon nanomaterials require vacuum systems to generate plasmas using an arc discharge,[3,12] laser ablation[13] or glow discharge.[14] These methods suffer in bulk production from not only the high investment and running costs of the vacuum equipment but also from low yield of the desired products. The vacuum processes also yield, in addition to the desired nanomaterials, unwanted contaminants (amorphous carbon and disordered nanoparticles) so that a time consuming and costly purification steps must be carried out. Therefore, a process that allows the generation of nanotubes or nanoonions with minimum contamination is desirable. Recently, Ishigami *et al.*[15] proposed a high yield method for multiwalled carbon nanotubes that does not require vacuum systems. In their method, an arc discharge was generated in liquid nitrogen between two carbon electrodes. Although their method is superior to conventional ones in terms of simplicity, the rapid evaporation of the liquid nitrogen poses a problem. After their report, an even more economical technique using water instead of liquid nitrogen was used to successfully produce nanotubes.[16] Working independently on a water arc, we found that high concentration nanoonions can be obtained as

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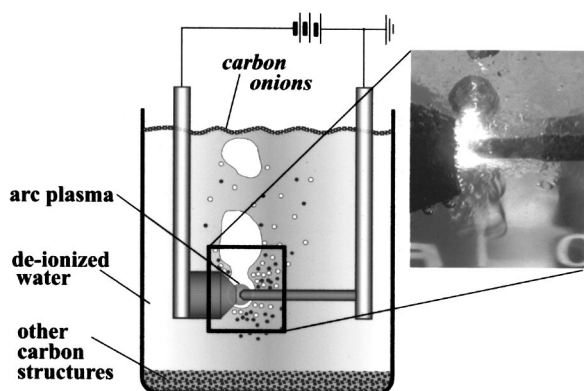[b)]Electronic mail: mc209@eng.cam.ac.uk

FIG. 1. Schematic of the apparatus used for arc discharge in water with a digital image of the discharge.

floating powder on the water surface while the rest of the product emitted is found at the base of the water.[11] This indicates that nanoonions tend to naturally segregate from the other products, yielding a higher purity product. In this article, we report further experimental details and several physical analyses of the floating powder and propose a model of the formation mechanism.

II. EXPERIMENT

In our method, a direct current (dc) arc discharge was generated in de-ionized water between two carbon electrodes. Our apparatus consisted of two graphite electrodes submerged in 2500 cm^3 of distilled water (resistance $= 1.4 M\Omega$ with a gap of 1 mm) in a Pyrex beaker. The arc discharge was initiated by contacting the 99.9% pure grounded anode (6 mm diameter) with a cathode (12 mm tip diameter) of similar purity submerged to a depth of 3 cm in distilled water. The discharge voltage and current were 16–17 V and 30 A, respectively. The arc discharge in water was found to be stable and could be run for several tens of minutes so long as a cathode–anode gap of ≈ 1 mm was maintained. The discharge in our case can be characterized as an anodic arc as the smaller anode electrode is consumed. The anode consumption rate for these conditions was approximately 117.2 mg/min whereas the cathode consumption was negligible.

A schematic of our apparatus is shown in Fig. 1. The relevant components of the apparatus are labeled. A digital image of the arc discharge in water is also shown. The bright area between the electrodes indicates the arc plasma region. The plasma can also be seen to surround the anode, indicating the direction of the plasma expansion. In addition, fine black powder emitted from the plasma ball region can also be readily observed visually. The evaporation rate of the water during arc discharge was measured to be 99 cm^3/min. This is significantly less than that for liquid nitrogen (300 cm^3/min), making this process more cost effective and economical. Similar to in the case of a conventional fullerene reactor, the carbon plasma in our case is generated by thermal evaporation of the anode. Therefore, unlike cathodic arc plasmas, here the carbon vapor is generated by thermionic rather than thermofield emission. The material collected from

the water surface was weighed without purification to obtain the production rate and was found to be 3.6 mg/min. Under the same condition, the production rate of the sediment products was found to be 15.9 mg/min.

III. RESULTS

The floating powder from the water surface was characterized by several microscopy techniques. High-resolution transmission electron microscopy (HREM) was performed on a JEOL 4000EX microscope operated at 400 kV. Unpurified material from the water surface was sprinkled onto holey carbon TEM grids for investigation. A typical HRTEM image of the material is shown in Fig. 2. Many nested onion-like particles with diameters of 30–35 nm can be seen in their agglomerated form. In addition, elongated nested particles, similar to multiwalled nanotubes can also be observed. The elongated structure and the onion are shown in greater detail in the upper and lower panels of Fig. 2, respectively. It should be noted that our more detailed study of the floating powder reported here shows two types of onion structure. The first is a well crystallized onion structure with well defined concentric shells like demonstrated in our initial report.[11] Here in Fig. 2 we show not so well crystallized onions along with elongated fullerene-like structures that are also present in the floating powder product of the water arc. It should also be mentioned that observations using a lower energy 200 kV TEM also showed the presence of onions, indicating that electron beam transformation is not the cause of the observed onions. Scanning electron microscopy (SEM) studies were performed on a Hitachi S800-FE microscope operated at 20 kV. To prepare the SEM sample, a silicon plate was directly dipped into the water to collect the raw material and was dried in an oven at 100 °C. Figures 3(a) and 3(b) show low and high magnification images taken using the SEM. It is readily seen that the spherical particles are agglomerated into clusters. The diameters of the particles estimated from Fig. 3 ranged from 4 to 36 nm. Also, in the inset of Fig. 3(a) is a "ball and bat" figure showing an elongated nanotube an spherical onion.

The floating powder was also analyzed with a differential scanning calorimeter (DSC) (Seiko Instruments, DSC-2). The measurement was performed at an elevated temperature rate of 5 K/min from room temperature to 500 °C in air. No significant endothermic and exothermic heat was detected in this temperature range except water evaporation. This indicates that the particles produced by arc discharge in water are free of volatile impurities.

The specific surface area of the floating powder was determined by nitrogen gas adsorption based on the Brunauer–Emmett–Teller (BET) adsorption isotherm using an automated surface area analyzer (Coulter, OMNISORP100). The result showed an extremely large value of 984.3 m^2/g, significantly larger than that reported for single and multiwalled carbon nanotubes (SWNTs and MWNTs).[17–19] We have tabulated the surface area values for different carbon materials in Table I. It can be seen from Table I that the floating powder produced by the water arc has a specific surface area that is approximately 3–5.5 times higher than that of other materi-
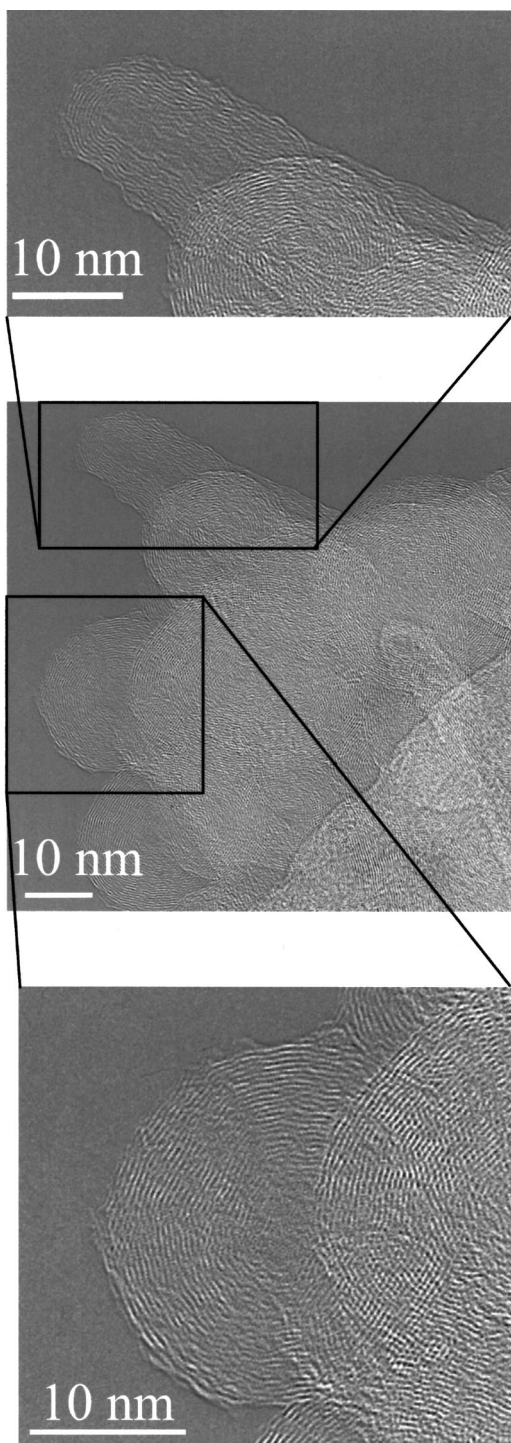
FIG. 2. HRTEM images of onions and elongated nanoparticles produced by the arc discharge in water and collected as the floating powder on top of the water surface.
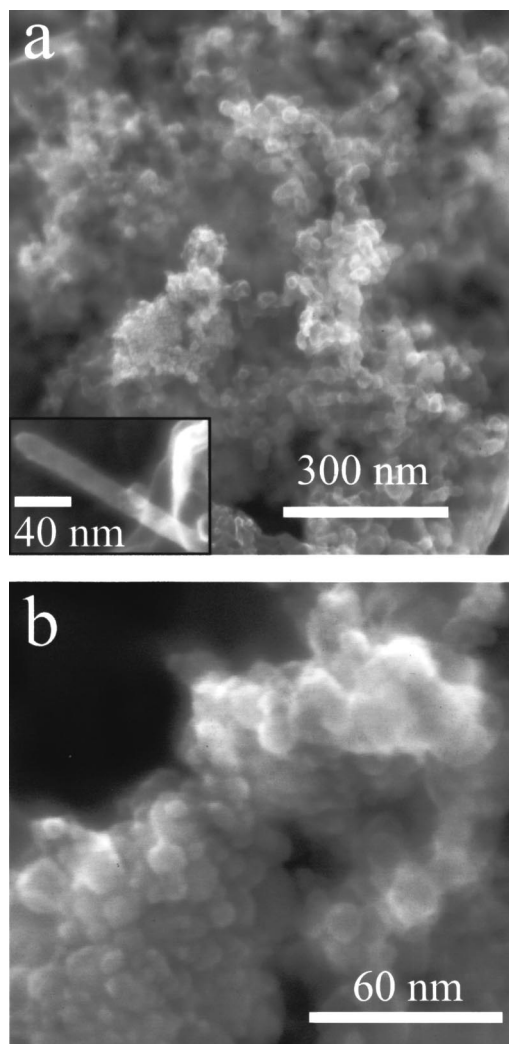

FIG. 3. SEM images of the floating powder produced by arc discharge in water. (a) Low magnification image of the floating powder. The inset shows an elongated and a spherical (ball and bat) particle. (b) High magnification SEM image of (a).

mean diameter is determined to be 3.7 nm. This value compares well to the smallest diameter onion we have measured using microscopy. The diameter value determined from adsorption is calculated under an assumption that the adsorption of nitrogen gas molecules occurs on the apparent surface area of the spherical particles. However, the real surface of the poorly crystallized onions is ''rough'' due to structural defects in the shells, as observed in the HRTEM image. This ''surface roughness'' increases the overall surface area of the particle. Since r_m is inversely proportional to S as in Eq (1),

als. The mean particle diameter can be derived from a simple correlation, assuming that the nanoparticles are uniformly spherical, according to

$$S = \frac{4\pi r_m^2}{4\rho\pi r_m^3/3},\qquad(1)$$

where S, r_m and ρ are the specific surface area, mean particle radius and particle density, respectively. If 984.3 m^2/g and a measured density of 1.64 g/cm^3 are used for S and ρ, the

TABLE I. Specific surface area comparisons of various types of carbon materials.

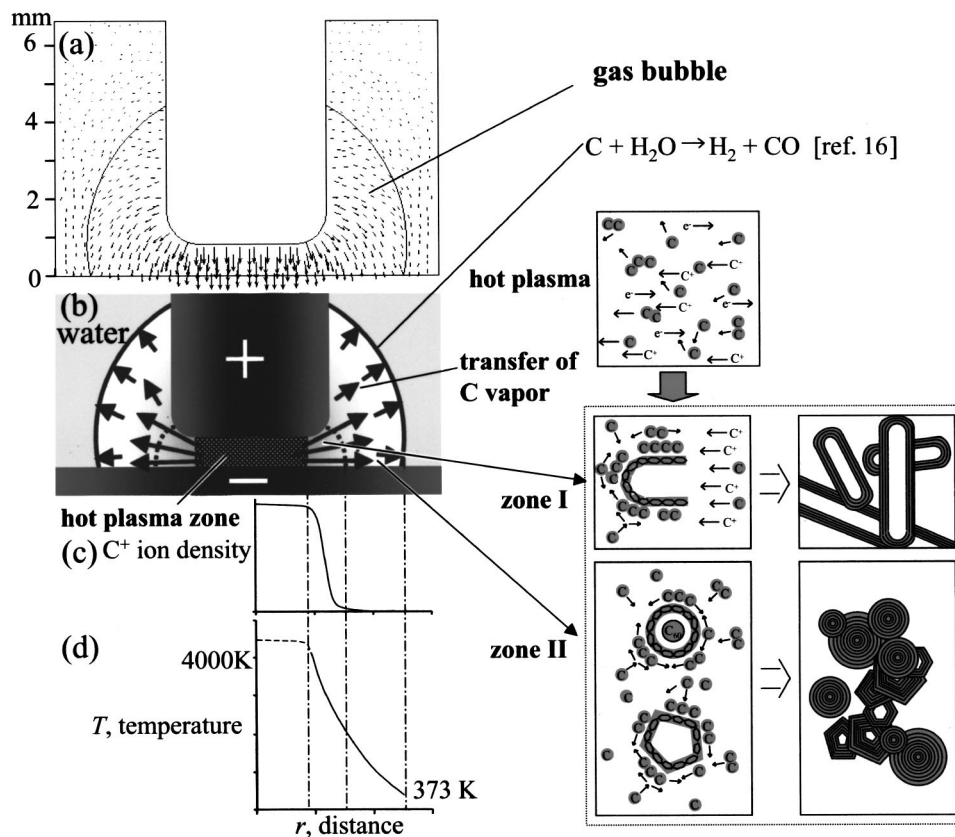| Reference	This work	Hernadi *et al.* (Ref. 17)	Inoue *et al.* (Ref. 18)	Ye *et al.* (Ref. 19)
Sample	Carbon onion and MWNT	SWNT and MWNT	MWNT	Bundles of SWNTs
Specific surface area	984 m^2/g	312 m^2/g	178 m^2/g	285 m^2/g

FIG. 4. Proposed formation mechanism of onions in a water arc. (a) Relative electric field strength, shown by arrows, between a rod anode (17 V) and a flat cathode (ground) in a gas bubble surrounded by water. (b) Direction of thermal expansion from plasma to the water interface. (c) Qualitative ion density distribution. (d) Temperature gradient obtained from Eq. (3) assuming q_c, Q_R, and $dT/dt = 0$. The formation of elongated nanoparticles in zone (I) and onions in zone (II) is also shown schematically.

adsorption enhancement can result in a smaller calculated mean particle diameter compared to the actual particle diameter.

IV. MODEL FOR THE WATER ARC

A. Gas bubble formation

Two types of structures, carbon onions and elongated structures, were obtained in the water arc used in this study. Based on this result, we propose an initial model to explain the production mechanism of the two types of structures. Figure 4 describes our model of the reaction zone. There is a plasma zone between electrodes surrounded by a gas bubble due to vaporization of the surrounding liquid as the arc temperature is estimated to be around 4000 K (the sublimation temperature of carbon). In fact, this gas bubble can be regarded as a microwater-cooling reaction chamber that enables rapid quenching of the arc discharge. The main gas components are CO and H_2 produced by the reaction of C atomic vapor and H_2O at the gas–liquid interface as[16]

$$C + H_2O \rightarrow CO + H_2. \tag{2}$$

To measure the gas bubble formation rate, the vapor was trapped in a collection Pyrex dish placed above the discharge beaker. The trapped vapor was allowed to condense but no condensation occurred, indicating that gas bubbles did not comprise water vapor. From Eq. (2), the stoichiometric mole fraction of CO is 50%. From the measured volumetric formation rate and this mole fraction value, we estimate the CO production rate to be 0.01 mol/min. As stated above, the corresponding production rates of the floating powder and

the sediment products are 3.6 and 15.9 mg/min, respectively, and the anode consumption rate is 117.2 mg/min. This indicates that approximately 83% of C was lost from the reaction system at a rate of 0.008 mol/min during arc discharge. This loss of carbon is attributed to the formation of CO. The discrepancy between the two values, 0.01 and 0.008 mol/min, may be caused by overestimation of the CO gas production rate due to other gas production by electrolysis. For higher accuracy in the mass balance, more elaborate gas analyses are necessary and they will be reported in the future. To produce CO at the gas–liquid interface, C atomic vapor must be present at this interface. It is therefore reasonable to expect that C atomic vapor exists wholly in the bubble surrounding the discharge.

B. Nanoparticle formation

The extremely sharp temperature gradient in this gas bubble from the hot plasma region to the gas–water interface is essential to cause rapid solidification of the vaporized carbon. The temperature at the hot plasma is estimated to be approximately 4000 K (the melting and boiling points of graphite are 3823 and 4203 K, respectively), while the temperature at the gas–water interface is the boiling point of water, 373 K. To estimate the approximate temperature gradient, we simply assume that the heat transfer occurs in a radial direction from the center of the plasma. Then the equation of heat balance can be expressed as

$$-\frac{d}{dr}(4\pi r^2 q_k) - \frac{d}{dr}(4\pi r^2 q_c) + 4\pi r^2 Q_R = 4\pi r^2 \rho C_\rho \frac{dT}{dt},$$
$$\tag{3}$$

where r, q_k, q_c, Q_R, ρ, C_ρ, T, and t are the distance from the arc center, heat transfer rate by thermal conductivity, heat transfer rate by convection, reaction heat, density of gas, specific heat of gas, temperature, and time, respectively. To simplify the calculation, q_c, Q_R, and dT/dt are assumed to be zero. If q_k is expressed by Fourier's law of thermal conductivity with a proportional constant k as $q_k = -k dT/dr$ with boundary conditions, $T = 4000$ K at $r = 2$ mm and $T = 373$ K at $r = 5$ mm, the average temperature gradient in the gas bubble is estimated to be 1209 K/mm. It is noted that this simple calculation is only to give a rough approximation of the temperature gradient, and we do not intend to analyze it in detail at this stage. In fact, q_c, Q_R, and dT/dt should be significant in the real system and all parameters must be highly space and time dependent. Also, the expansion rate of C vapor from the hot plasma zone to the cold region can be estimated by a simple approximation. If all the graphite consumed in the anode is assumed to be converted to C vapor, the volumetric C vapor expansion rate is calculated to be 5.30×10^{-5} m^3/s at 4000 K if ideal gas conditions with 1 atm pressure are assumed. If the hot plasma zone between electrodes with a 1 mm gap is assumed as a cylindrical zone with a 2 mm diameter, the expansion velocity can be obtained by dividing this volumetric expansion rate by the surface area of this assumed hot plasma zone, resulting in a velocity of 4.2 m/s. This high expansion velocity enables C vapor to transfer into the cold zone of the bubble readily. The cold zone can be categorized into two parts: (I) that where the quenching of C vapor occurs within the ion current adjacent to the hot plasma zone and (II) that without the ion current outside zone (I). Although we have not obtained the distribution of the ion current density in our system at present, we provide a map of the simulated electric field in a configuration that is close to our electrode shapes in Fig. 4(a). This simulation does not include the effect of the C vapor expansion. In zone (I), elongated structures such as nanotubes are expected to be produced because of their epitaxial growth in the C ion current. On the other hand, in zone II, three-dimensional (3D) isotropic growth of nanoparticles is preferable because of the absence of an axis of symmetry. In this case, onions may be produced.

C. Floatation of carbon nanoparticles

Subsequent to the formation of onions, they cluster into larger van der Waals crystals. We find that these clusters readily float to the top of the water surface. We find that the floating powder remains separated at the surface of the water even after vigorous dispersion through ultrasonication. In order to investigate the mechanism responsible for floatation of the onion powder, we have attempted to measure the actual density of the powder. To calculate the true density, the true volume of the particles was estimated by soaking the particles in acetone to fill the void between particles. It resulted in a mean density of particles of 1.64 g/cm^3. It is noteworthy that it is higher than water although it is lower than graphite 2.25 g/cm^3. The density measured for our sample is comparable to that of well known caged nanoparticles such as C_{60} and nanotubes whose densities are 1.72 and 1.2–2.0 g/cm^3,

respectively.[20] Hence, floatation of the particles cannot be ascribed to their weight but more likely to their hydrophobic surface. In fact, the particles can be dispersed well in organic solvents such as acetone, toluene and *n*-hexane. In our arc-in-water system, onions are naturally agglomerated and float, being separated from the other large products that settle to the bottom of the beaker.

V. ROUTES TO CONTROL NANOPARTICLE CHARACTER

In order to maximize the fabrication rate of nanomaterials such as onions and nanotubes, several important aspects of the reaction should be optimized such as the current density, gas pressure, concentration of emitted species and temperature gradient in the reaction zone. It must be emphasized that not only the production rate but also the selectivity of onions to nanotubes can be controlled because the formation depends on the directionality at the particle formation zone caused by the ion current (see Fig. 4). One possible way to achieve this is to use a different electrode shape. If a narrow anode is used to decrease the relative area of the ion current zone compared to the isotropic quenching zone, the production of onions may increase. A study on the influence of the electrode shape is currently underway and the results will be reported elsewhere.

VI. CONCLUSIONS

In summary, we have successfully produced carbon onions in large quantities by an arc discharge in water. The arc discharge in water allows an alternative to conventional vacuum processes for fabricating onions in large quantity. HRTEM and SEM analyses show onions with diameters ranging from 4 to 36 nm in the floating powder. The measured specific surface area of the particles was found to be extremely high, 984.3 m^2/g, indicating that the particles produced by this method are promising for gas storage. The mean particle diameter was calculated to be 3.7 nm from the specific surface area. The discrepancy between the particle size estimated by microscopic analysis and the specific surface area is ascribed to surface roughness from defective shells in the onions. Also it was found that the surface of the particles is hydrophobic because the particles float on water in spite of their density, 1.64 g/cm^3, being higher than that of water. To explain the production of onions and nanotubes a model of the arc-in-water system in which there are two quenching zones was proposed. Based on this model, we propose that the physical characteristics of the nanoparticle products from the water-arc can be controlled to improve large quantity production.

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