Fe Nanoparticle Production by an Atmospheric Cold Plasma Jet *

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We present a simple method of producing Fe nanoparticles based on the dissociation of ferrocene by a simple single electrode atmospheric cold argon plasma jet. The system is driven by a sinusoidal ac-supply with a peak voltage of 0–30 kV and a frequency of 50 kHz. The average size of iron nanoparticles analyzed by scanning electron microscopy is about 10–30 nm for the gas phase samples, and 30–100 nm for the liquid phase samples. The method should be competitive due to its simplicity and low cost.

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Iron nanoparticles have attracted considerable interest because of their potential applications in water purification, special magnetic properties in micro- and nanoelectronics, and so on.[1–4] However, traditional processes usually need a long time or high cost. Dielectric barrier discharges (DBD) may be a good method to produce iron nanoparticles, but the system needs to be heated. In this Letter, we describe a system designed for producing iron nanoparticles by using an atmospheric single electrode cold argon plasma jet.

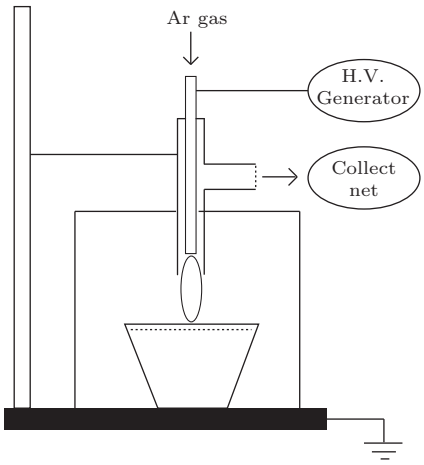


Fig. 1. Schematic of the experimental setup.

A schematic diagram of the experimental device is shown in Fig. 1. In this system a stainless tube is the powered electrode, of which the inner and outer diameters are 2 mm and 2.5 mm, respectively. A 30-mL corundum crucible is added with a mixture of 15 mL 5 ppm ferrocene/ethanol and 15 mL deionized water solution. Ar (99.999%) is the working gas. The stainless tube is connected to an ac-voltage source with a frequency of 50 kHz, a peak voltage of 0–30 kV and a power of 500 W. Voltage and current measurements are performed by using a high-voltage probe P6015A and a Pearson current coil (Pearson 4100) via a digital oscilloscope TDS220 (100 MHz). Gas phase particles are collected by a grounded 300 mesh stainless net. Morphology, primary particle size and energy dispersive x-ray spectra (EDX) of the iron particles are determined using a scanning electron microscope (SEM, JSM-6700F). The discharge images are taken by a digital camera (Cannon PowerShotA720). The optical emission spectrum of the plasma is obtained by a spectrometer (Acton 2500i). The position of the optical fiber is located at 1 cm from the quartz tube.

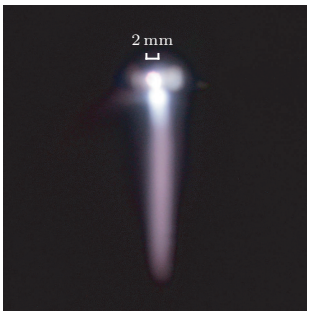


Fig. 2. Discharge photographs with peak value of applied voltage 5 kV, distance of 22 mm, the argon flow rate $Q_{\text{argon}} = 0.3$ L/min.

The energy for consecutive splitting of two Cp radicals from ferrocene requires about 4 eV, and the free electrons in the plasma jet may gain temperatures of several eV from the electric field, sufficient for ionization and initiating the dissociation of ferrocene.[3–6] According to the principle of plasma-enhanced deposition the plasma volume has a space charge controlled by its non-zero potential relative to ground, so charged particles in the jet were accelerated toward the grounded grid and are collected.[4]

A glow-like discharge mode will be sustained when the voltage varies from 3 to 5 kV and the distance between the HV electrode and the mixture solution surface is kept in the range of 8–30 mm. The maximum

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flow rate of argon is 0.5 L/min. In this experiment we take the single electrode as the jet generator, which is not sensitive to discharge distance d as DBD.[2,4]

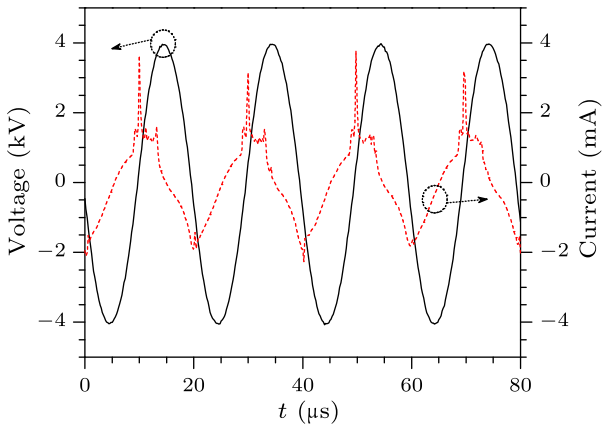


Fig. 3. Applied voltage V (black line), and current I (red line) vs time.

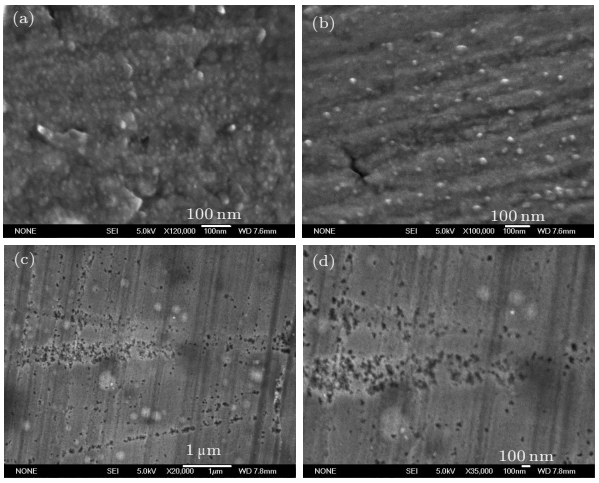


Fig. 4. SEM micrograph of the produced nanoparticles: (a) and (b) the gas phase samples, (c) and (d) the liquid samples, when $U = 5$ kV, $d = 22$ mm, and the argon flow rate $Q_{\rm argon} = 0.3$ L/min.

A homogeneous plasma is generated in the end of the stainless steel tube, as shown in Fig. 2. The plume length and discharge characteristics (glow-like or filamentary mode) may be modulated by the flow rate of argon and the voltage. The transition from corona to glow-like is easy due to the metastable state energy level of argon, so it is difficult to sustain a stable corona discharge for a long time. The discharge mode in Fig. 2 should be a glow-like one according to the voltage-current characteristic shown in Fig. 3. The solution temperature measured by a mercury thermometer is about 300 K after 30 min running (room temperature about 283–293 K). The Ar jet is of low temperature around 533 K by analyzing the spectrum.[7]

No Fe nanoparticles can be found without ferrocene, which proves that Fe nanoparticles are produced from the dissociation of ferrocene by plasma, not the ablation of the electrode. Gas phase Fe samples come from the particles that move with Ar gas flow and are deposited on the net, and liquid ones come from others that are dissolved in water. The diameters of particles produced by glow-like mode for gas phase samples shown in Figs. 4(a) and 4(b) are about 10–30 nm and 30–100 nm for the liquid phase samples of Figs. 4(c) and 4(d) due to coagulation in water. The big darker areas inside the liquid samples indicate that smaller diameter pure iron particles have a high contrast to white ferrocene particles. Some samples may be pure iron in the inert atmosphere circumstance, and are oxidized when removed from the test set-up and exposed to air. The gas and liquid phase particle diameters of filamentary discharge mode are about 50–70 nm and 80–200 nm, respectively. The diameter difference of glow-like and filamentary modes for the electron concentration and temperature of filamentary mode is higher than a glow-like one.[5] Figure 5 is the EDX-spectrum of the micrograph shown in Fig. 4(a). The Cr signal in the EDX spectra is due to background radiation hitting the stainless steel sample holder grid. The small carbon and oxygen peak could point to some ferrocene evaporating from the solution by plasma jet. The presence of the relatively high iron peak indicates that the particles consist of iron.

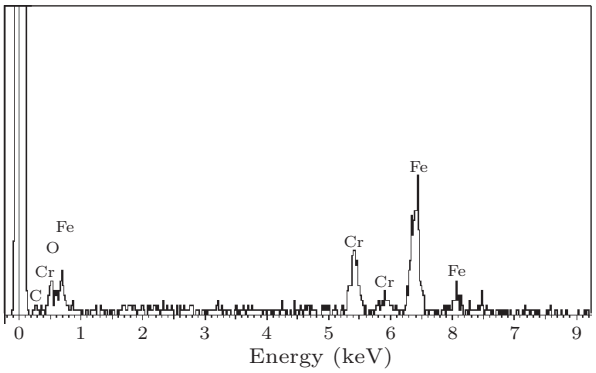


Fig. 5. EDX spectrum of the sample displayed in Fig. 4(a).

In conclusion, iron nanoparticles are successfully produced from the dissociation of ferrocene using a single electrode atmospheric pressure argon cold plasma jet. The particles are characterized by scanning electron microscopy. The system is not heated. The results prove that this is a hopeful method for metal nanoparticle synthesis due to its simplicity and low cost.

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