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Controlled formation of metallic nanoballs during plasma electrolysis

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Formation of spherical nanoparticles (hereafter “nanoballs”) in a gas/liquid mixed dual phase system during plasma electrolysis is reported. A gas/vapor sheath is formed at the electrode/electrolyte interface when the applied voltage is high enough to induce discharge plasma. Through this nonequilibrium process, the authors have produced Ni, Ti, Ag, and Au metallic nanoballs from the cathode mother materials with a certain size controllability. The electrode surface is partially melted by the local current concentration induced by electrothermal instability followed by an immediate cooldown, yielding nanoballs without contamination from electrolyte. © 2007 American Institute of Physics. [DOI: 10.1063/1.2760042]

Although material/chemical processes are usually conducted in the gas or liquid monophase, we may expect advantages in the gas/liquid mixed dual phase, such as in liquid discharge experiments. Because of the seminal work on discharge electrolysis,\textsuperscript{1–4} it has been widely recognized as a potential method for chemical and material engineering. A salient feature of this process is the non-Faradaic reactions\textsuperscript{1–3,5,6} ranging from polymerization\textsuperscript{7,8} to the formation of amino acids\textsuperscript{9,10} and degradation of harmful substances.\textsuperscript{11,12} The amount of product is generated over Faraday’s law, which strictly predicts that the amount is exactly equal to the amount of current, mainly through anodic plasma electrolysis. Theoretical models to explain non-Faradaic reactions have been proposed.\textsuperscript{1–3,6,8} Recently, non-Faradaic hydrogen evolution has been confirmed as the direct pyrolytic decomposition of water molecules to apply it for the hydrogen economy.\textsuperscript{13} From the viewpoint of material engineering, an oxide coating method has been developed under the anodic plasma electrolysis condition as a more inexpensive, faster, and easier method as compared with previous procedures.\textsuperscript{14} Furthermore, the method has a potential to enrich a certain isotope.\textsuperscript{15,16}

In this letter, we report metallic nanoballs formation at the electrode surface by plasma electrolysis with a relatively low cell voltage of less than 160 V. The experimental setup simply consisted of a glass cell to induce glow discharge in an electrolytic solution under atmosphere pressure without a vacuum chamber or pumps. The discharge electrode was not the anode, but cathode, which could discharge at a lower cell voltage (~140 V) than the anode.\textsuperscript{6,14} Several metallic wires, viz. Ni, Ti, Ag, and Au, were electrolyzed in a 0.1 mol/dm$^3$ K$_2$CO$_3$ solution. The counter electrode was a Pt mesh whose surface area was much larger than that of the working electrode in order to concentrate the voltage drop at the cathode/electrolyte interface.

It is shown in Fig. 1(a) that glow discharge with light emission occurred only near the cathode surface area where excited atoms drop to a stable level by emitting unique energy photons as visible light. Figure 1(b) then shows the current-voltage relationship during electrolysis. We defined regions 4 and 5 as the plasma regions: (1) conventional region, (2) breakdown point, (3) transitional region, (4) partial plasma region, and (5) full plasma region. Region 1 is the standard electrolysis region with normal electrode reactions where current increases according to Ohmic law. Since the IR loss was concentrated at the cathode/electrolyte interface, the temperature near the cathode increased rapidly and generated a vapor sheath with hydrogen when the cathode temperature exceeded the boiling point of the electrolyte (regions 2 and 3). The current cannot increase any more thereafter and thus decreases because the electrode and elec-

FIG. 1. (Color online) Typical current-voltage relation curve and schematic diagram before and during plasma electrolysis. (a) Pictures of Ni electrode with a diameter of 1.5 mm during plasma electrolysis. (b) Current-voltage relation during plasma electrolysis with Ni electrode. (c) A schematic diagram of plasma electrolysis; a thin gas/vapor layer is formed at the metal/solution interface, where a high applied voltage induces the glow discharge.
tretary for atom species, the color of the emission level by emitting photons. Since the excitation energy is high, atoms drop down immediately to a stable energy level after impact a neutral atom to dissolve and excite it. The energy of the electron is the glow discharge. Electrons in the plasma electrolysis process are constant at a low level during the plasma electrolysis process, which is predicted as 80–200 V.14 Since the current keeps almost 120–160 V in each case, while this voltage is theoretically critical voltage over the full plasma region, which is almost constant. The electrolyte do not touch each other through the unstable region 4. If the cell voltage is sufficiently high, a glow discharge with intense light emission starts in the gas film and the light emission area expands to the whole area of the electrode in region 5.

This plasma electrolytic process is schematically illustrated in Fig. 1c to show a thin gas/vapor layer formed at the metal/solution interface. The generation of the vapor/gas sheath is a key factor because the ignition condition is determined by the thickness of a sheath and the gas pressure, namely, Paschen’s law.17,18 The electrochemical conditions, i.e., the type and surface area of the electrode, and the type and concentration of the electrolyte, do not influence the critical voltage over the full plasma region, which is almost 120–160 V in each case, while this voltage is theoretically predicted as 80–200 V.14 Since the current keeps almost constant at a low level during the plasma electrolysis process, this is classified as a glow discharge. Electrons in the plasma layer are accelerated under a high electric field and impact a neutral atom to dissolve and excite it. The electronically excited atoms then, drop down immediately to a stable energy level by emitting photons. Since the excitation energies are characteristic for atom species, the color of the emitted light depends on the sort of electrodes and electrolytes. However, the Pt anode does not change from the normal anode reaction.

After plasma electrolysis, the electrode surfaces were observed by a scanning electron microscope (SEM) (JEOL JSM-6500F). Nanoballs with diameters ranging from 10 nm to 1 μm were formed where the discharge covers, as shown in Figs. 2(a)–2(d). (a) Ni, (b) Ti, (c) Ag, and (d) Au electrode surfaces. These particles are distributed evenly over the entire cathode surface without a deviation in number and diameter, as are the discharge characteristics. Some nanoballs were scattered in the solution during the discharge process and precipitated at the bottom of the cell. After rinsed with purified water, they were collected and deposited on a Cu microgrid with a diameter of 3 mm for transmission electron microscopy (TEM) (JEOL JEM-2010F) observation. TEM images and electron diffraction patterns of corresponding metals are shown in Figs. 2(e)–2(h) and Figs. 2(i)–2(l), respectively.

Some particles’ surfaces were oxidized through the nanoball formation process due to the high temperature environment or the after treatment exposure to the air, especially in the case of Ti particles. Ti particles have TiO2 surface layers, whose composition is determined by energy dispersive x-ray analysis. The electron diffraction patterns are shown on the left side of Figs. 2(i)–2(l), while the corresponding numerical simulation ones with an assumption of powder samples were displayed on the right. Experimental electron diffraction patterns of Ni, Ag, and Au agree with those of the monometals, while that of TiO2 corresponds to rutile structure. The x-ray diffraction supports the previous results.

Almost all particles greater than 10 nm in diameter are perfectly spherical, which minimizes the total surface area. For the sake of universality, we can apply the above process to four different metal electrodes, namely, Ni, Ti, Ag, and Au, as shown in Figs. 2(a)–2(b). The process used was exactly the same in all cases. The size distribution obtained was different in each case. At present, we believe that the electrode material plays an important role in determining the particle formation processes and diameter distribution.
The TEM observation reveals lattice defects of dislocations and grain boundaries or twins inside the even smaller particles. These results indicate that the electrode surface was locally heated and momentarily exceeded the melting point, and the molten metal yielded to a spherical shape due to surface tension. The metal immediately cools down to the electrode surface for four different voltage conditions in the case of Ni electrodes. The error bars represent the standard deviation.

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