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Pulsed-laser Irradiation of Carbonaceous Materials in $AgNO_3$ Solution and Its Application to Preparing Silver-activated Carbon Electrodes

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We irradiated a glassy carbon electrode in $AgNO_3$ solution using a 532 nm pulsed laser to prepare a silver-activated electrode. The UV–visible spectrum of the solution evidenced the production of Ag particles, and transmission electron microscopic images showed the formation of carbon–silver composite on the solid carbon surface. The reduction potential of O_2 measured with the prepared electrode by differential pulse voltammetry shifted positively by 0.05 V in $NaClO_4$ solution, which indicated that the present irradiation procedure effectively activated the glassy carbon electrode.

We reported previously[1] that when carbon particles suspended in $AgNO_3$ solution were irradiated by pulsed laser at 532 nm, a characteristic plasmon absorption peak ascribed to the formation of Ag nanoparticles appeared in the solution and that transmission electron microscopic (TEM) images of the recovered solid materials showed the coexistence of entangled long fibrils and/or thin shells of carbon with Ag nanoparticles. Thus the pulsed laser irradiation as mentioned above may be employed for preparing silver-activated carbonaceous materials.

Silver metals and nanoparticles combined with carbonaceous materials are thought to be usable for constructing a potential electrocatalytic system for O_2 reduction reaction (ORR) necessary for fuel cells, in particular relevant to alkaline fuel cells,[2] and also for chlor-alkali electrolysis.[3,4] The catalytic activity of Ag is well established in alkaline solutions,[2] although not so much studied in lower pH regions. In spite of many attempts, Pt remains as the catalyst of choice for acid-based fuel cells.

The present authors feel that the above-mentioned laser irradiation method is applicable to preparing O_2 gas-diffusion cathodes for fuel cells and electrolysis cell. This is a new extension of laser technology. So far very few laser irradiation techniques have been applied to preparing electrodes, except for studies concerning the morphology change of the electrode surface by laser irradiation.[5] The laser irradiation procedure is simple and may also be less subject to contamination than other fabrication procedures. Since improved cathode performance in alkali is often attributed to a lower degree of specific anion adsorption, solutions containing the weakly adsorbing ClO_4^- anion could have properties similar to alkaline solutions for ORR. Thus in the present study, we tried to prepare a model electrode activated by carbon–silver composite (or Ag particles entangled with carbon fibrils) on the electrode surface by irradiating a glassy carbon electrode (GCE) in $AgNO_3$ solution. Then we investigated its electrochemical behavior by differential pulse voltammetry (DPV) in $NaClO_4$ solution under O_2 atmosphere.

In the irradiation procedure, a GCE (outer diameter 6 mm, and inner diameter 3 mm: obtained commercially from BAS Inc.) was fixed at the bottom of a vertically settled acrylic tube of ca. 1.5 cm inner diameter by using a rubber plug, keeping the upper end surface of the electrode parallel to the bottom. Then typically, 3 mL of 0.01 mol dm^{-3} $AgNO_3$ solution was poured into the tube. The 532 nm pulsed laser light from a Nd:YAG laser (Spectra-Physics, GCR-170; repetition rate, 10 Hz; pulse length, nominally 7 ns) with a beam cross section of 0.5 cm^2 was introduced into the solution along the downward direction and irradiated the upper end surface of the GCE immersed in the $AgNO_3$ solution.

With the irradiation progress, the $AgNO_3$ solution somewhat darkened in parallel with a solution color change to brown. The black solid curve of Figure 1 of the UV–visible spectrum (JASCO, V-550) of the irradiated solution shows the Ag particle plasmon peak centered around 424 nm. The relatively long tail extended up to at least 900 nm indicates the presence of suspended carbon particles. Thus the silver ion is thought to have been reduced to yield Ag nanoparticles under the irradiation in the presence of carbon surface and suspended carbon fragments, as discussed previously.[1] The morphology change of the surface of the GCE and the fragmentation of some carbonaceous material from the surface under the laser irradiation are fully expected, considering our previous results[6] dealing with the irradiation of suspended carbon particles up to the size of 5 µm. Formation of carbon onions from the suspended carbon black by millisecond pulsed laser irradiation was also reported very recently by Hu et al.[7]

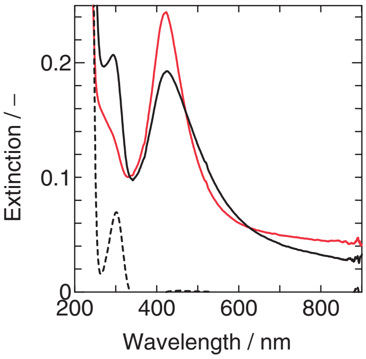

Figure 1. UV–visible spectrum of the $AgNO_3$ solution used for the laser irradiation in the presence of GCE: 0.01 mol dm^{-3} $AgNO_3$ solution was used for the laser irradiation under 30 (black dotted line) and 60 mJ pulse^{-1} (black solid line) for 5 min. The red line is the spectrum obtained from a 5 µm diameter GCP suspension (2×10^{-3} mol dm^{-3} concentration based on atomic carbon) in 0.01 mol dm^{-3} $AgNO_3$ solution after the irradiation under 100 mJ pulse^{-1} for 10 min.

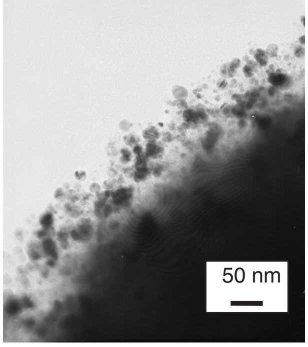

Figure 2. TEM image of a 5 µm diameter GCP recovered from the GCP suspension (2×10^{-3} mol dm^{-3} concentration based on atomic carbon) after the irradiation under 100 mJ pulse^{-1} in 2×10^{-3} mol dm^{-3} $AgNO_3$ solution for 10 min.

As a comparison, the spectrum obtained from irradiation of a 5 µm diameter glassy carbon particle (GCP, Tokai Carbon Co., Ltd.) suspension in 0.01 mol dm^{-3} $AgNO_3$ solution is also shown by the red curve in Figure 1. Although the peak width is somewhat narrow, the total appearance is very similar and the peak maximum is around 423 nm.

In order to confine the formation of carbon–silver composite on the electrode surface, we measured the TEM image of an irradiated GCP in place of the electrode rod. For the latter, it was difficult to prepare a good TEM sample. The TEM image (measured with a JEOL, JEM-2010F microscope, with an acceleration voltage of 200 kV) obtained for the sample from the irradiation of a carbon particle suspension is shown in Figure 2. The sample was prepared under the same condition as adopted for the measurement of the UV–visible spectrum in Figure 1. The morphology change of the surface and the entangled structure are seen. The diameter of the particulate matter on the carbon surface is 17 ± 7 nm (1σ), which is in fair agreement with the estimated Ag particle size of 37 nm from the peak maximum of the solution spectrum in Figure 1, employing the relationship between the peak maximum and Ag particle diameter suggested by Evanoff and Chumanov.[8] The presence of metallic silver was evidenced by the selected area electron diffraction patterns as shown in Figure 3 where larger particles are also seen. Considering from the similar UV–visible spectra between the GCE and the GCP irradiation shown in Figure 1, it is certain that a kind of carbon–silver composite (or Ag particles entangled with carbon fibrils) is produced also on the GCE surface.

Concerning the mechanism, the laser irradiation on the GCE produces a carbon particle suspension. A certain kind of carbon–silver composite is produced through the reduction by the irradiated carbon suspension, which then deposits on the solid surface. The activated carbon surface under irradiation may also reduce the silver ions and trap them on the surface.

DPV was conducted on the prepared electrode as the working electrode with an electrochemical analyzer (BAS Inc., ALS/CHI model 430A) using 0.1 mol dm^{-3} $NaClO_4$ solution as the electrolyte, Pt wire as the auxiliary electrode and Ag|AgCl|3.0 mol dm^{-3} NaCl (0.209 V vs. normal hydrogen electrode (NHE)) as the reference electrode in the presence and absence of O_2 in the atmosphere. The prepared electrode with the laser irradiation in 0.01 mol dm^{-3} $AgNO_3$ solution was rinsed several times with pure water before setting it in the measurement cell. The atmosphere in the cell was controlled by bubbling or flowing the required gas into/over the cell electrolyte. For comparison, the electrochemical behavior was also measured for a GCE without any irradiation, one prepared with irradiation in pure water, and a Ag electrode (outer diameter 6 mm, and inner diameter 1.6 mm: obtained commercially from BAS Inc.).

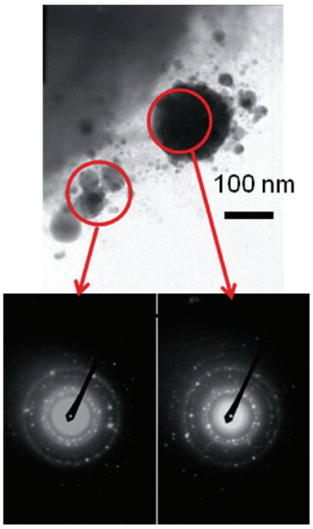

Figure 3. TEM image with the selected area electron diffraction patterns of a 5 µm diameter GCP recovered from the GCP suspension (2×10^{-2} mol dm^{-3} concentration based on atomic carbon) after the irradiation under 100 mJ pulse^{-1} in 2×10^{-3} mol dm^{-3} $AgNO_3$ solution for 10 min.

Figure 4 shows the results for the above 4 electrodes. Figure 4a is measured under Ar; Figure 4b, under air; and Figure 4c, under 100% O_2. The peaks located in the potential region of 0 to −0.5 V (vs Ag|AgCl) should be related to ORR. Indeed, the above-mentioned experimental peaks do not appear in the absence of O_2. The half-wave potential $E_{1/2}$ against the Ag|AgCl electrode under air for the nonirradiated GCE is estimated to be −0.28 V, for irradiation in pure water, −0.29 V, for irradiation in $AgNO_3$ solution, −0.23 V, and for Ag electrode, −0.15 V, respectively. The value of $E_{1/2}$ is estimated from Figure 4b according to the relation,

$$E_{1/2} = E_p - \Delta E_{pulse}/2 \qquad (1)$$

where E_p is the experimental peak potential of the DPV spectrum, and ΔE_{pulse} is the pulse step width for the measurement (in the present experiment, 0.05 V). The electric current for the electrode irradiated in pure water is considerably smaller than the value for nonirradiated GCE. The current seems to be recovered in the case of the irradiation in $AgNO_3$ solution. The above-mentioned variation in the current may be attributed to some change in the surface structure and/or area due to laser irradiation, but the quantitative analysis is a future problem.

The standard equilibrium potential for the reaction

$$O_2 + e^- = O_2{}^- \qquad (2)$$

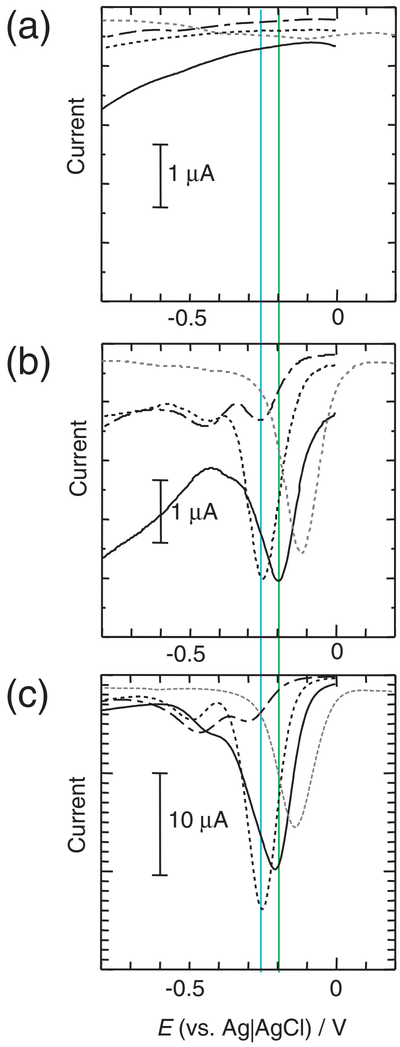

Figure 4. DPV curves of a GCE without any irradiation (dotted line), one prepared with irradiation in pure water (dashed line), one prepared with irradiation in 0.01 mol dm^{-3} $AgNO_3$ solution (bold line) and a Ag electrode (gray-colored dotted line) under Ar (a), air (b), and 100% O_2 (c) atmosphere: the laser irradiation was conducted at 60 mJ pulse^{-1} for 5 min. The two vertical lines connect the same electrode potential values through the three figures.

is reported to be −0.31 V vs. NHE(pH 0).[9,10] The corresponding ΔG is 30 kJ mol^{-1}. In general, ORR is a multielectron reaction including a number of elementary steps. The final products in acid solutions are H_2O and/or H_2O_2 through the overall reactions as

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (3)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (4)$$

Although the detailed reaction mechanism is not agreed, there is a general consensus that the addition of the first electron to O_2 via reaction (2) is the initial important step for the overall reaction. When the electrode adsorbs $O_2{}^-$, the corresponding potential should change by the amount $\Delta G(O_{2,add}{}^-)/F$, where the numerator is Gibbs adsorption free energy of $O_{2,add}{}^-$ and F is Faraday constant. Because the bonding of the Ag–$O_{2,add}{}^-$ is expected to be relatively weak, a relatively small anodic potential shift is expected.

The reaction (2) is considered to be relevant also to the measured electrode potentials in the present study. Although the detailed reaction progress is not certain, the important finding is the anodic shift of the peak for the case of the GCE irradiated in $AgNO_3$ solution, compared to the case of irradiation in pure water. This shows that there is an interaction between the formed carbon–silver composite and the reaction (2), although the electrode potential of the prepared electrode does not reach the potential of the Ag electrode. Thus the present irradiation procedure should be indeed useful to activating GCE, though detailed study on the relationship between the fabrication procedure of the electrode and the degree of the activation is remained for the future.

In conclusion, we propose the present laser irradiation method so as to study the catalytic activity of carbon–metal composite for fuel cell and electrolysis cell applications and also to prepare practical electrode materials. It is important to notice that the reduction of metal ions by irradiating the solution in the presence of electrode materials is not limited to silver alone.

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