

Electronic supplementary Information

Enhancement of Electrocatalytic Activity of Gold Nanoparticles by Sonochemical Treatment

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1. Theoretical Calculations

To obtain structural information on gold nanoparticles (NPs) at different temperatures, we performed classical Molecular Dynamics simulations. The embedded atom method potential [1] was employed to model the Au–Au atomic interactions. Nose-Hoover thermostat [2], consistent with the canonical ensemble, was applied at each time step. The initial structure of the gold NP had cuboctahedral (C_h) symmetry, and was ~ 3 nm in diameter. To avoid dependence on the heating rate, we increased the temperature step-wisely with 200 K per step from 300 K to 1100 K. For each one of the temperature steps, as shown in Figure S1, the thermally equilibrated structure was obtained by performing 10^4 iterations (1 fs per iteration). The initial structure displays the ideal C_h symmetry with well-defined vertices, lines, and faces [Figure 1a]. The C_h symmetry was maintained until $T = 700$ K [Figure 1b-1d]. At 900 K, the surface started to show significantly degraded symmetry [Figure 1e] and finally, melted at 1100 K [Figure 1f]. We also checked the structures with radial distribution functions [Figure S2] and the mean square displacements [Figure S3].

Next, we investigated H_2 adsorption properties of the two structures which have the C_h symmetry at 300 K and the molten surface at 1100 K. In these calculations, we performed the first-principles total energy calculations based on the density functional theory [3] using the plane wave basis set [4]. The ultrasoft pseudopotential [5] was adopted with the cutoff energy of 30 Ry, and the generalized gradient approximation was employed for the exchange-correlation effect. The supercell size was $15 \times 15 \times 15 \text{ \AA}^3$, which was large enough to exclude undesirable interactions between supercells. The scalar relativistic effects for Au were taken into account. Only 20 Au atoms near the H_2 molecule were considered for the calculations. The positions of the hydrogen molecule and four Au atoms were relaxed until the residual Hellman-Feynman forces became smaller than 0.02 eV/\AA .

Our computational results demonstrate that the bond length of H₂ molecule is increased to ~0.83 Å and the distance between a Au atom and H₂ is ~1.85 Å in the case of the molten gold NP (at 1100 K). Compared with the GGA calculation result on the bond length of H₂ in vacuum (0.75 Å), the bond length was increased by 11 %. Our Löwdin population analysis shows that each hydrogen atom donates 0.2 e⁻ to the gold cluster. For the gold NP with C_h symmetry, on the other hand, the change in the bond length of H₂ was negligible. Even in the edge adsorption configuration, the bond length of H₂ was about 0.77 Å. In this case, electron transfer between the gold NP and H₂ was also negligible.

2. Preparation of Au/C. Gold(III) chloride trihydrate, (HAuCl₄; Aldrich, 99.9+ %; 0.0246 g) and trisodium citrate (Na₃C₆H₅O₇, Aldrich, 0.0184 g) were dissolved in 250 ml distilled water. A cold NaBH₄ solution was added dropwise to this solution to obtain gold NPs. 0.0191 g of a carbon support (Ketjan Black) was added in 100 ml of so-obtained gold colloid solution. The solution was stirred vigorously at room temperature for 48 h. After the completion of the impregnation of gold NPs onto the carbon support, which was determined by the disappearance of the characteristic burgundy color of the gold NPs, the Au/C product was filtered, washed with distilled water, and placed in a vacuum desiccator for drying over a period of 10 h.

3. Preparation of Au/C(s). 0.0215 g Au/C was dispersed in 100 ml distilled water in an ultrasound vessel. The solution was irradiated by a high-intensity ultrasound (Sonic and Materials, VC-500, amplitude 25 %, 20 kHz) under an air condition for 30 min. The resultant powder was filtered, washed with distilled water, and dried in a vacuum desiccator for 10 h.

4. Preparation of working electrodes. 3 mg Au/C or Au/C(s) sample was dispersed in 1.5 g distilled water. 5 μ l of the suspension was dropped onto the working surface of a rotating disk electrode (RDE; AUTOLAB) made of glassy carbon ($d = 3$ mm, area = 0.071 cm²) and dried in air. A 5 μ l Nafion® solution (1 wt %) was applied to cover the working electrode for mechanical protection during the rotation of the RDE. Based on the elemental compositions by energy dispersive X-ray spectroscopy (Figure S5), each electrode contained about 1.5 μ g of Au NPs.

5. Cathodic treatment and HOR test. The working electrode with Au/C or Au/C(s) covered was cleaned electrochemically by sweeping in the potential range of 0.0 - 0.5 V at a scan rate of 500 mV/s in a N₂-saturated electrolyte (0.5 M, HClO₄). For the cathodic treatment, the electrode was subjected to a fixed potential at -0.6 V or -0.3 V for 600 s. Ag/AgCl and Pt mesh electrode were used as reference and counter electrode, respectively. After the cathodic treatment, the electrolyte was replaced with a fresh one and was saturated with H₂ gas by bubbling H₂ for 30 min. The HOR measurement was conducted by the linear sweep voltammetry at a scan rate of 5 mV/s. The rotation rate of the RDE was 1600 rpm. All the measurements were conducted at a controlled temperature of 30 \pm 0.5 °C.

6. Instruments for characterization. X-ray diffraction patterns were recorded on a DC/Max-2000 diffractometer (Rigaku) operating with a Cu K α radiation. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM-3011 model with an operation voltage of 300 kV. Energy Dispersive X-ray spectra were obtained with a JEOL JSM-6700F scanning electron microscope. Low temperature TEM images were obtained on a cryogenic TEM (FEI-TECNAI F20, located at Korea Institute of Science and Technology) with an acceleration voltage of 200 kV.

REFERENCE

1. Foiles, S. M.; Baskes, M. I.; Daw, M. S. *Phys. Rev. B* 1986, **33**, 7983.
2. Hoover, W. *Phys. Rev. A* 1985, **31**, 1695.
3. Kohn, W.; Sham, L. J. *Phys. Rev.* 1965, **140**, A1133.
4. Ihm, J.; Zunger, A; Cohen, M. L. *J. Phys. C* 1979, **12**, 4409.
5. Vanderbilt, D. *Phys. Rev. B* 1990, **41**, R7892.

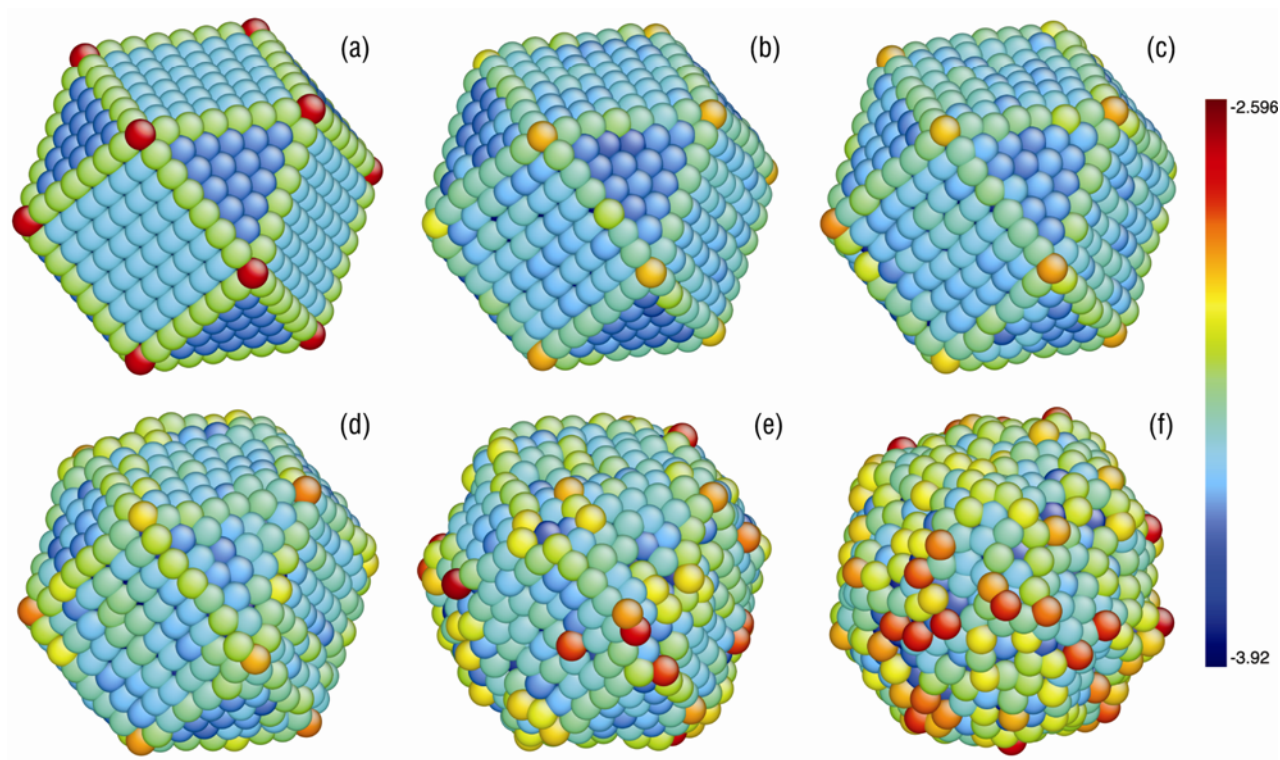


Figure S1. Potential energies of gold atoms of calculated structures of gold NPs equilibrated at 0 K (a), 300 K (b), 500 K (c), 700 K (d), 900 K (e), and 1100 K (f)

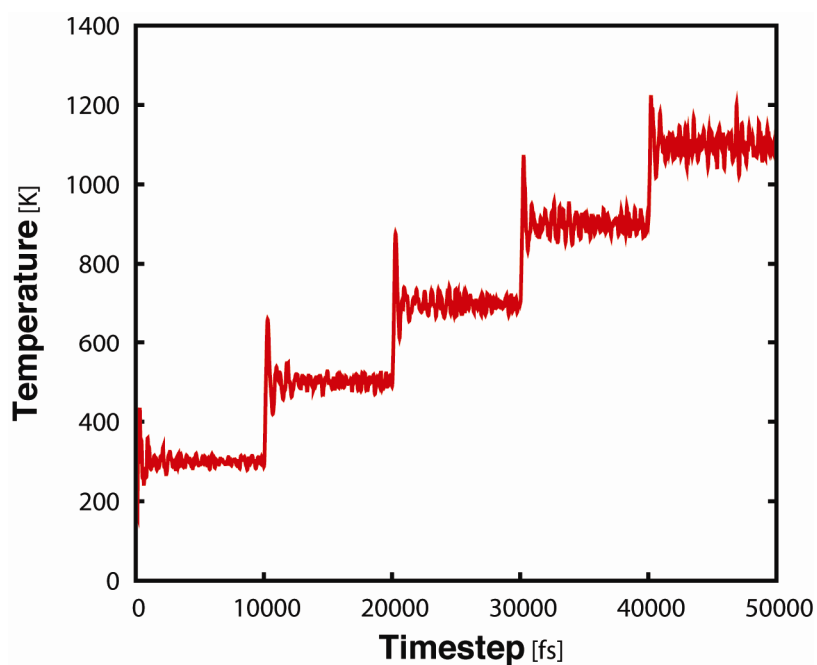


Figure S2. Plot of the equilibration processes used to obtain the structures of a gold NP at $T = 300$ K, 500 K, 700 K, 900 K, and 1100 K. For each temperature step, 10,000 iterations were used.

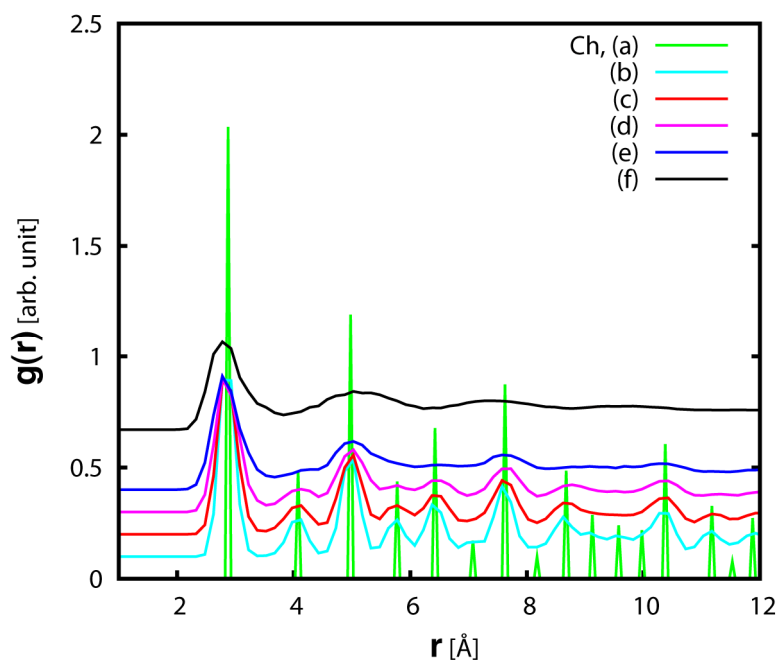


Figure S3. Radial distribution functions calculated for the structures shown in Figure 1. At high temperatures, the curves are comparable with those of liquid.

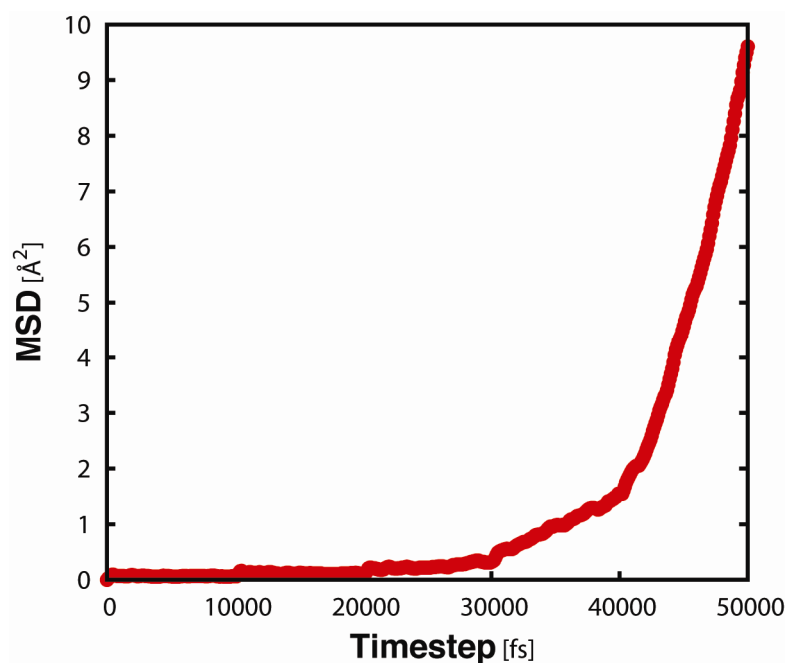


Figure S4. Mean square displacements of atoms throughout the calculations to reach the final 1100 K structure. Different slopes indicate different diffusivities. Therefore, we can infer that the gold NP of this size melts continuously without structural transition during the heating.

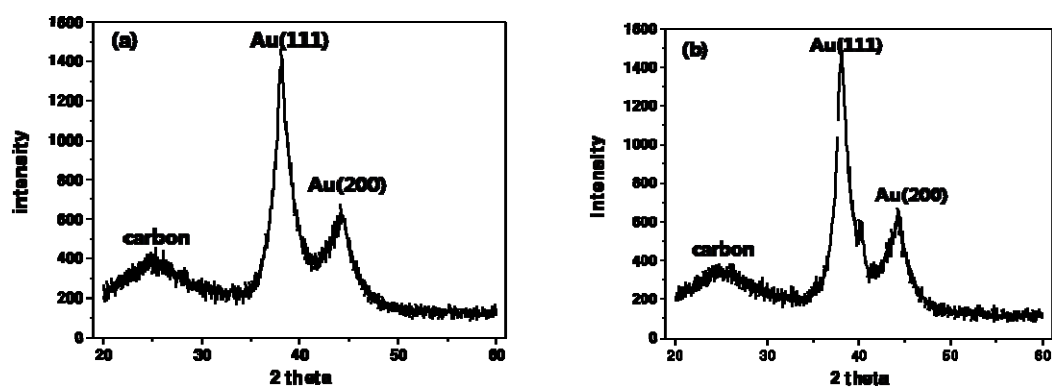


Figure S5. XRD patterns of Au/C (a) and Au/C (s) (b).

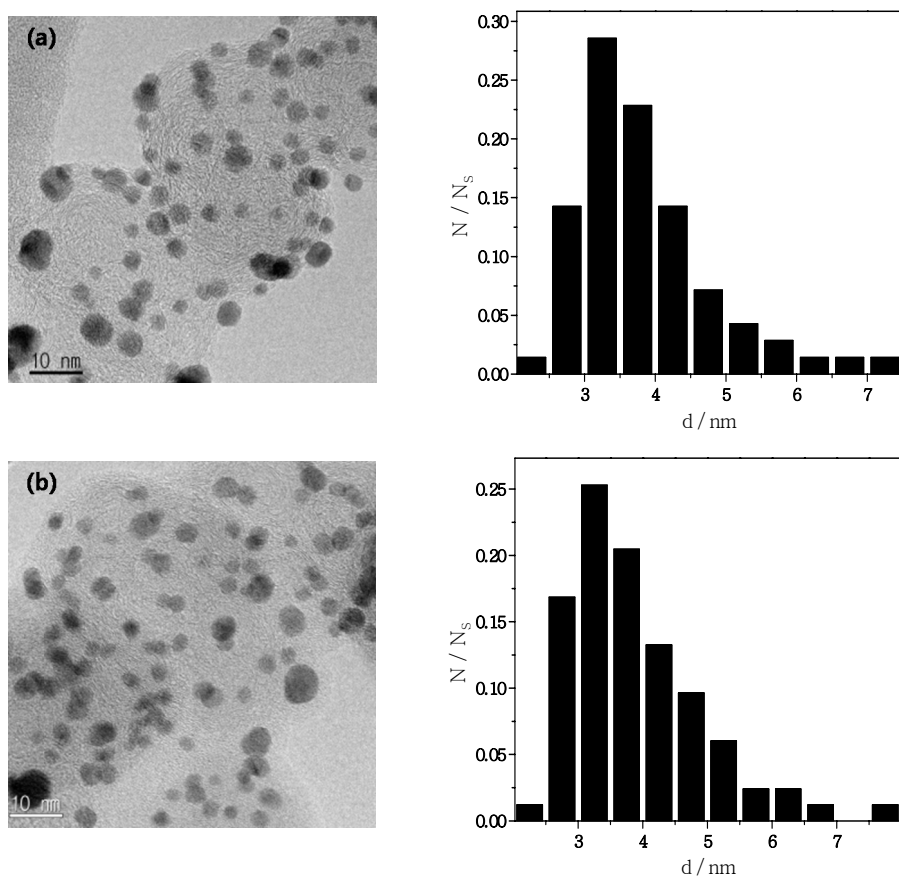


Figure S6. Room temperature TEM images and histograms of the size distribution of Au/C (a) and Au/C(s) (b).

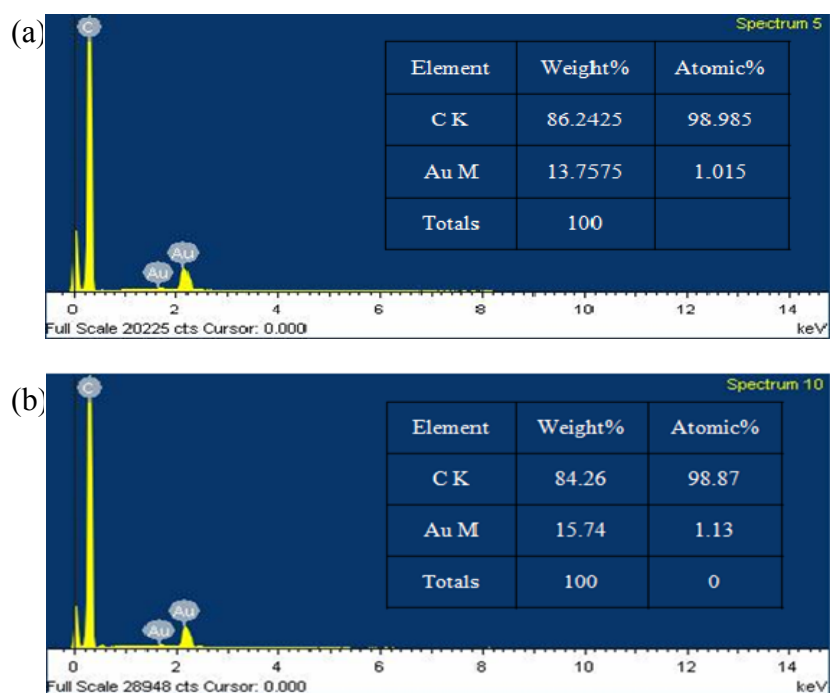


Figure S7. EDX spectra of Au/C (a) and Au/C(s) (b). The composition data are averaged values of measurements on five different locations for each sample.

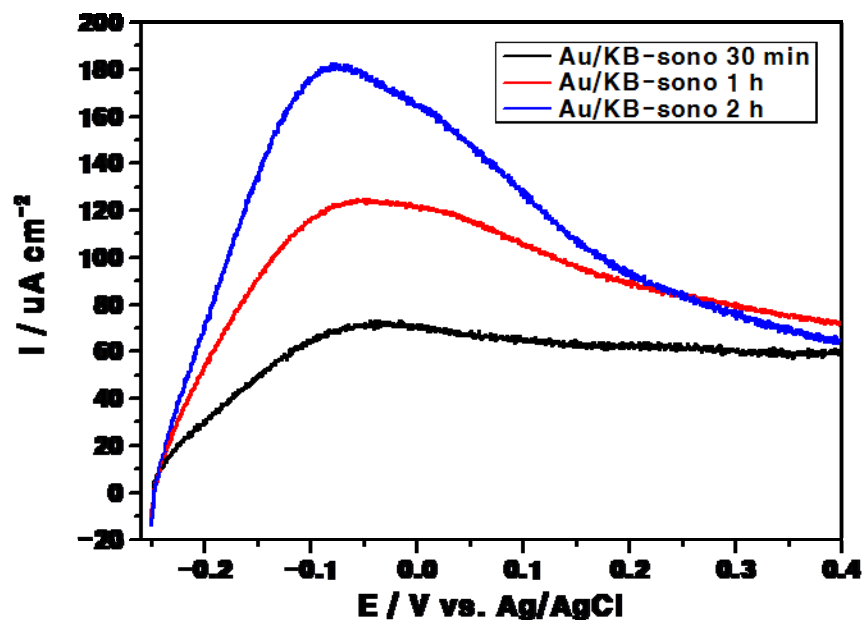


Figure S8. HOR plots of Au/C(s) prepared with different time periods of sonication.

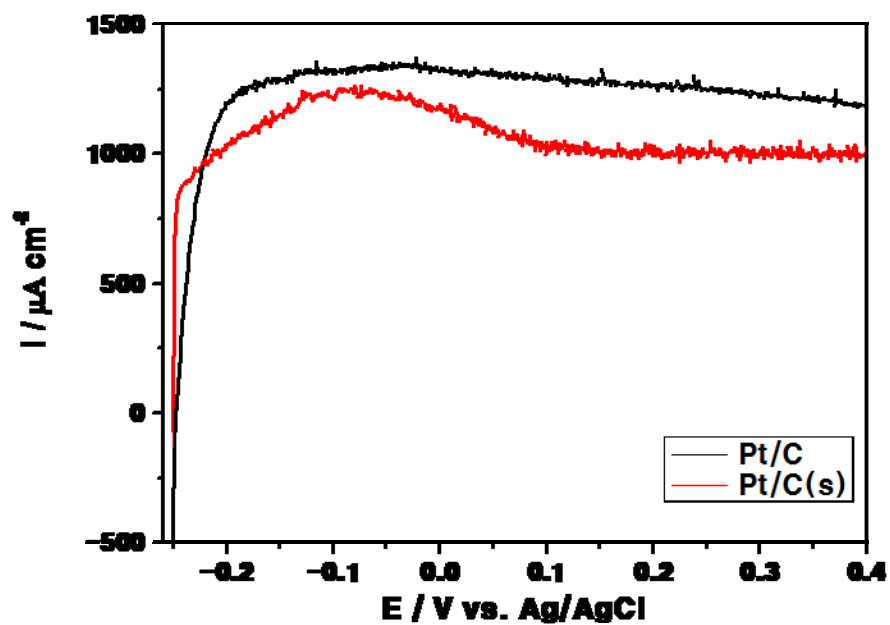


Figure S9. HOR plots of electrodes prepared with Pt nanoparticles loaded on carbon supports with sonication (Pt/C(s)) and without (Pt/C).