Supplementary Information

Monodisperse Pt and PtRu/C_{60} Hybrid Nanoparticles for Fuel Cell Anode Catalysts

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Experimental

All reactions were carried out under an argon atmosphere with the use of standard Schlenk techniques. Platinum acetylacetonate (98%, Strem), ruthenium acetylacetonate (98%, Strem), C_{60} (99.5%, SES research), 1,2-hexadecanediol (90%, Aldrich), 1,2-dichlorobenzene (99%, Aldrich), 1,2-dichlorobenzene-d_4 (98 atom% D, Aldrich), oleic acid (99%, Aldrich), benzylether (99%, Aldrich), acetic acid (99.0%, Junsei), toluene (99%, Junsei), ultrapure water (Milli-Q, >18 Ω), Nafion alcohol solution (5.0 wt%, Fluka), methanol (99%, Junsei), sulfuric acid (99%, Aldrich) and Vulcan carbon (Vulcan XC-72R, Carbot) were used without further purification. Oleylamine (technical grade, Aldrich) was purified by vacuum distillation over CaH_2.

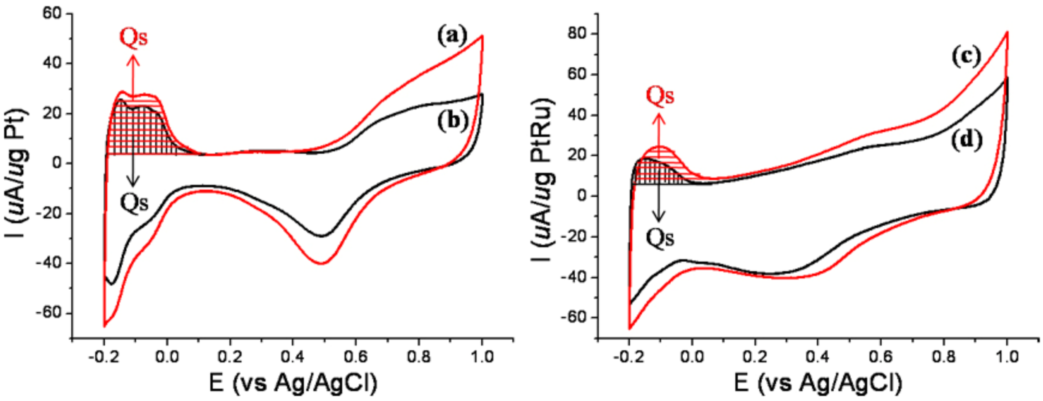
***Synthesis of Pt/C_{60} hybrid nanoparticles*:** Platinum acetylacetonate (250 μmol), C_{60} (10 μmol), 1,2-hexadecanediol (500 μmol), oleylamine (900 μmol), and oleic acid (900 μmol) were mixed with benzylether (10 mL) in a 100 mL two-necked round-bottom flask, and the mixture was heated at 50 °C under an argon atmosphere for 1 h. The reaction mixture was slowly heated to reflux at a rate of 8.3 °C/min for 30 min and allowed to reflux for 30 min to yield a black dispersion. The mixture was cooled to room temperature, and the product was precipitated by adding ethanol (12.5 mL). Centrifugation at 14,000 rpm for 30 min and repeated washing with ethanol and toluene yielded Pt/C_{60} hybrid nanoparticles. The particles could be readily dispersed in various hydrocarbon solvents such as toluene, hexane, and chlorobenzene. For checking the C_{60} concentration effect, the reaction followed the procedure identical to that of Pt/C_{60} hybrid nanoparticles except the C_{60} usage of 0, 1.9, 4.5, 7.8, and 15 μmol.

Synthesis of PtRu/C_{60} hybrid nanoparticles**:** The synthetic procedure for PtRu/C_{60} hybrid nanoparticles were identical to that for the Pt/C_{60} hybrid nanoparticles, otherwise platinum acetylacetonate (125 μmol) and ruthenium acetylacetonate (125 μmol) were used as metal precursors.

Synthesis of Pt/C_{60} particulates without surfactants**:** Platinum acetylacetonate (250 μmol), C_{60} (10 μmol), and 1,2-hexadecanediol (500 μmol) were mixed with 1,2-dichlorobenzene (10 mL) in a 100 mL two necked round-bottom flask, and the mixture was stirred at room temperature under argon atmosphere for 1 h. The reaction mixture was slowly heated to reflux at a rate of 4.4 °C/min for 40 min and allowed to reflux for 12 h to yield a black dispersion. The mixture was cooled to room temperature, and was thoroughly washed with ethanol and chlorobenzene at 70 ^{o}C in order to remove C_{60} and organic residues completely. The addition of oleylamine (900 μmol) and oleic acid (900 μmol) to the solid materials yielded a stable dispersion of Pt/C_{60} particulates in toluene.

Catalyst preparation**:** Pt and PtRu/C_{60} hybrid nanoparticles (30 wt%) and Vulcan carbon (70 wt%) were dispersed in toluene (100 mL) by the help of sonication. After solvent evaporation, the products were dried in air for 1 h. The resulting dark powders were mixed with acetic acid (50 mL), and vigorously stirred at 80 °C for 10 h. The resulting catalysts were collected by centrifugation, washed with a copious amount of ethanol, and then dried at room temperature in air for 24 h. The purified Pt and PtRu/C_{60} hybrid catalysts have metal loading contents of 27.1 and 27.0 wt%, respectively, measured by inductively coupled plasma spectroscopy.

Electrochemical measurement**:** Linear sweep voltammetric and chronoamperometric analyses were conducted using a platinum wire counter electrode and a Ag/AgCl (in 3 M NaCl) reference electrode in a three-electrode cell at room temperature. All potentials are reported with respect to Ag/AgCl. The solutions were purged with Ar gas for 30 min prior to use. Potential control and sweeps were established using an Autolab potentiostat (Eco chemie, Netherlands). The glassy carbon (GC) electrode with a 3 mm diameter of the GC core (Bioanalytical Systems, Inc.) was polished with a 0.05 mm Al_2O_3 paste and washed with ultrapure water. For the preparation of electrode, 5.0 mg of the catalyst was dispersed ultrasonically in a mixture of a Nafion alcohol solution (100 μL) and ultrapure water (25 mL). The resulting suspension (5.0 μL) was drop-casted onto a working electrode surface, and carefully dried in an oven at 70 °C for 20 min so that the catalyst could be uniformly coated over an entire cross-section of the 6 mm diameter area. The geometric area of the GC electrode was 0.0706 cm^2, and the catalyst loading on the electrode was 14.16 $\mu g/cm^2$. The surface area measurements of the catalysts in 0.5 M H_2SO_4 were carried out from -0.2 to 1.0 V. The electrochemically active surface area (ESA) of the catalysts was obtained from the surface charge (Q_s), which could be calculated from the area under the CV curve as shown in the following figures.[4a]



Surface area measurements of (a) Pt/C_{60} hybrid nanoparticles on Vc, (b) E-TEK Pt catalysts, (c) PtRu/C_{60} hybrid nanoparticles on Vc, and (d) E-TEK PtRu catalysts in an electrolyte of 0.5 M H_2SO_4 aqueous solution (scan rate = 0.050 V/s).

For linear sweep voltammetry and chronoamperometry of methanol oxidation, the electrolyte solution was fit to 1 M CH_3OH in 0.5 M H_2SO_4. For the chronoamperometry experiments, the working electrode was treated at the potential of 1.0 V for 2 s, followed by a sudden decrease of the potential to 0.0 V for 2 s in order to remove any oxides and hydroxides adsorbed on the surface. The current transients were recorded at 0.3 and 0.2 V for the Pt and PtRu/C_{60} hybrid catalysts, respectively.

Characterization: Transmission electron microscopy images were obtained either on an Omega EM912 operated at 120 kV (low resolution) or on a Philips F20 Tecnai operated at 200 kV (high resolution). The selected area electron diffraction (SAED) patterns and energy dispersive analysis data of X-ray emission (EDS) were also obtained on the Philips F20 Technai. X-ray diffraction data were collected using a Rigaku D/MAX-RB diffractometer at 12 kW with a graphite-monochromatized Cu-Kα radiation at 40 kV and 120 mA. UV-Vis spectra were measured on a JASCO V-530 UV-Vis spectrophotometer. ^{13}C (400MHz) NMR spectrum was recorded on a Bruker AVANCE-400 spectrometer. Differential scanning calorimeter data were measured on a NETZSCH DSC 404 C. Infrared spectra were obtained on a Bruker EQUINOX-55 FT-IR spectrophotometer. The metal loading contents of the hybrid catalysts were analyzed by inductively coupled plasma spectroscopy (ICP, X-series, Thermo).

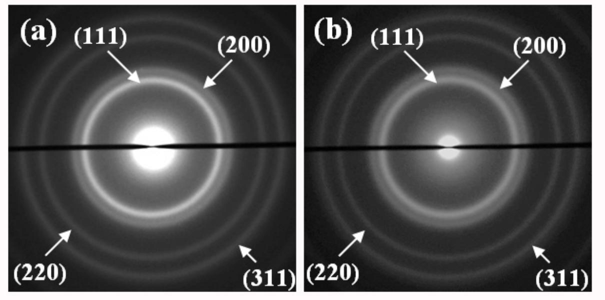


Fig. S1 SAED patterns of (a) Pt/C_{60} and (b) PtRu/C_{60} hybrid nanoparticles.

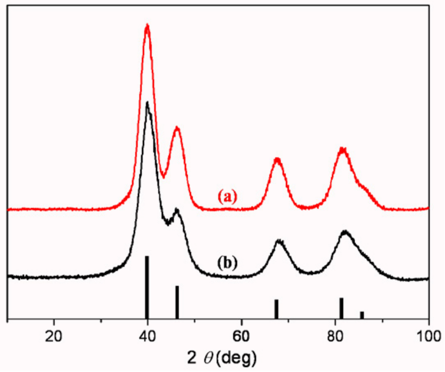


Fig. S2 XRD patterns of (a) Pt/C_{60} and (b) PtRu/C_{60} hybrid nanoparticles. The standard peaks from the JCPDS card are shown as a bar diagram at the bottom.

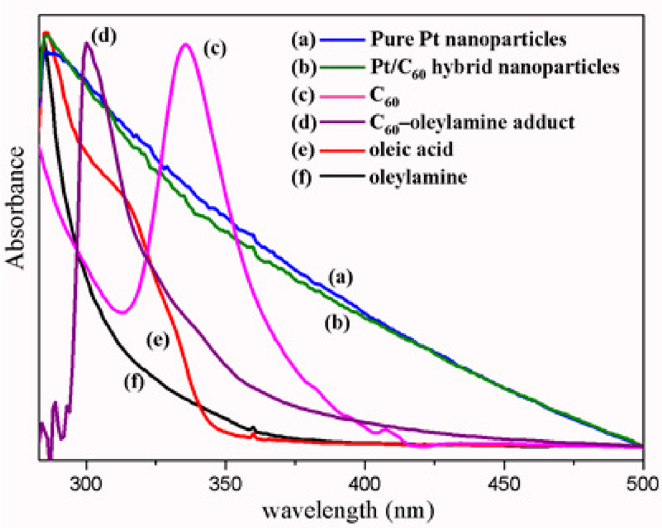


Fig. S3 UV-Vis spectra of (a) Pt nanoparticles, (b) Pt/C_{60} hybrid nanoparticles, (c) pure C_{60}, (d) C_{60}–oleylamine adduct, (e) oleic acid, and (f) oleylamine.

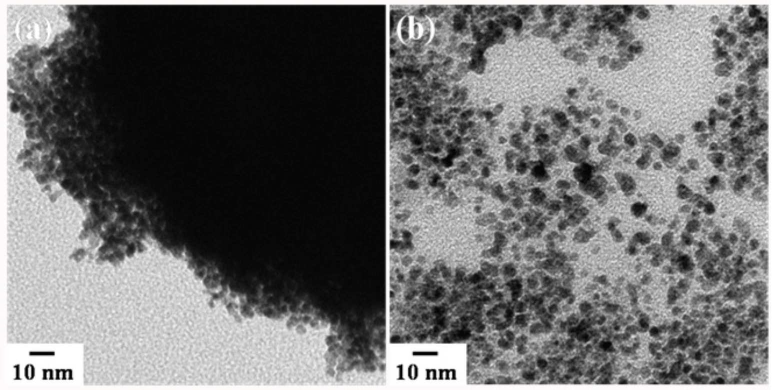


Fig. S4 TEM images of Pt/C_{60} particulates (a) before and (b) after the addition of oleylamine and oleic acid.

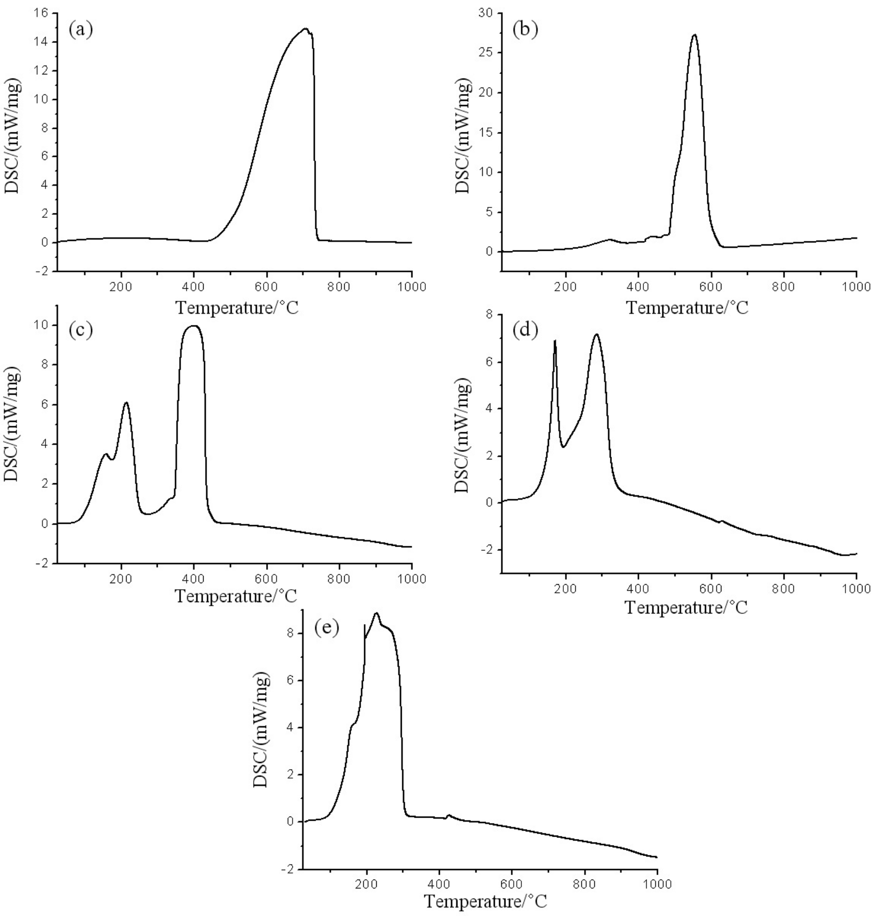


Fig. S5 DSC curves of (a) pure C_{60}, (b) C_{60}-oleylamine adduct, (c) pure Pt nanoparticles, (d) Pt/C_{60} particulates, and (e) Pt/C_{60} hybrid nanoparticles.

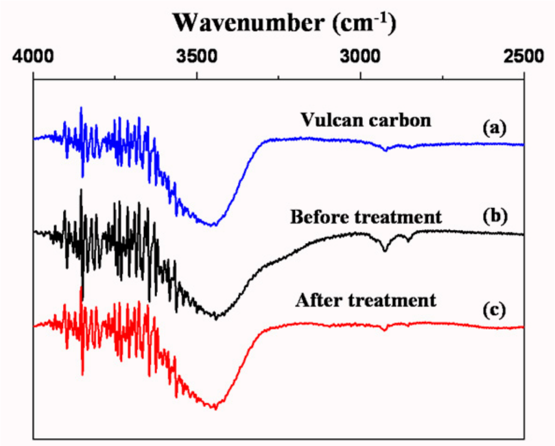


Fig. S6 FTIR spectra of (a) Vulcan carbon and Pt/C_{60} hybrid catalysts (b) before and (c) after acetic acid treatment.

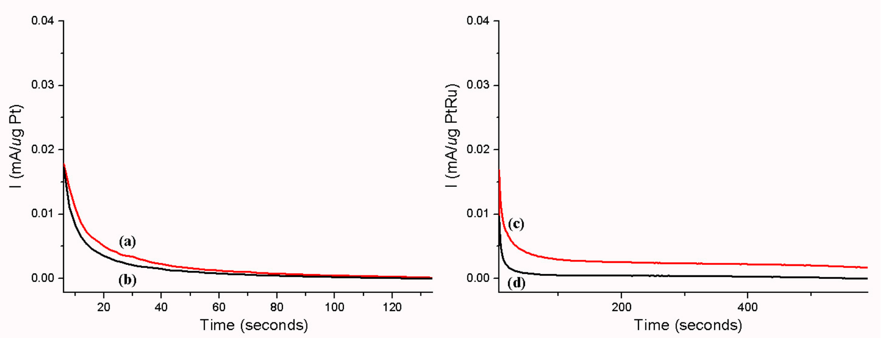


Fig. S7 Chronoamperometry measurements of (a) Pt/C_{60} hybrid catalysts and (b) E-TEK Pt catalysts at 0.3 V, and (c) PtRu/C_{60} hybrid catalysts and (d) E-TEK PtRu catalysts at 0.2 V in an electrolyte of 1 M CH_3OH and 0.5 M H_2SO_4 aqueous solution.

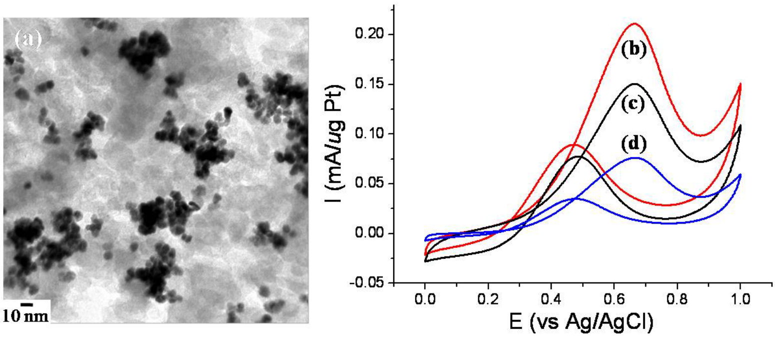


Fig. S8 TEM image of (a) Pt nanoparticles (7.0±1.9 nm) prepared without C_{60} on Vc and linear sweep voltammograms (scan rate = 0.050 V/s) of (b) Pt/C_{60} hybrid catalysts, (c) E-TEK Pt catalysts, and (d) Pt nanoparticles on Vc.

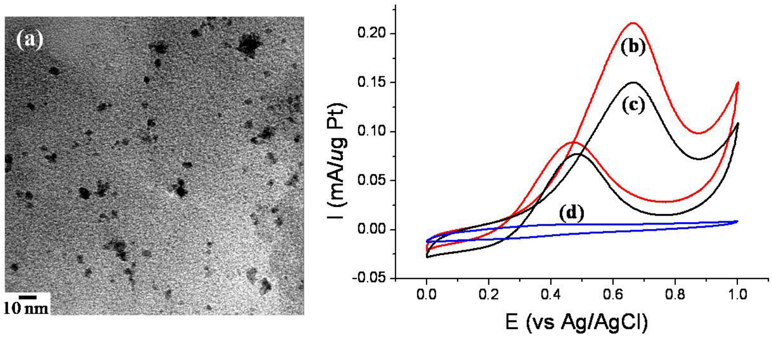


Fig. S9 TEM image of (a) Pt(3.5±0.9 nm)/C_{60} composite with an excess of C_{60} and linear sweep voltammograms (scan rate = 0.050 V/s) of (b) Pt/C_{60} hybrid nanoparticles on Vc, (c) E-TEK Pt catalysts, and (d) Pt/C_{60} composite.