

Iridium Nanocrystal Synthesis and Surface Coating- Dependent Catalytic Activity

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Supporting Information.

Chemicals. All chemicals were of the highest purity available and used without further purification. Oleic acid ($C_{18}H_{34}O_2$, 65%), oleylamine ($C_{18}H_{37}N$, 70 %), dioctylether ($[CH_3(CH_2)_7]_2O$, 97%), trioctylphosphine or TOP ($C_{24}H_{51}P$, 90 %) were purchased from Fluka. Tetraoctylammonium bromide or TOAB ($C_{32}H_{68}N Br$, 98 %), tetraoctylphosphonium bromide or TOPB ($C_{32}H_{68}P Br$, 97 %), decane ($C_{10}H_{22}$, 99 %), 1-decene ($C_{10}H_{20}$, 94 %) and 1,2 hexadecanediol ($C_{16}H_{34}O_2$, 90%) were purchased from Aldrich. (Methylcyclopentadienyl) (1,5-cyclooctadiene) iridium ($(C_6H_7)(C_8H_{12})Ir$, 99 %) was purchased from Strem.

All solvents used were of analytical grade and purchased from Aldrich.

Oleic Acid and Oleylamine Capped Iridium. Iridium nanocrystals capped with oleic acid and oleylamine were produced in a method similar to Sun *et al.*'s for FePt.²⁴ In a 25 ml- three neck, round bottom flask, 7.5 ml of dioctylether was used to dissolve 0.195 g of hexadecanediol. 0.08 μ l of oleic acid and 0.085 μ l of oleylamine were added. Septa were placed on two of the

necks of the flask, while a condenser and a stopcock valve connected to the third. The flask was connected to a schlenk line, and three freeze-pump-thaw cycles were performed on the contents, to remove oxygen. This flask was heated up to 290 °C under nitrogen flow. 0.19 g of (Methylcyclopentadienyl) (1,5-cyclooctadiene) iridium was measured into another 25 ml- three neck, round bottom flask, and 1 ml of dioctylether was added. The flask was prepared using the same method as the first to remove oxygen, but kept at room temperature. The contents of this flask were then injected into the 290 °C flask, and the reaction was allowed to proceed for 2 hours. The product was a dark brown liquid that, after cleaning by centrifuging the product in alternating solutions of hexanol and chloroform, resulted in brown precipitate. The nanocrystals redisperse in various non-polar organics solvents including chloroform, cyclohexane and toluene. The size distribution could be narrowed by size selective precipitation using ethanol as an antisolvent.

Trioctylphosphine Capped Iridium. Iridium particles were synthesized with TOP as the capping ligand by using a similar injection method, with flasks prepared as in the previous method. 0.39 grams of hexadecanediol were dissolved into 10 ml of TOP in a 25 ml- three neck, round bottom flask which was deoxygenated and brought to 290 °C. 0.38 g of (methylcyclopentadienyl) (1,5-cyclooctadiene) iridium was added to a second 25 ml- three neck, round bottom flask with 2 ml of TOP, deoxygenated and then injected into the 290 °C flask. After heating for 1.5 hours, the solution cooled and a brown product was extracted and cleaned by centrifuging in alternating hexanol and chloroform solutions.

Tetraoctylammonium Bromide or Tetraoctylphosphonium Bromide Capped Iridium.

Iridium particles with TOAB and TOPB ligands were synthesized using only one 25 ml- three neck, round bottom flask. 0.2 g of hexadecanediol, 7 ml of dioctylether, 0.2 g of (methylcyclopentadienyl) (1,5-cyclooctadiene) iridium, and 0.76 g of either TOAB or TOPB were measured into the flask. The solution was freeze-pump-thawed for three cycles, and heated up to 270 °C for 30 minutes. The product was a black liquid and particles were isolated using one rinse in ethanol. Rinsing the solution multiple times in ethanol resulted in the removal of capping ligands from the iridium surface, so exposure to ethanol and other antisolvents was kept at a minimum.

Catalysis. 1-decene hydrogenation reactions were carried out in a 100 ml round bottom flask that acted as a batch reactor. Three psig of hydrogen gas were bubbled into 1-decene at 75 °C. Iridium nanoparticles in 1-decene were injected into the flask as to create a 1000:1 decene to iridium mass ratio. Initially the reaction temperature dropped to 70 °C but stabilized back at 75 °C after 1 minute. Aliquots of the solution were removed every minute for the first 20 minutes of the reaction, then every 5 minutes until one hour, and at every 10 minutes after that. Aliquots were placed in screw cap gas chromatography vials. Particles were later recovered by vacuum evaporation of the liquid away from the particles.

Transmission Electron Microscopy. High resolution transmission microscopy (HRTEM) images were obtained using a JEOL 2010F microscope operating at 200 kV. Low resolution transmission microscopy (LRTEM) images were obtained using a Phillips EM208 microscope

operating at 120 kV. The samples were prepared by drop casting dilute solutions of iridium particles in chloroform on 200 mesh carbon-coated copper grids.

Powder X-Ray Diffraction. Powder X-Ray diffraction (XRD) was performed on a Bruker-Nonius Powder Diffractometer using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Iridium samples in chloroform were drop cast on a quartz substrate.

Small Angle X-Ray Scattering. Small angle X-ray scattering (SAXS) measurements were performed using a rotating copper-anode generator by Bruker Nonius, Molecular Metrology, Inc. operated at 3.0 kW on iridium nanocrystals dispersed in cyclohexane. X-rays accessed the sample through the Kapton windows of the sample holder. The scattering angle was calibrated using a silver behenate ($\text{CH}_3(\text{CH}_2)_{20}\text{COOAg}$) standard. The experimental SAXS data was corrected for background scattering and sample absorption.

Gas Chromatography/ Mass Spectroscopy. The catalytic properties of oleic acid and oleylamine, TOP, TOAB, and TOPB particles were determined by analyzing the hydrogenation reaction aliquots using a Hewlett Packard 5890 series II gas chromatography mass spectrophotomer (GCMS). The GCMS was calibrated to determine the relative amounts of 1-decene and decane in each aliquot, and in this way the hydrogenation reaction progress and rate were monitored.