

Supporting Information

Epoxidation of Stilbene using Supported Gold Nanoparticles: Cumene Peroxyl Radical Activation at the Gold Nanoparticle Surface

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Materials and Methods

Reagents. Cumene, cumene hydroperoxide (CHP), (technical grade 80%, largely cumene impurity), cumyl alcohol (98 %; 2-phenyl-2-propanol), *tert*-butyl hydroperoxide solution in H₂O (80%), *trans*-stilbene, *trans*-stilbene oxide, *cis*-stilbene, *cis*-stilbene oxide, and optima grade acetonitrile were purchased from Sigma-Aldrich and used as received. TiO₂ P25 was a gift from Evonik Degussa. AUROLite™ 1% AuNP@TiO₂ extrudates were purchased from Strem Chemicals and ground with a mortar and pestle prior to use. Optima grade heptane and 2-propanol used in HPLC analysis were purchased from Fisher Chemicals and used as received.

Instrumentation. The size of supported AuNP nanoparticles was determined using a JEM-2100F FETEM transmission electron microscope (TEM) from Jeol Ltd. Analysis of the reaction mixture (cumyl alcohol, acetophenone and cumene hydroperoxide) was carried out using a normal phase Agilent 1100 HPLC (eluent 99:1 heptane/2-propanol). The amount of *trans*-stilbene, *trans*-stilbene oxide, *cis*-stilbene, *cis*-stilbene oxide were determined using a Waters HPLC fitted with a reverse phase C-18 silica column and employing an eluent mixture of 60:40 acetonitrile:water. EPR spectrum were recorded on an Joel FA-100 spectrometer.

Experimental Details

Characterization of commercial AuNP@TiO₂. The size of the commercial AuNP@TiO₂ (Figure S1) was analyzed by SEM and determined to be 2.3 nm from an average of 50-100 particle measurements.

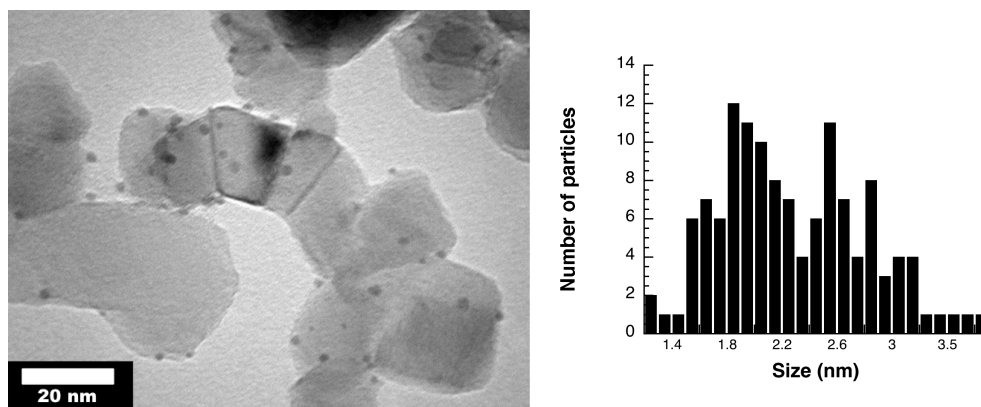


Figure S1. TEM (left) and size distribution histogram (right) of AuNP@TiO₂ commercial. The average size was determined to be 2.3 nm ± 0.5 as determined from 50-100 measurements.

Epoxidation of *cis*-stilbene . In a 50 mL, two-neck round bottom flask, 0.1 g of catalyst, 94 µl (0.5 mmol) of *cis*-stilbene and 7.8 µl (0.05 mmol) of an aqueous solution of *tert*-butyl hydroperoxide were added to 10 mL of cumene. 500 µl (0.32 mmol) of *tert*-butyl benzene were added as an internal standard and the reaction heated to 80°C. After 24 hours, the reaction was analyzed using both normal and reverse phase HPLC. Normal phase chromatography was used to assess the yields of peroxidation products (acetophenone, cumyl alcohol and cumene hydroperoxide) and reverse phase HPLC to examine the epoxidation products were (*cis*-stilbene oxide and *trans*-stilbene oxide) Control reactions were carried out using the support itself (TiO₂ P25) and in the absence of heterogeneous materials (*tert*-butyl hydroperoxide initiator only).

EPR spin-trap experiments. In a 50 mL, two-neck round bottom flask, 0.1 g of catalyst and 7.8 µl (0.05 mmol) of an aqueous solution of *tert*-butyl hydroperoxide were added to 10 mL of cumene and the reaction heated to 80°C. Aliquots of the reaction were added to a solution containing 50 mg (0.44 mmol) of type out the full chemical name (DMPO) spin trap. This solution was then centrifuged and the EPR spectrum recorded. Control EPR experiments performed using no catalyst and TiO₂ are presented in Figures S2 and S3, respectively. Note the absence of an EPR signal when no supported AuNP are present.

Figures S2 and S3 are control experiments related to Figure 1 in the main article.

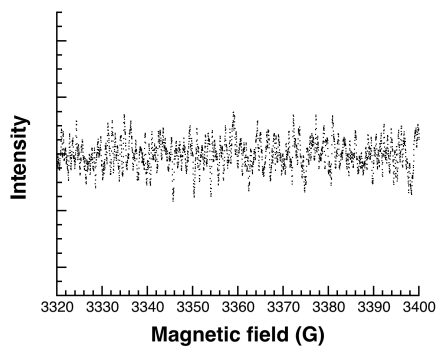


Figure S2. EPR spectrum recorded for the DMPO spin-trap experiment done in absence of catalyst (*tert*-butyl hydroperoxide initiator only).

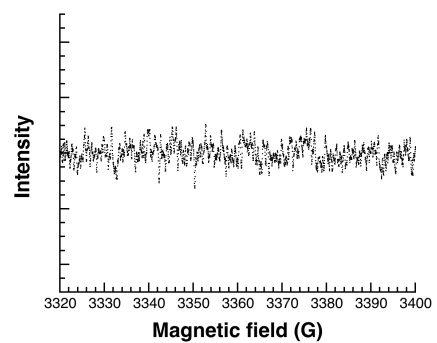


Figure S3. EPR spectrum for the DMPO spin-trap experiment done in the presence of TiO_2 .