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Supporting information for:

Heterogeneous Photocatalytic C-C Coupling: Mechanism of the Plasmon-mediated Reductive Dimerization of Benzyl Bromides by Supported Gold Nanoparticles

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Experimental

Reagents. Gold(III) tetrachloroauric acid hydrate ($HAuCl_4 \cdot 3H_2O$), diamond nanopowder (DNP), 4-NitroBenzyl Bromide (4-NBB), Triethylamine (TEA), N,N-diisopropylethylamine (DIPEA) and diisopropylamine (DIPA) were purchased from Sigma-Aldrich and used as received. TiO_2 P25 was a gift from Evonik Degussa. AUROlite 1% AuNP@TiO_2 was purchased from Strem Chemicals and was ground using a mortar and pestle prior to use. The average size of the AuNP was determined to be 2.3 nm by TEM (Figures S1 and S2). The diffuse reflectance spectrum of the catalyst is shown in figure S3.

Catalyst preparation. AuNP@TiO_2 extrudates were ground with a mortar and pestle prior to use.
The support of the commercial material was tested as catalyst after the AuNP was completely removed from the commercial AuNP@TiO_2 by cyanide etching.[1]
Briefly, 1 g of AuNP@TiO_2 were placed together with 50 mL of an aqueous solution of KCN (1M). The mixture was stirred, the color of the solid turned from violet to white in a couple of hours. In order to get rid of the residual cyanide and gold ions, the solid was washed several times with milliQ water. After dried under vacuum, the TiO_2 was placed into the oven at 40°C for 2 days. The lack of the plasmon band on the diffuse reflectance spectrum suggests complete removal of Au(0) (Figure S3).

The preparation of 1% AuNP@HO-DNP was performed as follow: first, the Fenton reaction has been used to purify commercial DNPs by the selective mineralization of the soot.[2] Once the DNP Fenton treated particles (HO-DNP) were obtained, the preparation of AuNP on HO-DNP at 1% nominal loading and 1% AuNP@TiO_2 was performed based on a method already published by our group.[3] In brief, 20 mg of the solid support (HO-DNP or TiO_2 from the commercial catalyst) and 1 mL of Milli-Q water were placed in a 20 mL glass vial and sonicated for 1 min prior to use. Next, 3 mL of polymorphic AuNP was subjected to 532 nm laser drop ablation and collected in the support/water slurry with continuous stirring. The suspension was left to separate for 2−3 h, and the supernatant was discarded. The resulting solid was washed with 4 mL of water and centrifuged at 3000 rpm for 30 min. This process was repeated three times, and the resultant solid was submitted to lyophilization for 14 h in a Labconco Freezone 4.5 lyophilizer. TEM and spectroscopic characterization of these materials are shown in figures S1, S2 and S3.

Sample Preparation for 530 nm LED Plasmon Irradiation. The samples used for plasmon-mediated catalysis experiments containing Au@TiO_2 composite were prepared using *ca.* 5 mg of the composite, 20 mg of 4-NBB (0.09 mmol) and 0.18 mmol of the desired amine in 3 mL of strictly deareated dichlorometane (DCM). The reaction was analyzed by HPLC-PDA by diluting 20 µL of the solution with 0.78 mL of acetonitrile using CH_3CN:H_2O 80:20 as mobile phase. HPLC results were extracted at λ_{max} = 275 nm for both 4-NBB and 4,4'-dinitrobibenzyl.

Catalyst Recyclability Experiments. The supported AuNP composites were tested for potential reuse in the reductive dimerization of 4-NBB performing the reaction at least three times. The reaction was scaled up to facilitate catalyst recovery and reuse. Following excitation, the samples were placed in a 15 mL centrifuge tube, and centrifuged at 2500 rpm for 10 min to recover the

supported Au catalyst. The catalyst was rinsed three times with AcN by consecutive stirring and centrifuging steps.

Instrumentation. Irradiated samples were analyzed using a Waters Integrity HPLC in tandem with a reverse phase C18 Zorbax column using a 80:20 AcN/Milli-Q H_2O eluent mixture and a 0.35 mL/min flow rate. The light-emitting diode system (LED) consisted of four, 10 W 530 nm LedEngin LZ4-40G110 emitters attached to aluminum heat sinks in a custom design irradiator (Figure S7) using a thermal bath with water/ethanol circulation for temperature control (set T= 5°C). The intensity of each emitter at the distance the sample is placed was measured (480 mW/m^2). Figure S5 shows the spectrum from the LED recorded at close range and illustrates the level of contamination from shorter wavelengths.

A solution of 4-NBB with the proper amine and supported AuNP in deareated DCM were combined in a quartz cuvette, capped and sealed, and irradiated for varying amounts of time (0−21 hs). The reaction work-up is explained above. The temperature within the LED reactor raised the DCM boiling point (39°C). Conventional heating experiments were performed in a capped glass flask for 22 h using water bath heated to 39°C on a conventional laboratory hot plate to mimic temperature conditions within the liquid-cooled LED apparatus.

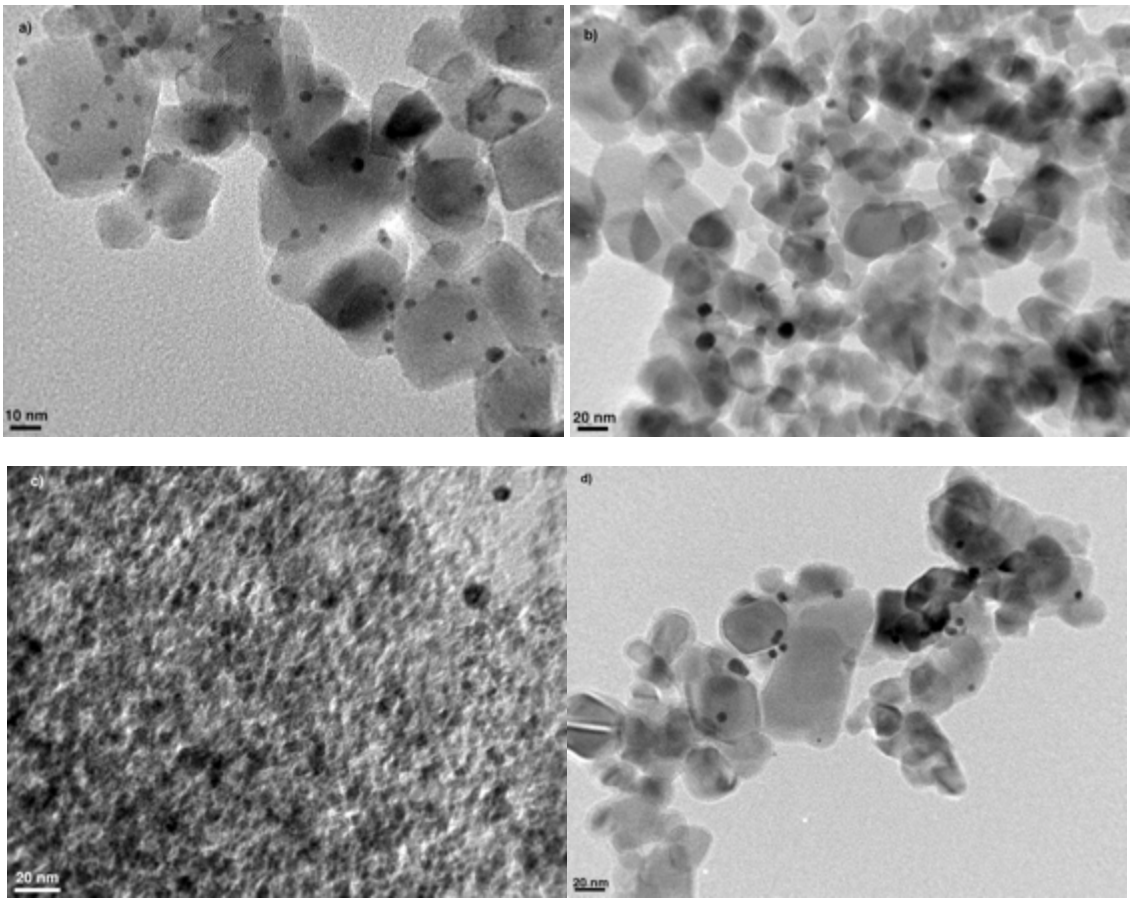

Figure S1. TEM image of a) commercial 1% AuNP@TiO_2, b) homemade 1% AuNP@TiO_2, c) 1% AuNP@HO-DNP, and d) commercial 1% AuNP@TiO_2 after 3 reused cycles.

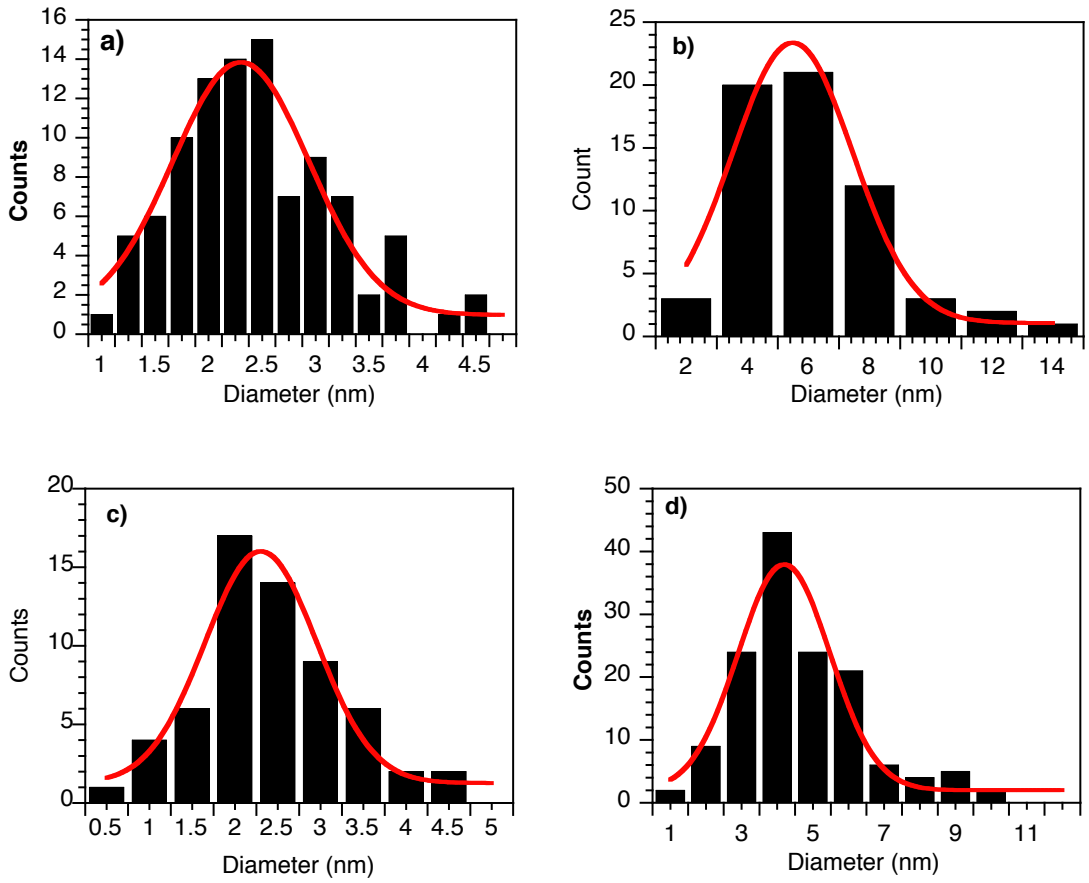

Figure S2. Size distribution histograms obtained following around 100 measurements of a) commercial 1% AuNP@TiO_2, b) homemade 1% AuNP@TiO_2, c) 1% AuNP@HO-DNP, and d) commercial 1% AuNP@TiO_2 after 3 reused cycles.

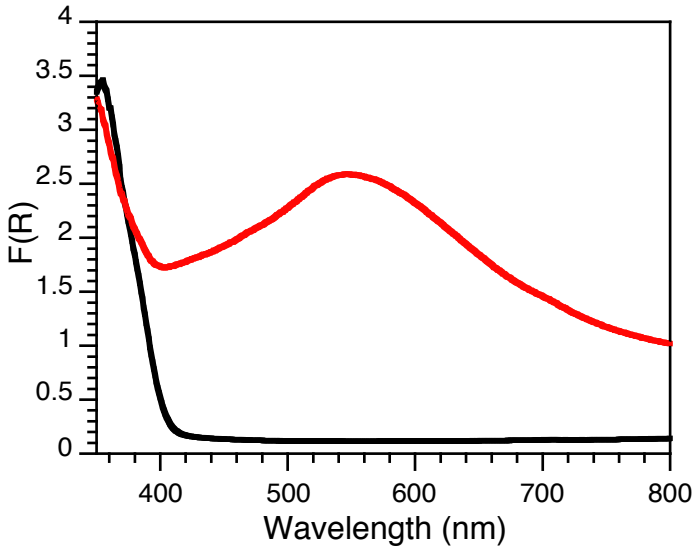

Figure S3. Diffuse reflectance spectra for TiO_2 obtained by gold etching (black) and commercial AuNP@TiO_2 (red)

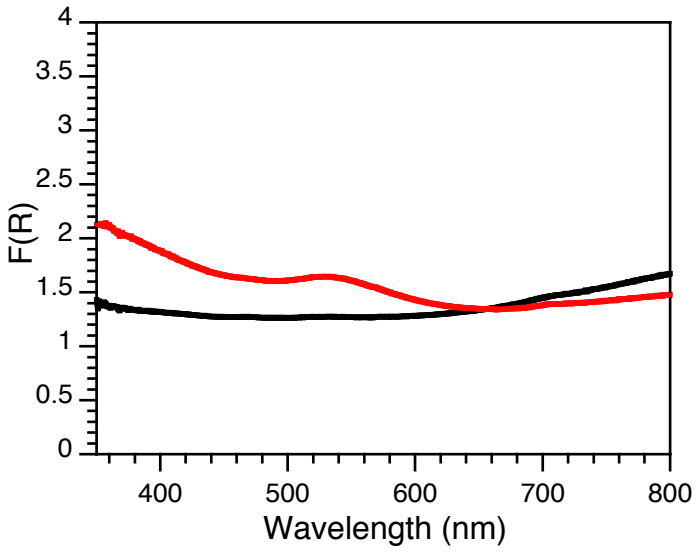

Figure S4. Diffuse reflectance spectra for HO-DNP (black) and 1% AuNP@OH-DNP (red)

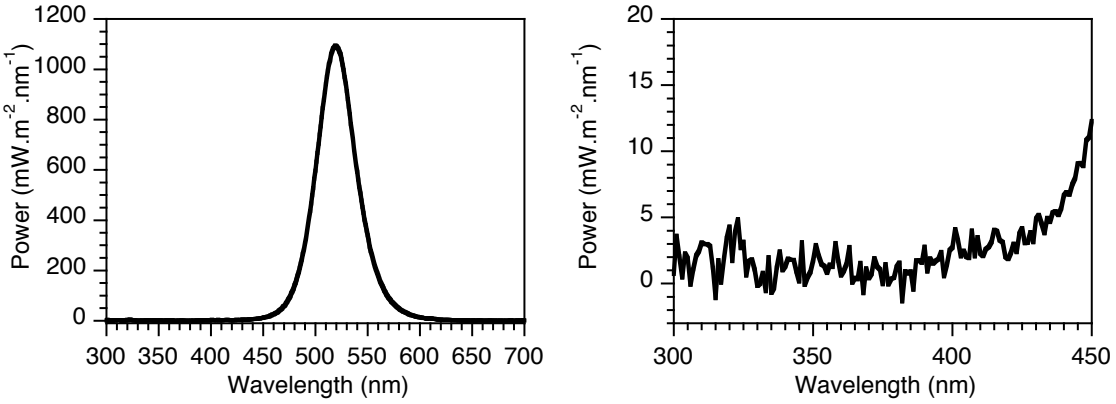

Figure S5. *Left*: Typical relative LED spectral power vs. wavelength at RT. *Right*: Zoom in the blue region.

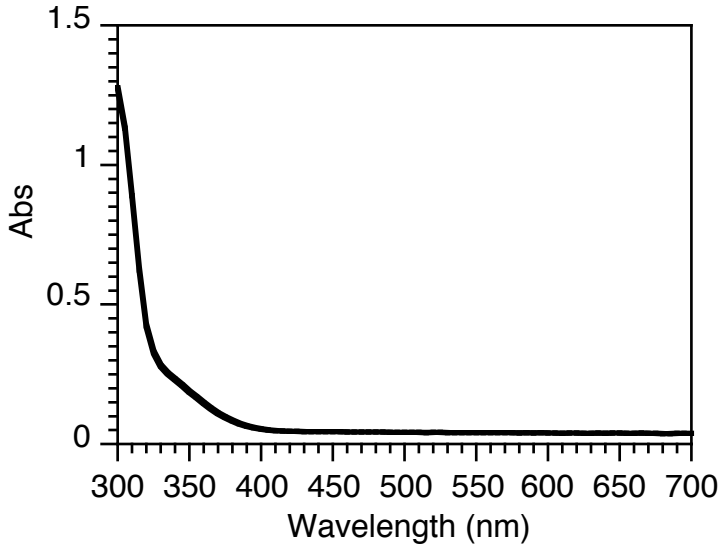

Figure S6. UV-vis spectrum of the reaction mix before irradiation.

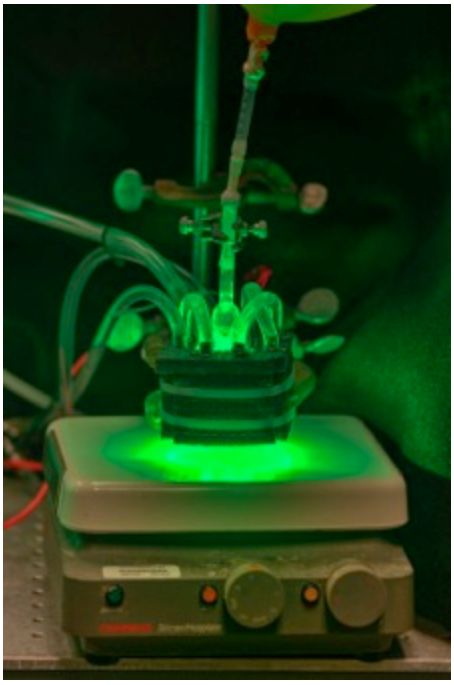

Figure S7. Photo depicting the LED apparatus used for plasmon-mediated catalysis

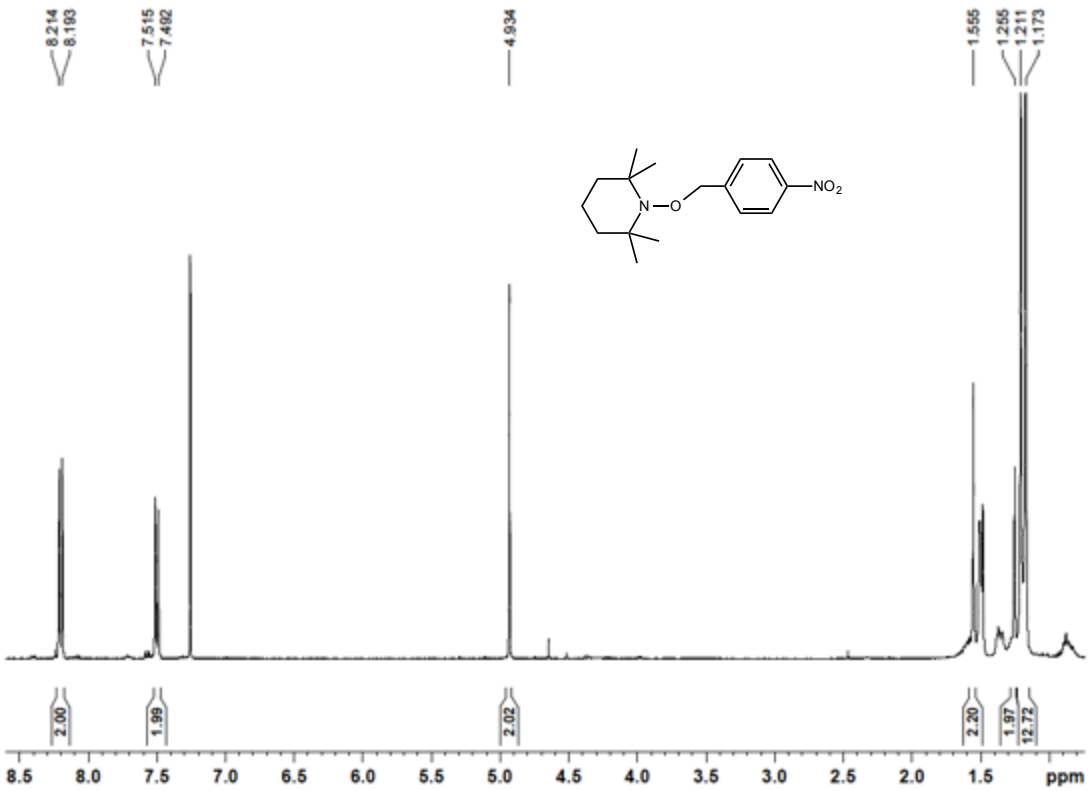

Figure S8. ^{1}H NMR spectrum of the TEMPO trapping adduct (400 MHz, CCl_3D).

Table S1. Evaluation of the time reaction needed to get complete conversion for the reduction of different substituted benzyl bromides.

#	R1	R2	% Yield of Ar-Ar	% Yield of Ar-H	Time (h)	Ar-Ar/Ar-H ratio
i	OCH_3	H	68	29	16	2.4
ii	H	H	69*	ND	18	>>
iii	CH_3	H	70	18	24	3.9
iv	Ph	H	74	ND	5	>>
v	NO_2	H	81	12	5	6.9
vi	H	NO_2	73	14	5	5.3

* 77 % conversion.

References

(1) Zhu, T.; Vasilev, K.; Kreiter, M.; Mittler, S.; Knoll, W. *Langmuir* **2003**, *19*, 9518.

(2) Martín, R.; Heydorn, P. C. n.; Alvaro, M.; Garcia, H. *Chem. Mat.* **2009**, *21*, 4505.

(3) Bueno-Alejo, C. J.; D'Alfonso, C.; Pacioni, N. L.; González-Béjar, M.; Grenier, M.; Lanzalunga, O.; Alarcon, E. I.; Scaiano, J. C. *Langmuir* **2012**, *28*, 8183.