Supporting information

Glass wool: a novel support for heterogeneous catalysis

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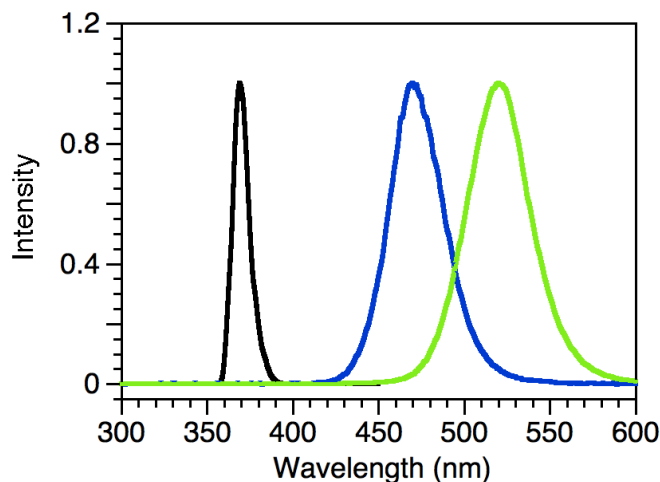1. EXPERIMENTAL DETAILS

1.1. Instrumentation

Figure S1. Normalized emission spectra of the LEDs used in this work: 368 nm (black), 465 nm (blue) and 532 nm (green).

1.2. Catalyst Preparation

1.2.1. Glass wool pre-treatments

1.2.1.1. Activation using harsh acid-conditions

Surface activation of SGW was performed using HCl 6M solution, sodium hydroxide NaOH 6M, MeOH:HCl solution[1] and piranha solution[2]. In order to determine the best activation method, the materials were subjected to AuNPs loading. This metal was selected as the formation of AuNP on the GW surface would turn the off-white color of GW into purple/pink when the particles are successfully anchored to the surface, thus giving an easy way to determine the metal modification. Among the different activation processes only two seemed to successfully attach AuNPs to the surface (pink color, see Figure 2i in MS), these are the treatments with HCl or NaOH. However, the last one changes drastically the mechanical properties of the GW, which after treatment becomes harder and brittle, converting the fibers in a fine powder. For this reason, only the treatment with HCl was considered for further work. Briefly, the SGW was soaked for 3 days in a 6M HCl solution and then recovered by filtration, washed several times with pure water until pH ~6 is reached. The resulting material was dried in the oven at 100°C overnight prior to further functionalization.

1.2.1.2. Activation using (3-Aminopropyl)triethoxysilane (APTES)

Both, the HCl-treated SGW and NGW surfaces were further modified by the addition of APTES. The APTES-amino groups are believed to facilitate the formation of siloxane bonds with surface Si-OH.[3-4] Briefly, APTES was grafted by immersing the NGW (or SGW) in a solution of 1% concentration of APTES in HPLC grade toluene and heating at 110 °C overnight to allow monolayer coverage.[5] After cooling down to room temperature, the mixture was stirred for 6 hours and then washed with toluene (3x) and acetone (3x) in order to remove weakly bonded silane molecules and hydrolyzes residual alkoxy linkages in the silanized layer. The resulting material was dried in the oven at 100°C overnight prior to metal decoration. We will refer with an asterisk all GW subjected to APTES modification (*i.e.*, GW*).

1.2.2. Metal decoration

1.2.2.1. Thermal methods

Ru@NGW* and Ru@SGW*: Ru supported on NGW activated with APTES (NGW*) was prepared as follows: 500 mg of NGW* and 50 mg of RuCl$_3$•xH$_2$O (enough for 3% Ru@NGW*, w/w%) were dispersed in 50 mL of Milli-Q water. The resulting mixture was stirred overnight in a fumehood prior to filtration and then washed with Milli-Q water at least five times to remove unreacted species. The resulting material was dried in an oven overnight at 100°C. The light grey fibers were characterized by SEM, XPS, ICP-EOS and EDS. Same protocol was followed for Ru supported on APTES-treated SGW (SGW*).

Pd@NGW*. Palladium supported on NGW activated with APTES was prepared using the protocol described for the synthesis of Ru@NGW. The material was prepared aiming for 2% Pd@NGW*, w/w%. The resulting brownish fibers were characterized by SEM, XPS, ICP-EOS and DRS.

1.2.2.2. Photochemical methods
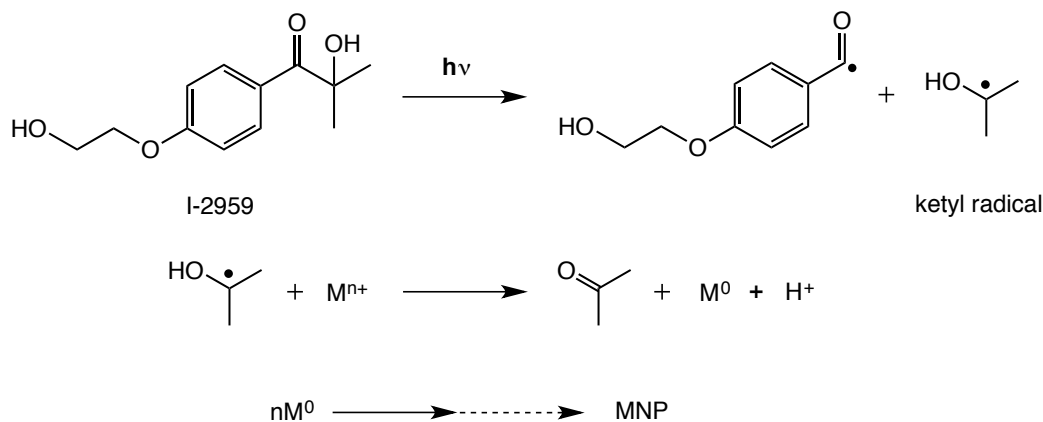
Scheme S1. Norrish Type I cleavage of the benzoin I-2959 forming ketyl radicals that subsequently can reduce metal cations into the corresponding metal species.

Synthesis of Pd@SGW. Palladium supported on SGW was prepared by photodeposition of $PdCl_2$ onto the SGW. In brief, 500 mg of activated SGW and $PdCl_2$ (22 mg, for 3% Pd@SGW, w/w%) were dispersed in 200 mL of Milli-Q water and sonicated for 15 min. Next, 24 mg of the I-2959 in 10 mL of EtOH 99% were added as a photo-initiator, the resulting mixture was purged with Ar for 15 min then irradiated in a Luzchem photoreactor equipped with 14 UVA bulbs for 1 h under vigorous stirring. The brownish/grey fibers were filtered and washed with Milli-Q water at least five times to remove unreacted $PdCl_2$ and dried in the oven overnight at 100°C. The resulting dark gray fibers were characterized by SEM, XPS, ICP-EOS and DRS.

Synthesis of Co@SGW. Cobalt supported on SGW was prepared by photodeposition of $CoCl_2$ onto HCl-treated SGW using the same procedure as for Pd@SGW utilizing enough Co precursor to obtain 3 % Co@SGW, w/w%. The resulting light gray fibers were characterized by SEM, XPS, ICP-EOS and DRS.

Synthesis of Cu@NGW. Copper supported on pristine NGW and on NGW* was prepared by photodeposition of $CuCl_2.2H_2O$ (enough amount for 5% Cu@GW w/w%) onto NGW (or NGW*) using the same procedure explained above for Pd@SGW. The resulting brownish/redish fibers were characterized by SEM, XPS, ICP-EOS and DRS.

Synthesis of Au@NGW. Gold supported on NGW* was prepared by photodeposition of HAuCl$_4$ (for 3% Au@NGW*, w/w%) onto NGW*. The resulting purple fibers were characterized by SEM, XPS, ICP-EOS and DRS.
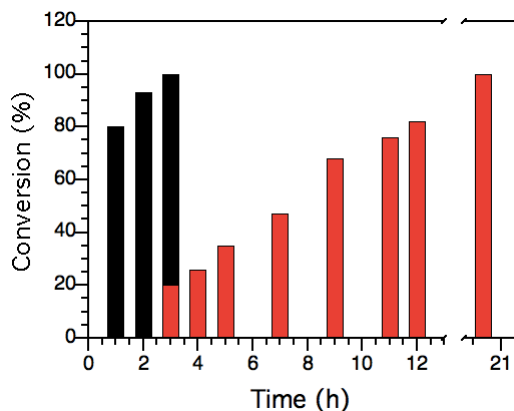
1.3. Catalytic reactions

Figure S2. Photoreductive dehalogenation of 4-chloromethylbenzoate catalyzed by Co@SGW (Black) and Pd@SGW (red) under conditions described in Table 3.
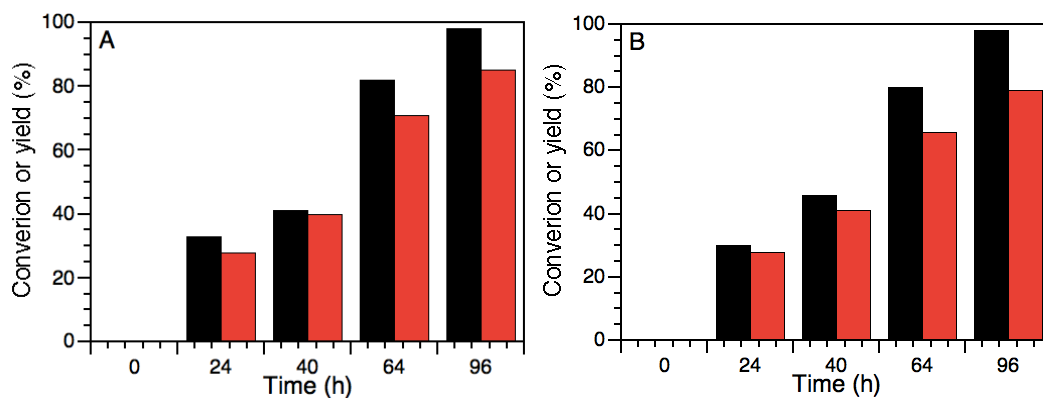

Figure S3. Kinetics of Reduction of nitrobenzene to aniline catalysed by (A) Ru@SGW* and (B) Ru@NGW*. Conversion (black) and yield (red).
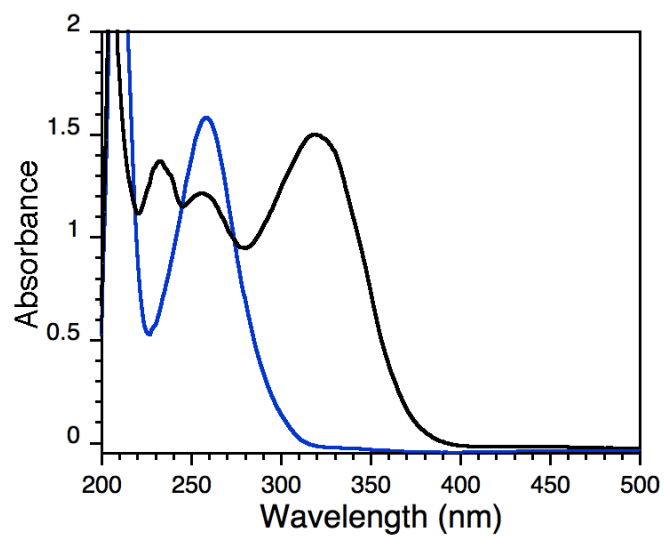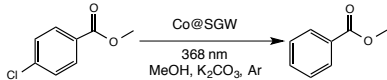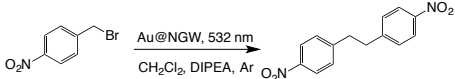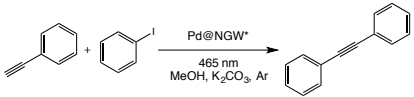
Figure S4. Photoreduction of nitrobenzene toward azobenzene catalyzed by Au@NGW* under conditions described in table 5, entry i. Absorption spectra of reaction mixture before (blue) and after 24 h of irradiation (black).

1.5. Catalyst Recyclability

Table S1. Catalyst reusability

Reaction	Catalyst	Cycle	Time (h)	% Conv	%Yield	Apparent rate (M h^{-1})
		1	3	100	>99	>13.3
		2	3	100	>99	>13.3
	Co@SGW	3	3	75	75	10.0
		3^a	4	100	>99	>10.0
		1	5	77	64	3.9
		1	7	100	80	>3.6
	Au@NGW*	2	5	58	43	2.9
		2^b	24	82	66	0.9
		1	5	100	90	6.0
	Pd@NGW*	2	5	90	68	5.4
		2^c	7	100	87	>4.3

[a] Remaining Co loading = (0.0276 ± 0.0004)%. [b] Remaining Au loading = (0.592 ± 0.007)%; Au particle size = (35 ± 12) nm. [c] Remaining Pd loading = (0.369 ± 0.007)%; Pd particle size = (28 ± 10) nm.

2. CHARACTERIZATION OF THE CATALYSTS

2.1. Electron microscopy characterization
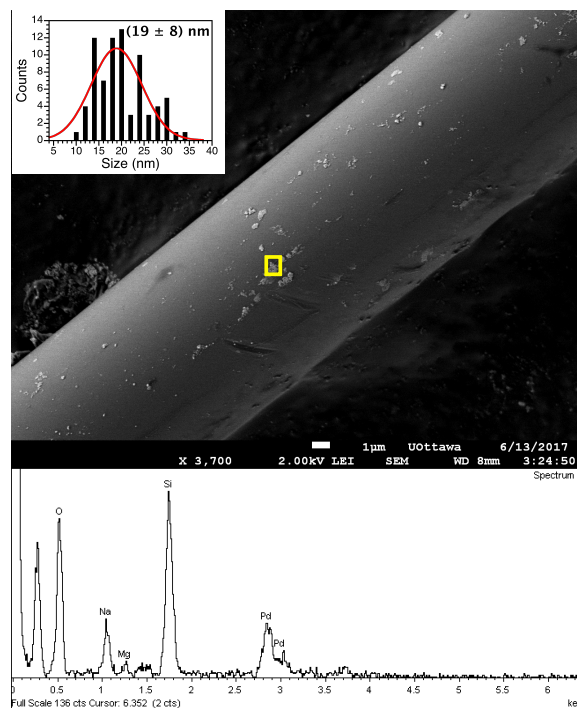
Figure S5. SEM image and particle size distribution (*top*) and EDS spectrum of the squared area (*bottom*) of Pd@SGW. Notice that agglomerated particles were not considered to determine particle size distribution.
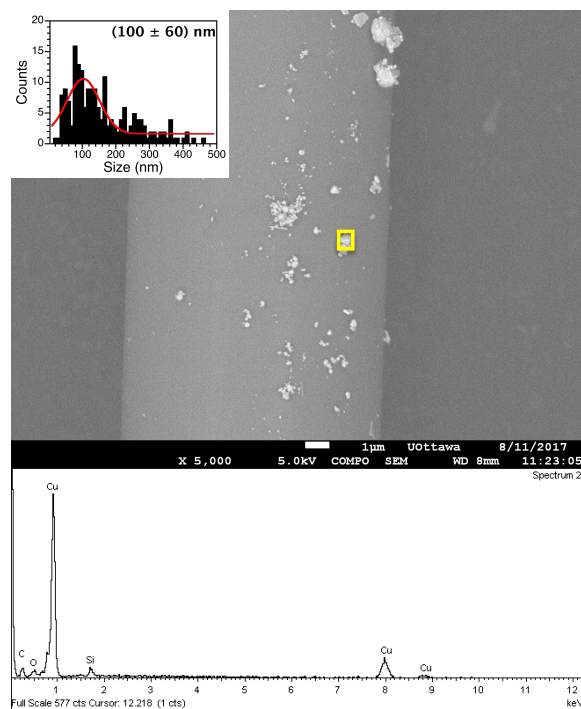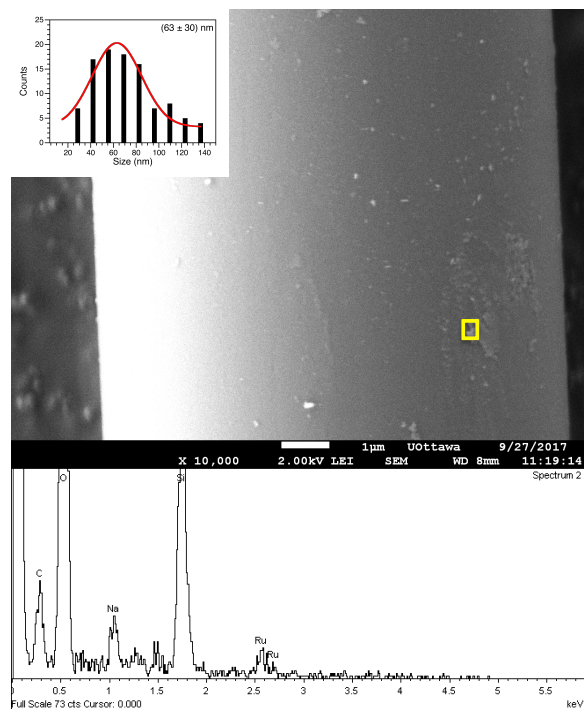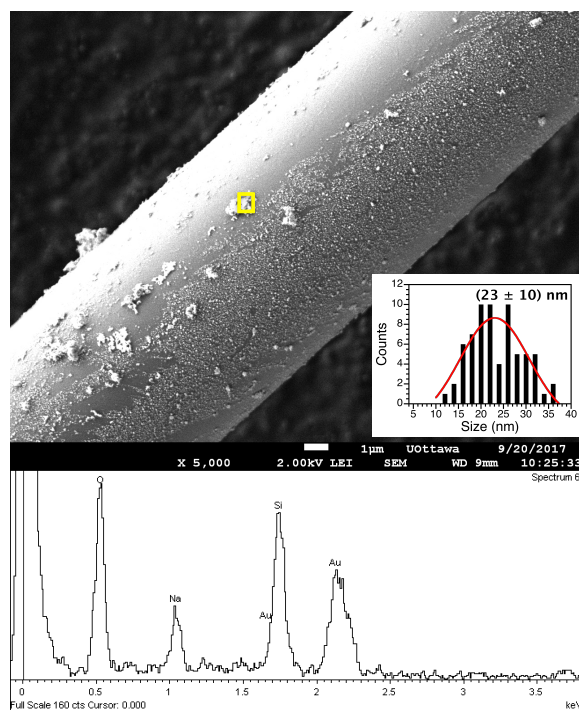
Figure S6. SEM image and particle size distribution (*top*) and EDS spectrum of the squared area (*bottom*) of Cu@NGW. Notice that agglomerated particles were not considered to determine particle size distribution.

Figure S7. SEM image and particle size distribution (*top*) and EDS spectrum of the squared area (*bottom*) of Ru@NGW*. Notice that agglomerated particles were not considered to determine particle size distribution.

Figure S8. SEM image and particle size distribution (*top*) and EDS spectrum of the squared area (*bottom*) of Au@NGW*. Notice that agglomerated particles were not considered to determine particle size distribution.

2.2. Diffuse reflectance spectroscopy
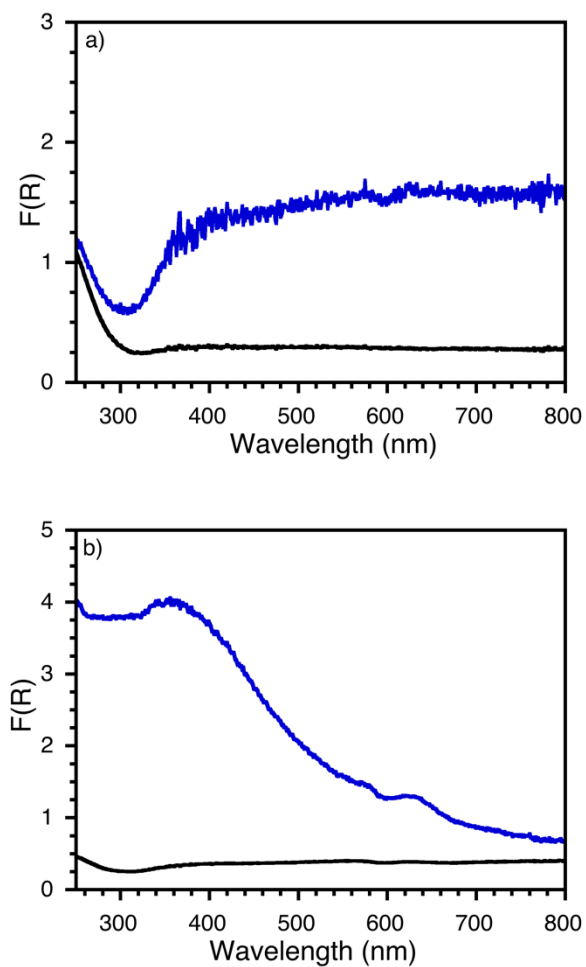
Figure S9. a) Diffuse reflectance spectra for HCl-treated SGW (black) and for Pd@SGW (blue) and b) for NGW* (black) and for Pd@NGW* (blue).
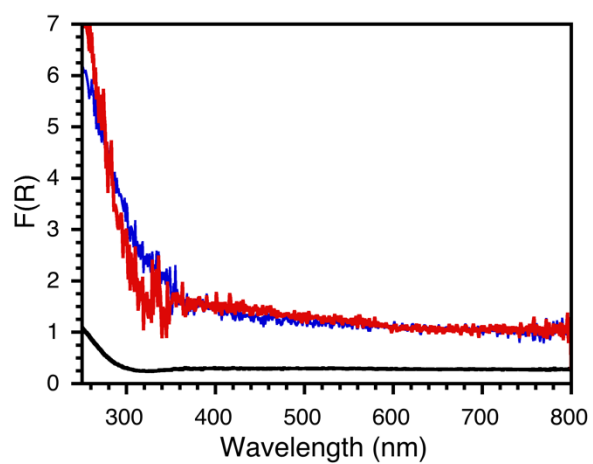
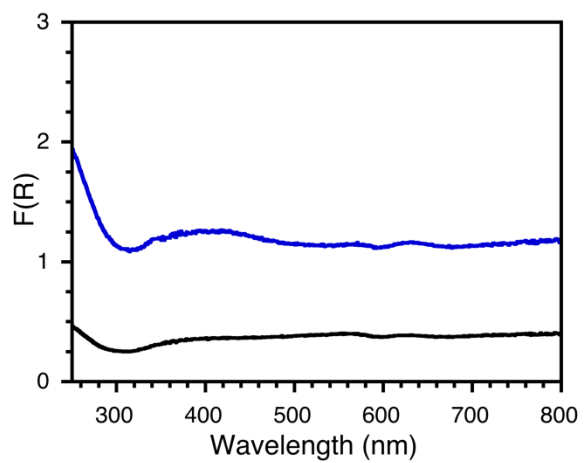Figure S10. Diffuse reflectance spectrum of treated NGW* (black), Cu@NGW* (blue) and Cu@NGW (red)

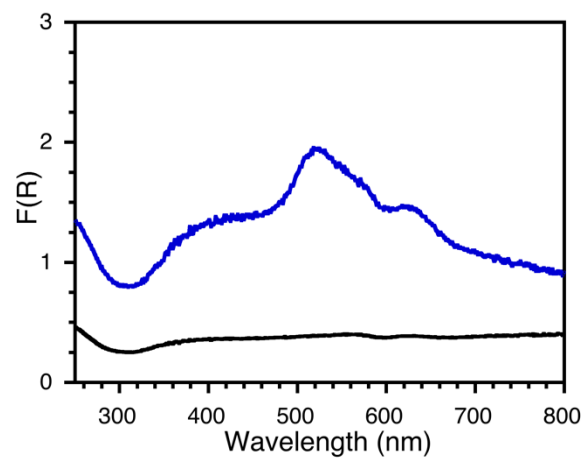Figure S11. Diffuse reflectance spectrum of treated NGW* (black) and Ru@NGW* (blue)

Figure S12. Diffuse reflectance spectrum of treated NGW* (black) and Au@NGW* (blue)
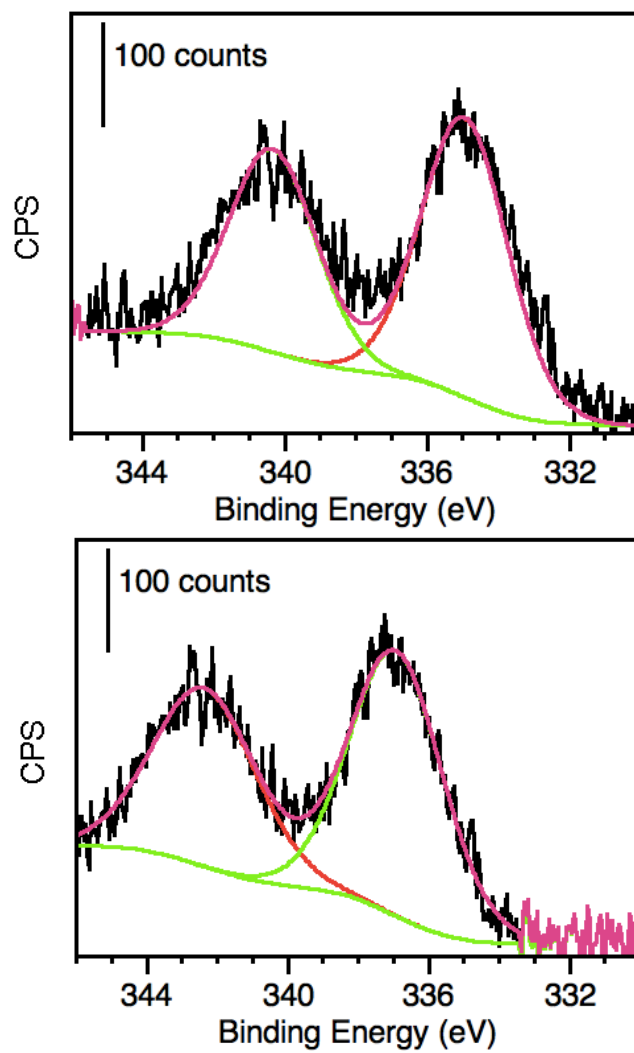
2.3. X-ray Photoelectron Spectroscopy

Figure S13. Deconvoluted Pd 3d HR-XPS spectrum for Pd@SGW (*top*) and Pd@NGW* (*bottom*) catalysts.
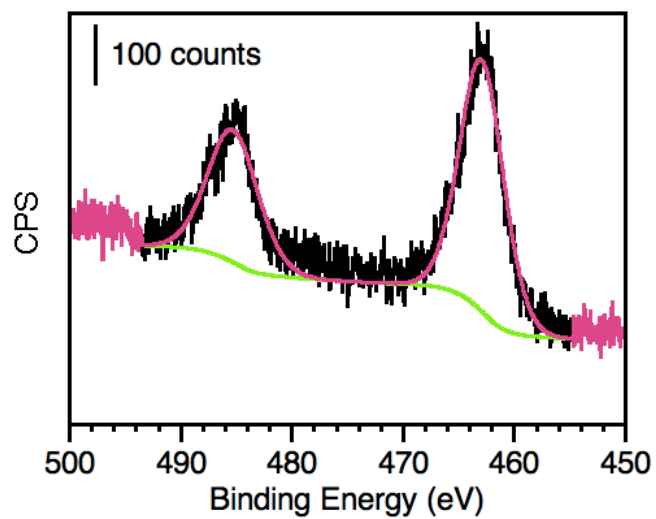
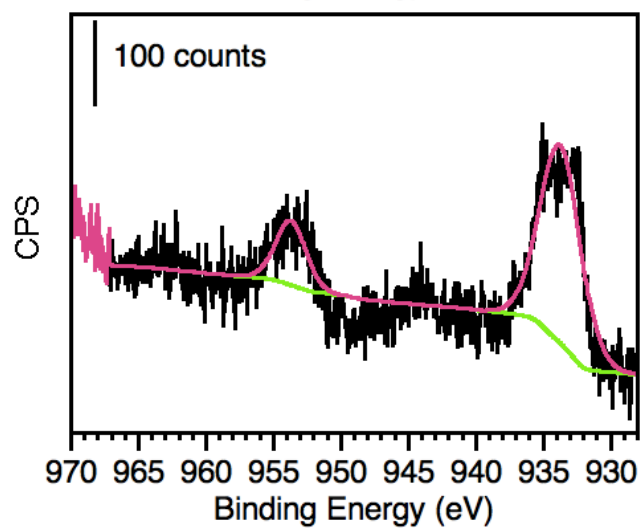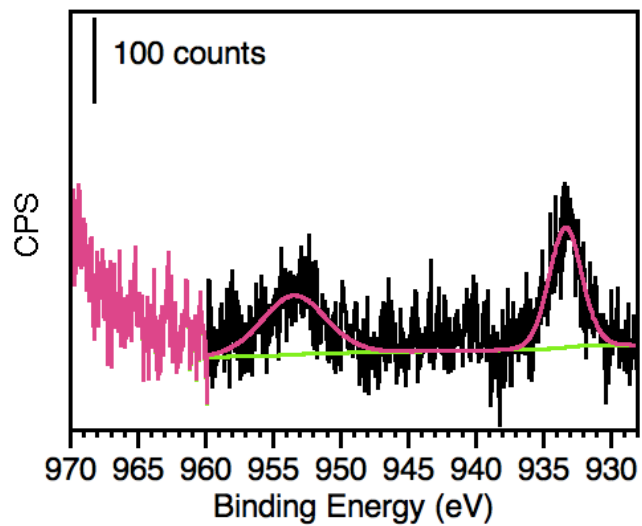Figure S14. Deconvoluted Ru 3p HR-XPS spectrum for Ru@NGW* catalyst.

Figure S15. Deconvoluted Cu 2p HR-XPS spectrum for Cu@NGW (*top*) and Cu@NGW* (*bottom*).
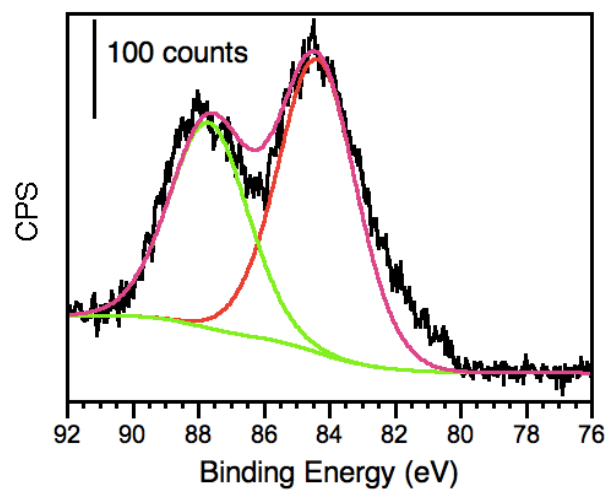
Figure S16. Deconvoluted Au 4f HR-XPS spectrum for Au@NGW* catalyst.
ICP-OES analysis

3. REFERENCES

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