Supporting Information

Plasmonic Au-Pd Bimetallic Nanocatalysts for Hot Carrier Enhanced Photocatalytic and Electrochemical Ethanol Oxidation

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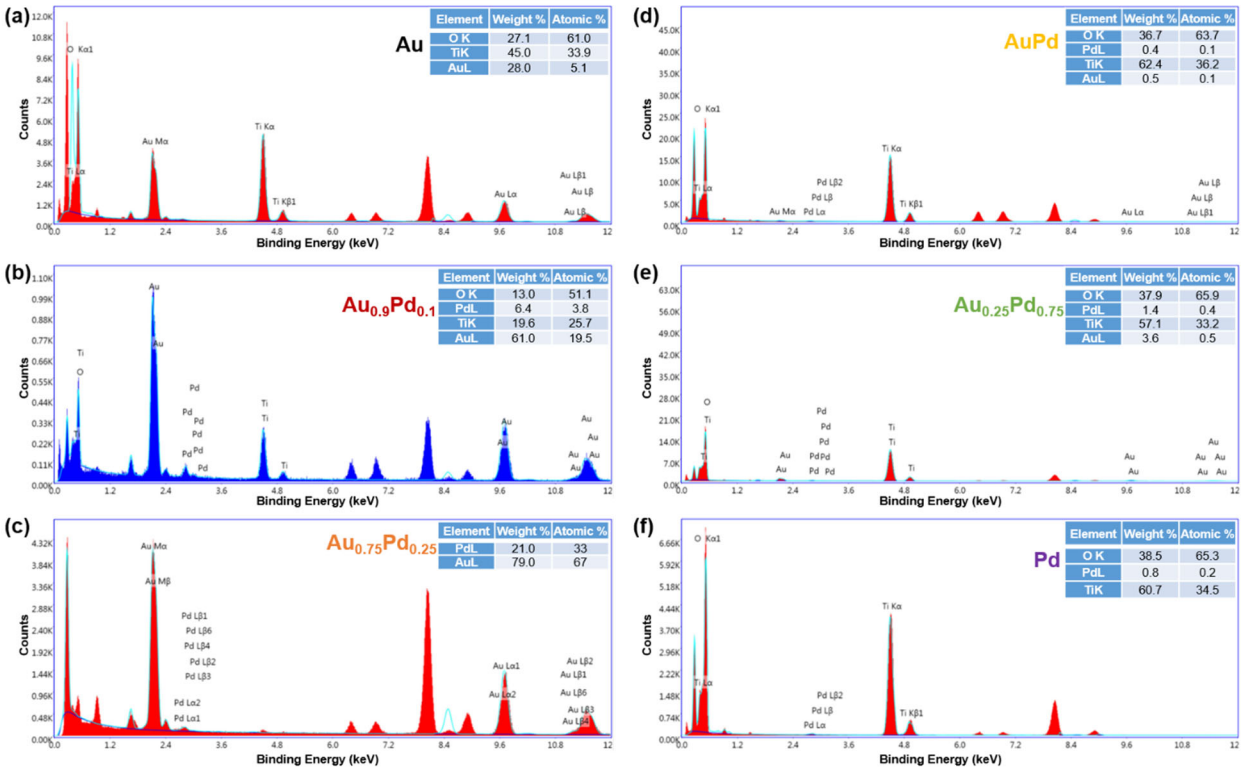

Figure S1. EDX spectra representative of $Au_{1-x}Pd_x$ NPs for (a) Au, (b) $Au_{0.9}Pd_{0.1}$, (c) $Au_{0.75}Pd_{0.25}$, (d) $Au_{0.5}Pd_{0.5}$, (e) $Au_{0.25}Pd_{0.75}$, and (f) Pd NPs on a TiO_2 support.

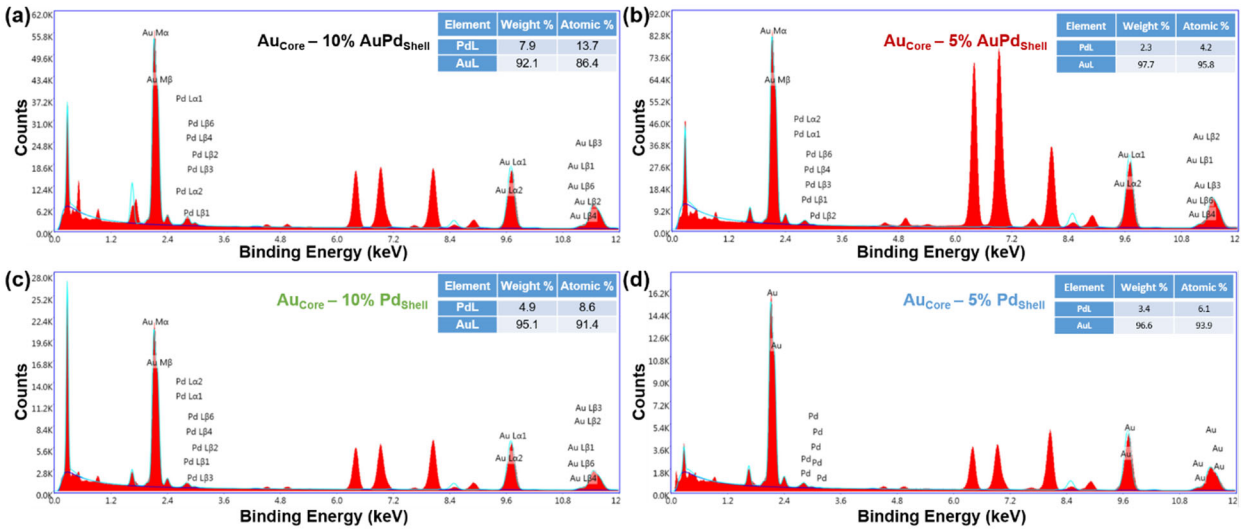

Figure S2. EDX spectra representative of Au$_{Core}$ NPs with (a) 10% Au$_{0.5}$Pd$_{0.5}$.Shell, (b) 5% Au$_{0.5}$Pd$_{0.5}$.Shell, (c) 10% Pd.Shell, and (d) 5% Pd.Shell.

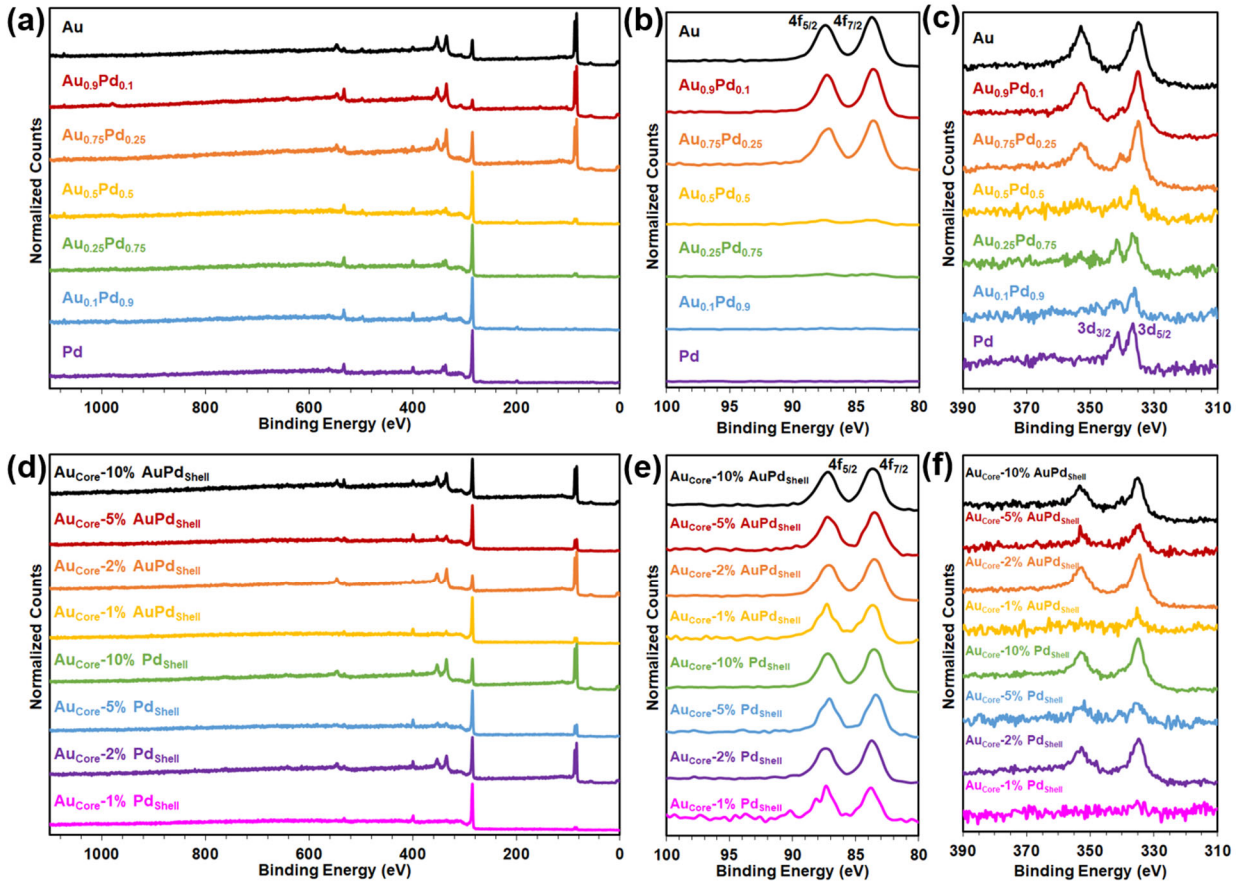

Figure S3. XPS survey scans, Au 4f and Pd 3d peaks of the (a-c) Au$_{1-x}$Pd$_x$ alloy and (d-f) Au$_{Core}$-Au$_{1-x}$Pd$_{x.Shell}$ NPs.

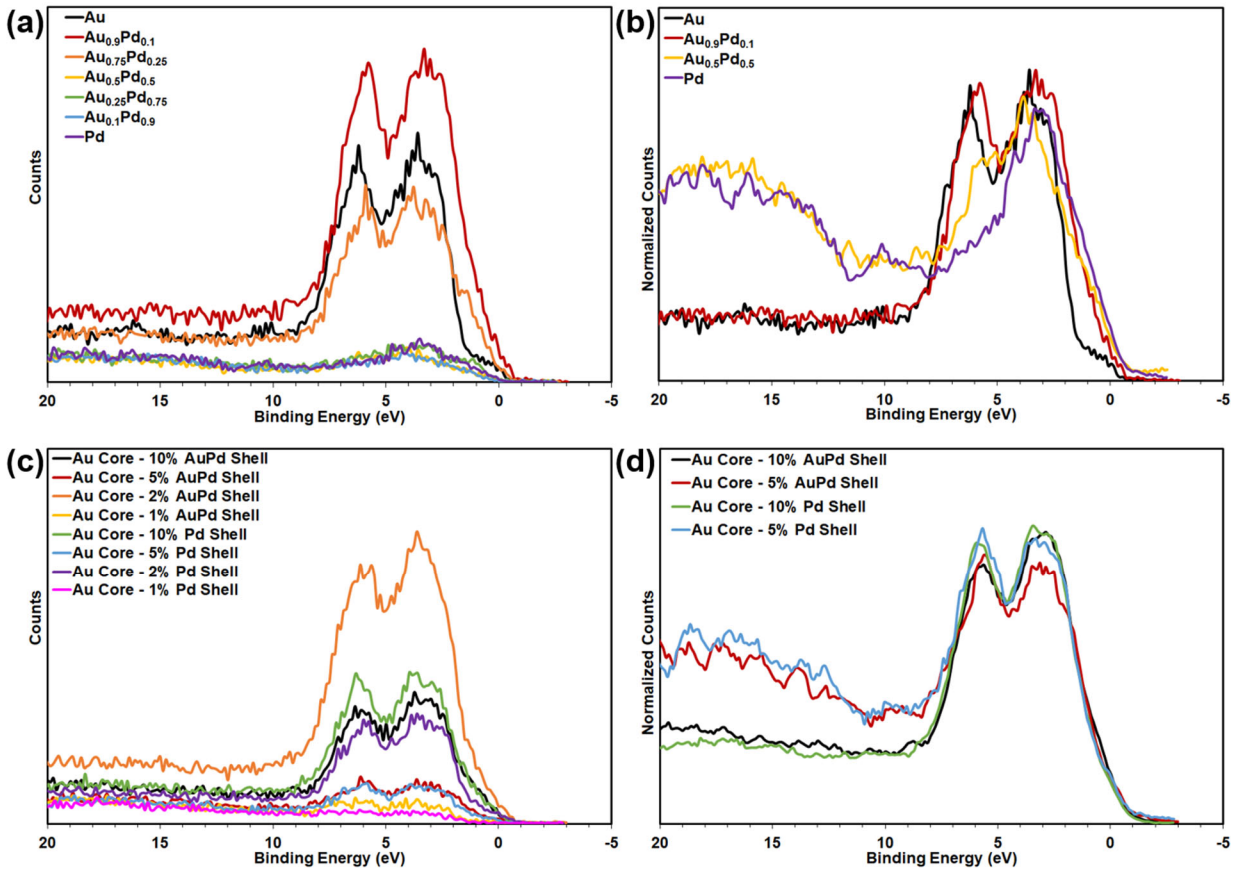

Figure S4. XPS scans of the VB region for (a-b) $Au_{1-x}Pd_x$ alloy and (c-d) Au_{Core}-$Au_{1-x}Pd_{x\,Shell}$ NPs.

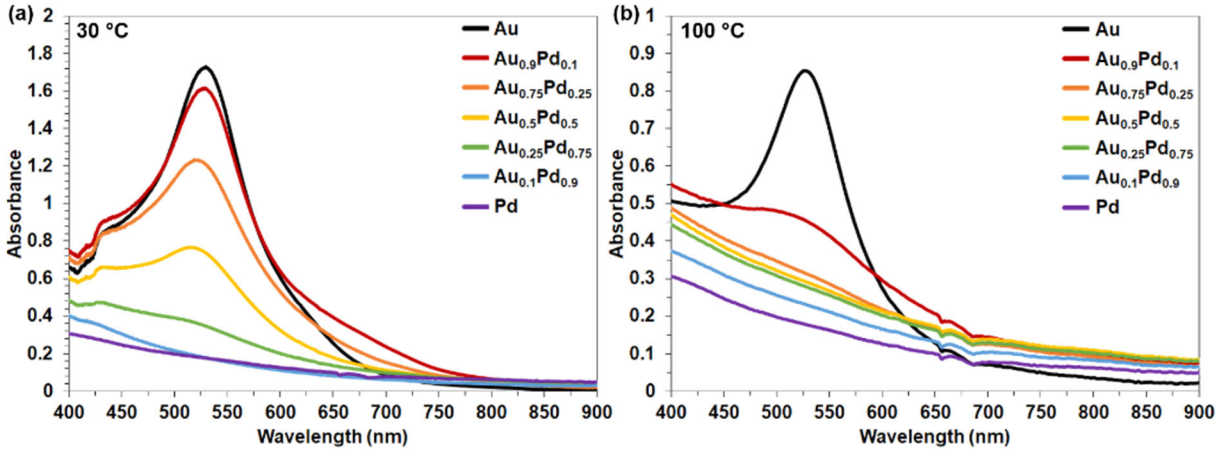

Figure S5. UV-Vis extinction spectra of $Au_{1-x}Pd_x$ NPs after synthesis at (a) 30 °C and (b) 100 °C.

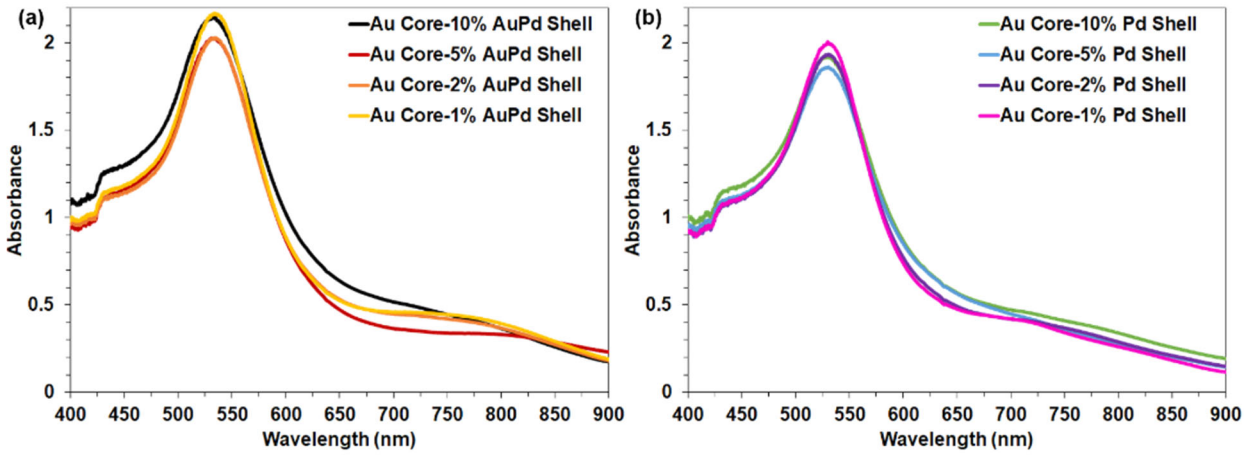

Figure S6. UV-Vis extinction spectra of Au_{Core} NPs with (a) 1-10% $Au_{0.5}Pd_{0.5}$.Shell and (b) 1-10% Pd.Shell after synthesis at 30 °C.

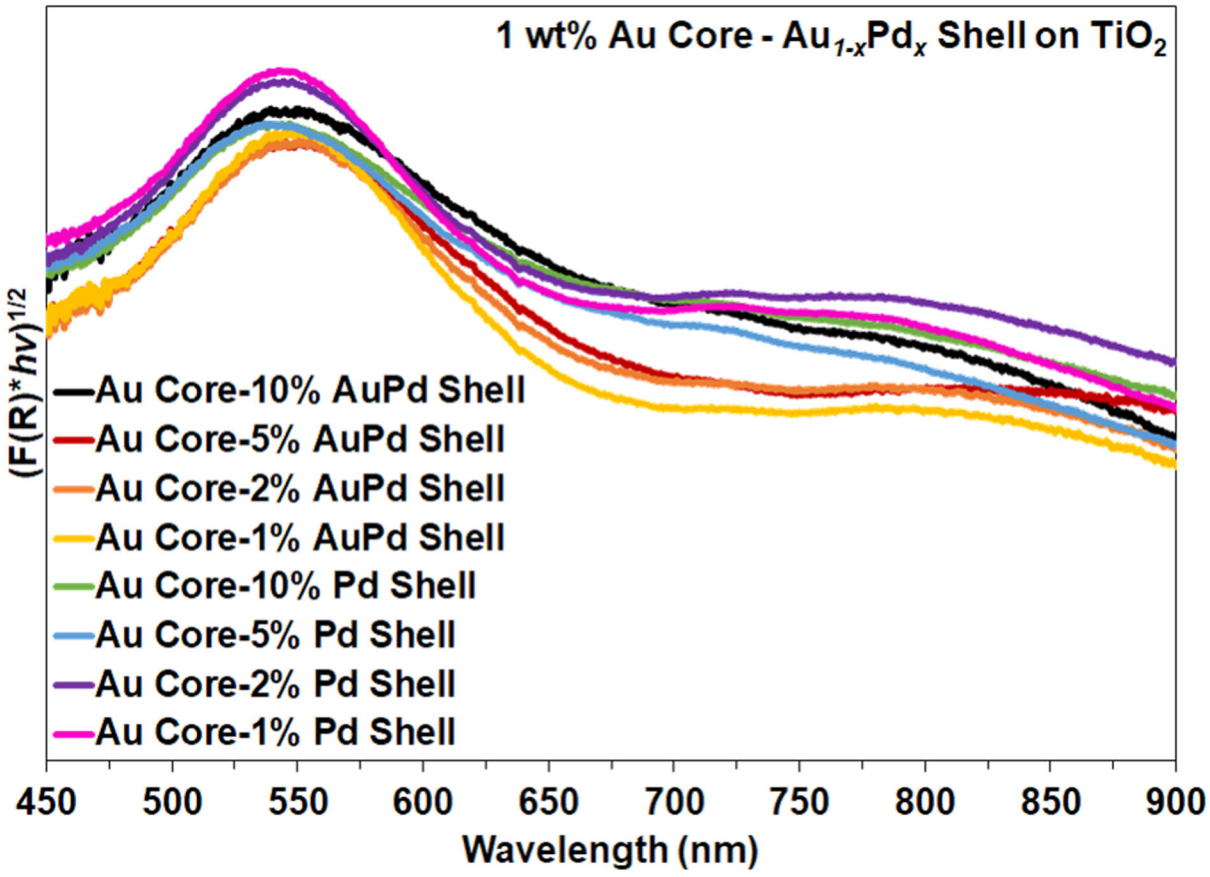

Figure S7. UV-Vis DRS of Au_{Core} NPs with 1-10% $Au_{0.5}Pd_{0.5}$.Shell and 1-10% Pd.Shell on TiO_2 supports.

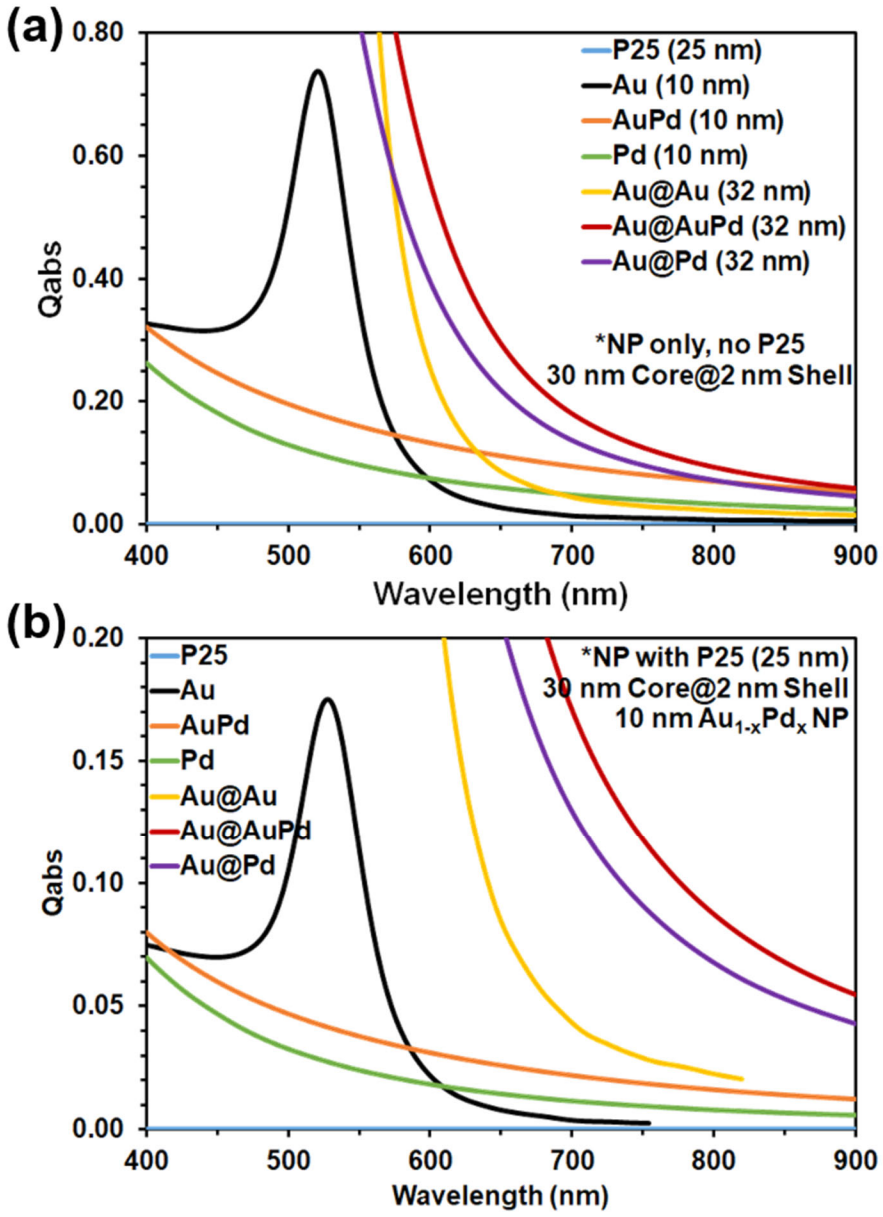

Figure S8. DDA simulated absorption spectra for spherical $Au_{1-x}Pd_x$ and Au_{Core}-$Au_{1-x}Pd_{x,Shell}$ NPs (c) without TiO_2 and (d) in contact with TiO_2. Rescaled spectra from Figure 4 in manuscript for clarity of nanomaterials with simulated low absorbance.

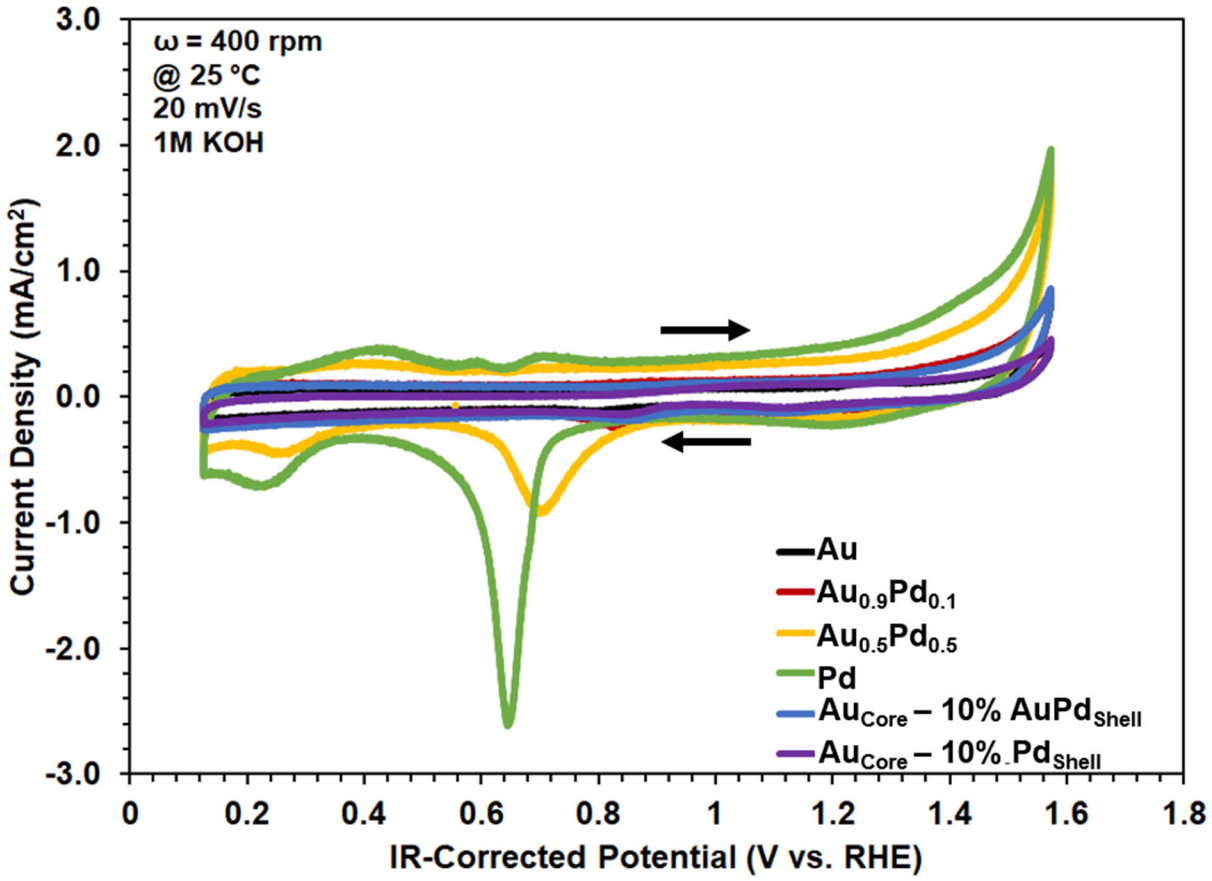

Figure S9. Electrochemical CVs in 1 M KOH supporting electrolyte (pH~14) catalysed by 60 µg of 20 wt% $Au_{1-x}Pd_x$ and Au_{Core}-$Au_{1-x}Pd_{x.Shell}$ NPs dispersed on carbon supports deposited onto a rotating disk, glassy carbon working electrode in the dark. Reference and counter electrodes were Ag/AgCl and a Pt coil, respectively.

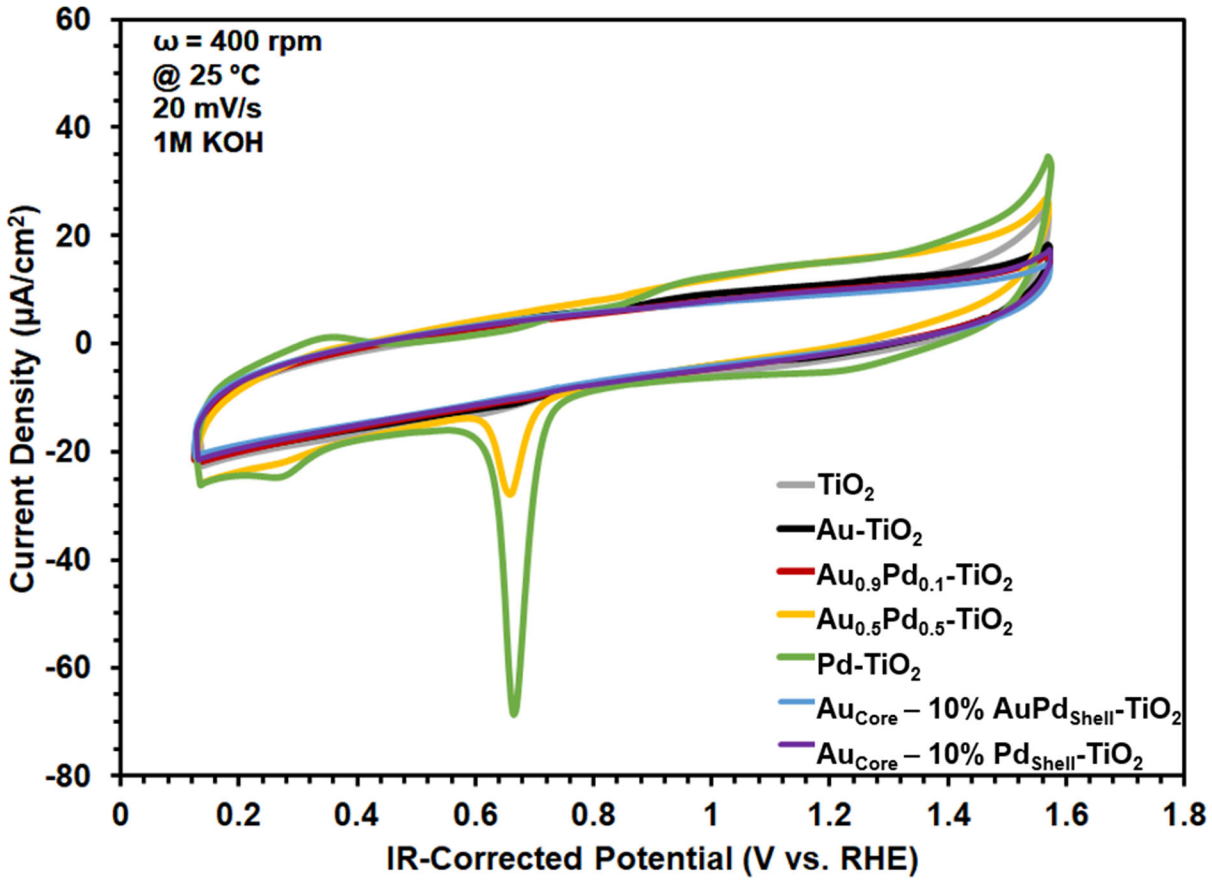

Figure S10. Electrochemical CVs in 1 M KOH supporting electrolyte (pH~14) catalysed by 60 µg of 1 wt% $Au_{1-x}Pd_x$ and Au_{Core}-$Au_{1-x}Pd_{x.Shell}$ NPs dispersed on TiO_2 supports deposited onto a rotating disk, glassy carbon working electrode in the dark. Reference and counter electrodes were Ag/AgCl and a Pt coil, respectively.

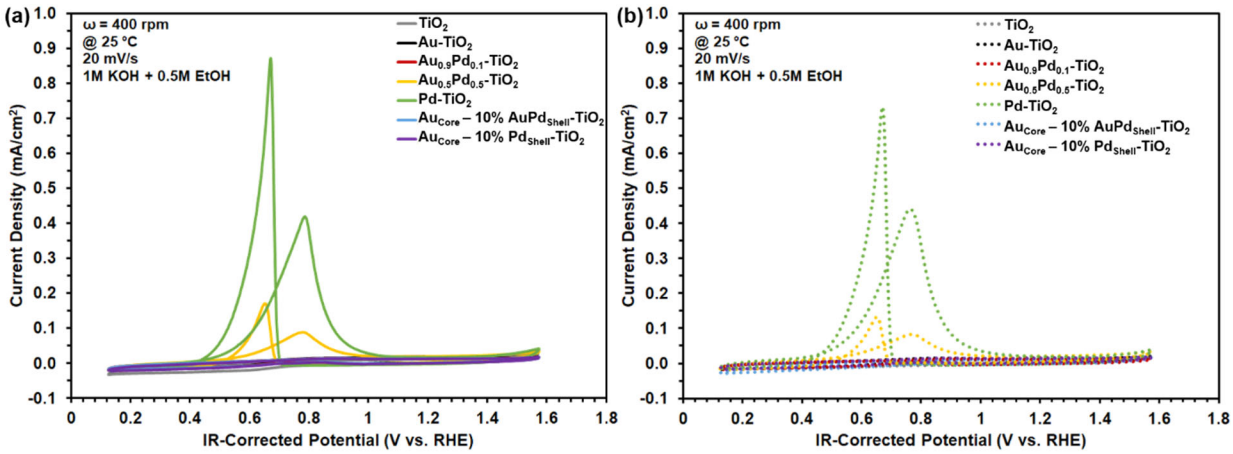

Figure S11. Electrochemical CVs of EtOH oxidation catalyzed by 1 wt% $Au_{1-x}Pd_x$ and Au_{Core}-$Au_{1-x}Pd_{x.Shell}$ NPs dispersed on TiO_2 deposited onto a rotating disk, glassy carbon working electrode immersed into 0.5 M EtOH with 1 M KOH supporting electrolyte. Reference and counter electrodes were Ag/AgCl and a Pt coil, respectively. CVs of the current density in the (a) dark and under (b) AM1.5G irradiation.

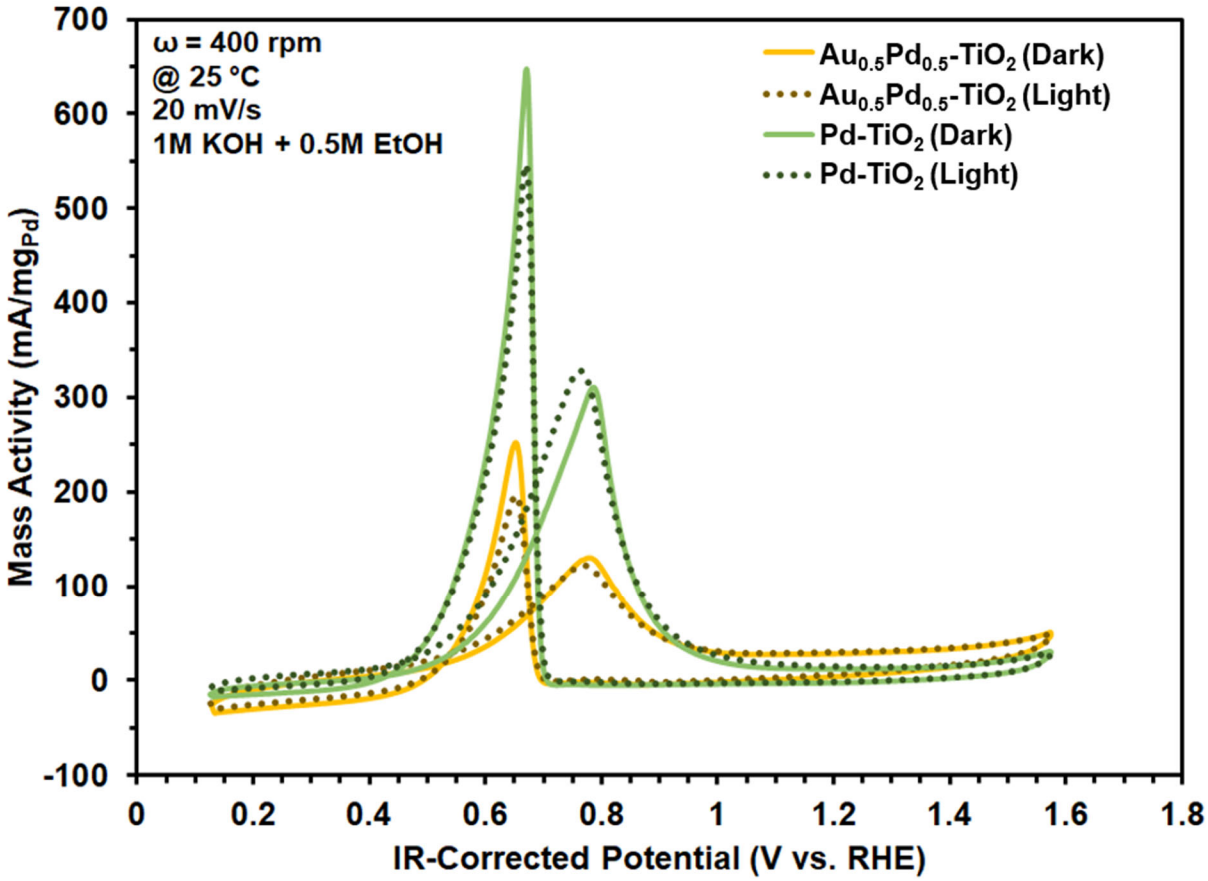

Figure S12. Electrochemical CVs of EtOH oxidation catalyzed by 1 wt% AuPd and Pd NPs dispersed on TiO_2 deposited onto a rotating disk, glassy carbon working electrode immersed into 0.5 M EtOH with 1 M KOH supporting electrolyte. Reference and counter electrodes were Ag/AgCl and a Pt coil, respectively. CVs of the mass activity (Pd) in the dark and under AM1.5G irradiation.

Table S1. Experimental and DDA calculated SPR peaks (λ_{Max}) for $Au_{1-x}Pd_x$ and Au_{Core}-$Au_{1-x}Pd_{x\text{-}Shell}$ NPs without TiO_2 and in contact with TiO_2

Composition	Experimental w/o TiO_2	Calculated w/o TiO_2	Experimental w/ TiO_2	Calculated w/ TiO_2
Au	526	521	547	528
$Au_{0.9}Pd_{0.1}$	526	-	545	-
$Au_{0.75}Pd_{0.25}$	-	-	539	-
$Au_{0.5}Pd_{0.5}$	-	-	532	-
$Au_{0.25}Pd_{0.75}$	-	-	512	-
$Au_{0.1}Pd_{0.9}$	-	-	452	-
Pd	-	-	450	-
Au-10% AuPd	529	519	550	522
Au-5% AuPd	535	-	550	-
Au-2% AuPd	535	-	553	-
Au-1% AuPd	534	-	550	-
Au-10% Pd	530	506	547	508
Au-5% Pd	530	-	539	-
Au-2% Pd	530	-	548	-
Au-1% Pd	530	-	543	-

Table S2. Mass activity of 1 wt% $Au_{1-x}Pd_x$ and Au_{Core}-$Au_{1-x}Pd_{x,Shell}$ NPs on TiO_2 supports under AM1.5G irradiation for 1 h determined from GC-MS-MHE analysis.

Sample	µmol CO_2/g	µmol CH_3CHO/g
TiO_2	87.11	0.60
Au	132.32	0.26
$Au_{0.9}Pd_{0.1}$	147.09	0.37
$Au_{0.75}Pd_{0.25}$	176.76	0.63
$Au_{0.5}Pd_{0.5}$	221.67	0.96
$Au_{0.25}Pd_{0.75}$	226.43	0.92
$Au_{0.1}Pd_{0.9}$	228.62	0.84
Pd	225.33	0.89
Au-10% AuPd	164.99	0.36
Au-5% AuPd	162.70	0.27
Au-2% AuPd	152.13	0.19
Au-1% AuPd	153.65	0.17
Au-10% Pd	283.28	1.06
Au-5% Pd	254.12	0.66
Au-2% Pd	249.02	0.72
Au-1% Pd	222.72	0.63

Table S3. Photocatalytic mass activities of 1 wt% $Au_{1-x}Pd_x$ and Au_{Core}-$Au_{1-x}Pd_{x,Shell}$ NPs for select compositions on TiO_2 supports under AM1.5G for 4 h and visible-light (>420 nm) for 1 h, determined from GC-MS-MHE analysis.

Sample	AM1.5G for 4h		>420 nm for 1 h	
	µmol CO_2/g	µmol CH_3CHO/g	µmol CO_2/g	µmol CH_3CHO/g
TiO_2			15.22	0.01
Au	292.35	1.82	19.24	0.19
$Au_{0.9}Pd_{0.1}$	394.63	1.84	21.64	0.01
$Au_{0.5}Pd_{0.5}$	455.67	3.86	30.34	0.02
Pd	327.98	3.57	32.63	0.09
Au-10% AuPd	403.13	1.61	30.03	0.03
Au-10% Pd	390.72	2.28	25.45	0.02

Table S4. Photo-induced current densities for 1 wt% $Au_{1-x}Pd_x$ and Au_{Core}-$Au_{1-x}Pd_{x,Shell}$ NPs dispersed on TiO_2 from chronoamperometry held at +0.72 V (vs. RHE) under 250 s on/off chopping of solar-simulated AM1.5G irradiation. Catalysts deposited onto a rotating disk, glassy carbon working electrode immersed into 0.5 M EtOH with 1 M KOH supporting electrolyte. Reference and counter electrodes were Ag/AgCl and a Pt coil, respectively.

Composition	Max I_{hv} ($\mu A/cm^2$)[a]	Avg. I_{hv} ($\mu A/cm^2$)[b]	I_{hv} ($\mu A/cm^2$) @ 1900 s
TiO_2	3.09	2.29	3.09
Au-TiO_2	1.46	1.31	0.69
$Au_{0.9}Pd_{0.1}$-TiO_2	1.39	1.31	0.74
AuPd-TiO_2	9.55	8.32	6.86
Pd-TiO_2	5.85	4.74	4.93
Au-10% AuPd-TiO_2	2.12	1.43	0.86
Au-10% Pd-TiO_2	2.17	1.97	0.96

[a]Overall maximum photocurrent magnitude measured.
[b]Average photocurrent magnitude measured during the first "light on" step.

Table S5. Photo-induced mass activities (Pd) for 1 wt% $Au_{1-x}Pd_x$ and Au_{Core}-$Au_{1-x}Pd_{x,Shell}$ NPs dispersed on TiO_2 from chronoamperometry held at +0.72 V (vs. RHE) under 250 s on/off chopping of solar-simulated AM1.5G irradiation. Catalysts deposited onto a rotating disk, glassy carbon working electrode immersed into 0.5 M EtOH with 1 M KOH supporting electrolyte. Reference and counter electrodes were Ag/AgCl and a Pt coil, respectively.

Composition	Max I_{hv} (mA/mg_{Pd})[a]	Avg. I_{hv} (mA/mg_{Pd})[b]	I_{hv} (mA/mg_{Pd}) @ 1900 s
$Au_{0.9}Pd_{0.1}$-TiO_2	10.30	9.76	5.53
AuPd-TiO_2	14.20	12.40	10.20
Pd-TiO_2	4.35	3.53	3.67
Au-10% AuPd-TiO_2	15.70	10.60	6.42
Au-10% Pd-TiO_2	16.10	14.70	7.15

[a]Overall maximum photocurrent magnitude measured.
[b]Average photocurrent magnitude measured during the first "light on" step.