Supporting Information

Peptide-directed Pd-decorated Au and PdAu Nanocatalysts for Degradation of Nitrite in Water

Imann Mosleh and Alireza Abbaspourrad*

Department of Food Science, College of Agricultural and Life Sciences, Cornell University, Stocking Hall, Ithaca, NY, 14853

* *E-mail: alireza@cornell.edu*

Table of Contents

Schematic of reaction setup

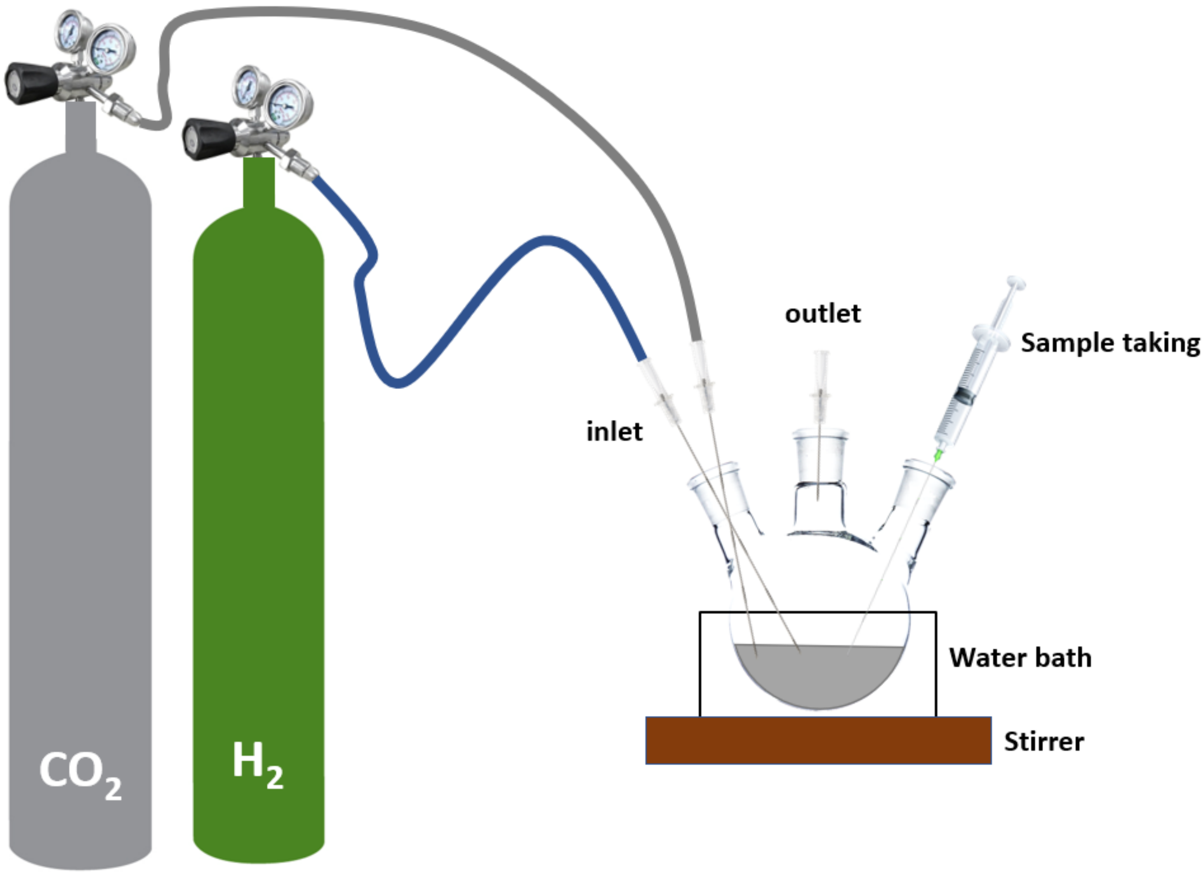

Fig. S1. Schematic of reaction setup for nitrite reduction reactions.

Nanoparticles preparation and their respective TOF values

Table S1. Comparison of the weight percent of palladium on TOF with respect to NP preparation.

Pd wt %	Pd-on-Au Nanoparticles		PdAu alloy Nanoparticles	
	Pd sc %	TOF (mol NO_2^{-1} mol $_{Pd}^{-1}$ min^{-1})	Pd_xAu_{100-x}	TOF (mol NO_2^{-1} mol $_{Pd}^{-1}$ min^{-1})
0	0	0	–	–
6.48	20	1.58	Pd_6Au_{94}	1.07
12.25	40	2.56	$Pd_{12}Au_{88}$	1.43
17.29	60	3.63	$Pd_{17}Au_{83}$	1.56
21.83	80	3.97	$Pd_{22}Au_{78}$	1.75
25.85	100	5.33	$Pd_{26}Au_{74}$	1.91
45.13	200	4.38	$Pd_{45}Au_{55}$	2.17
59.03	300	3.20	$Pd_{59}Au_{41}$	2.27
100	–	1.48	–	–

D-spacing measurements

Table S2. Measured d-spacing for different lattices and metallic PdAu alloys.

Pd_xAu_{100-x}	Measured d-spacing for different miller indices assignment (nm)			
	(111)	(200)	(220)	(311)
Pd_0Au_{100}	0.2351	0.2030	0.1440	0.1230
Pd_6Au_{94}	0.2344	0.2024	0.1436	0.1226
$Pd_{12}Au_{88}$	0.2337	0.2019	0.1432	0.1223
$Pd_{17}Au_{83}$	0.2331	0.2014	0.1428	0.1220
$Pd_{22}Au_{78}$	0.2326	0.2009	0.1424	0.1217
$Pd_{26}Au_{74}$	0.2321	0.2006	0.1422	0.1214
$Pd_{45}Au_{55}$	0.2299	0.1988	0.1408	0.1203
$Pd_{59}Au_{41}$	0.2283	0.1975	0.1398	0.1195
$Pd_{100}Au_0$	0.2236	0.1936	0.1369	0.1170

Nitrite reaction optimization

Table S3. Screening of nitrite reaction using peptide-based catalyst [a].

Entry	Temperature (°C)	Catalyst type	Pd loading (μg)	pH	Yield [b] (%)
1	25	$Pd_{26}Au_{74}$	7	6.5	-
1	4	$Pd_{26}Au_{74}$	7	6.5	-
2	4	$Pd_{26}Au_{74}$	19	6.5	-
3	4	$Pd_{26}Au_{74}$	40	6.5	-
4	4	80 sc%	40	6.5	-
5	4	80 sc%	40	5.5	4
6	4	80 sc%	400	5.5	8
7	15	80 sc%	400	5.5	33
8	25	80 sc%	80	5.5	73
9	25	Pd	80	5.5	28
10	25	$Pd_{26}Au_{74}$	80	5.5	35
11	25	100 sc%	80	5.5	97
12	25	100 sc%	40	5.5	97
13	25	100 sc%	20	5.5	53
14	25	$Pd_{26}Au_{74}$	40	5.5	34
15	25	$Pd_{26}Au_{74}$	20	5.5	21

[a] Reaction condition: $NaNO_2$ (40 mg/L), H_2 (100 mL/min), CO_2 (100 mL/min), catalyst, H_2O (20 mL), 600 rpm, 75 min. [b] Yields were determined by UV-Vis spectroscopy with Griess reagent as a nitrite concentration indicator.

Turnover frequency (TOF) calculation

TOF can be calculated following

$$TOF = \frac{k \times N_{0,NO_2^-}}{ss_{Pd}}$$

where k is the *pseudo*-first-order rate constant, N_{0,NO_2^-} is the initial number of NO_2^- ions, and ss_{Pd} is the number of active Pd surface sites. The N_{0,NO_2^-} can be obtained following

$$N_{0,NO_2^-} = \frac{C_{0,NO_2^-} \times V_{reactor} \times N_A}{MW_{NO_2^-}}$$

where C_{0,NO_2^-} is the initial NO_2^- concentration (g × NO_2^-/ L), $V_{reactor}$ is the volume of the reactor (0.020 L), N_A is Avogadro's constant, and $MW_{NO_2^-}$ is the molecular weight of NO_2^-. The number of Pd surface sites (ss_{Pd}) can be calculated following

$$ss_{Pd} = \frac{m_{catalyst} \times wt\%_{Pd} \times N_A \times \%SA}{MW_{Pd}}$$

where $m_{catalyst}$ is the mass of catalyst (g), $wt\%_{Pd}$ is the weight percent of each Pd in each catalyst ($g_{Pd}\ g_{catalyst}^{-1}$), $\%SA$ is the ratio of surface atoms to total atoms in the particle, and MW_{Pd} is the molecular weight of Pd (106.42 g mol^{-1}).

It is worth to mention that the total number of Pd atoms in the reactor for each batch reaction can be calculated from following

$$m_{catalyst} \times wt\%_{Pd} \times N_A$$

XPS data

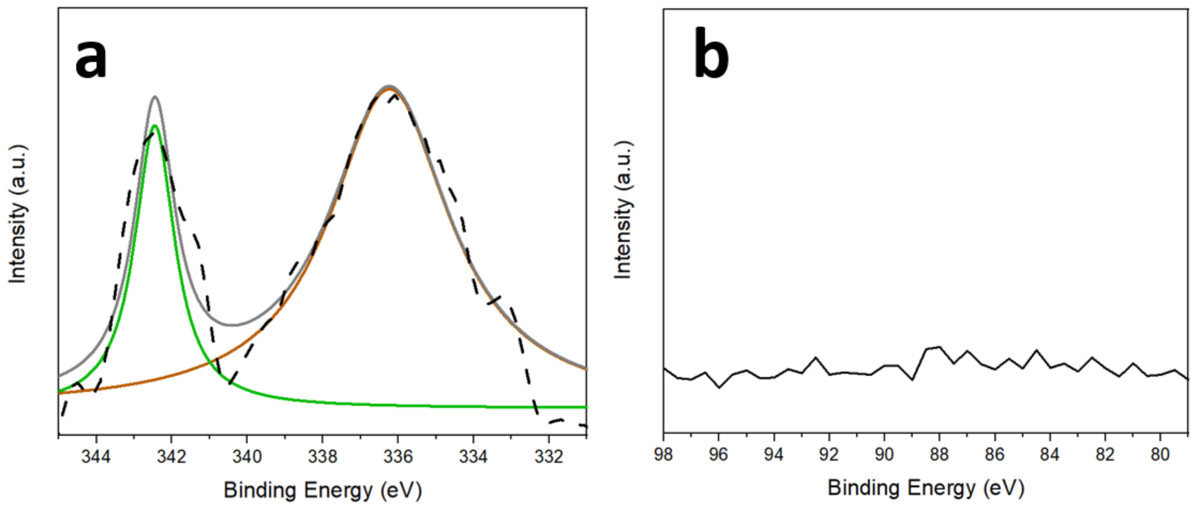

Fig. S2. a) Pd 3d and (b) Au 4f XPS spectra of MLPA NPs.

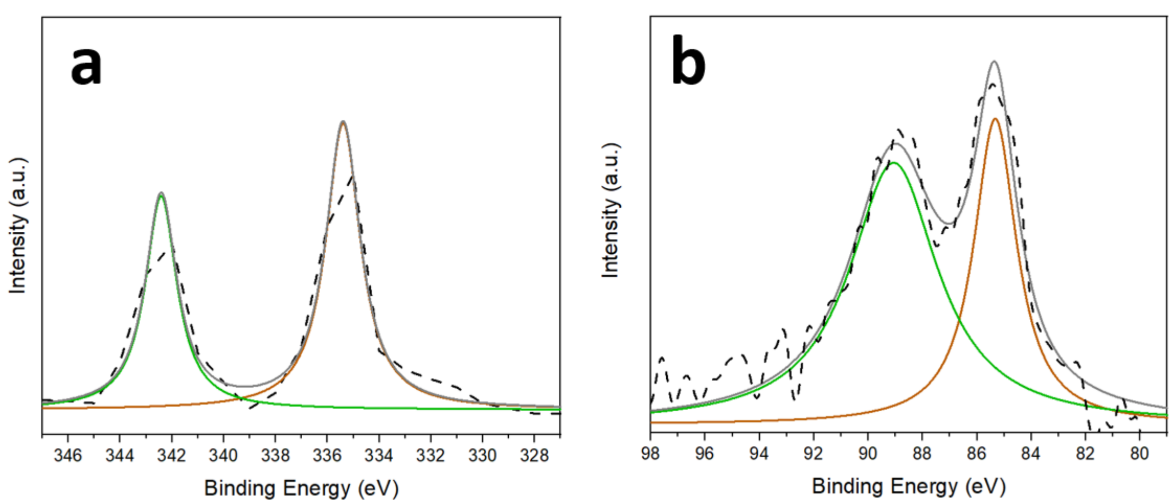

Fig. S3. a) Pd 3d and (b) Au 4f XPS spectra of $Pd_{26}Au_{74}$ NPs.

Nitrogen Selectivity analysis

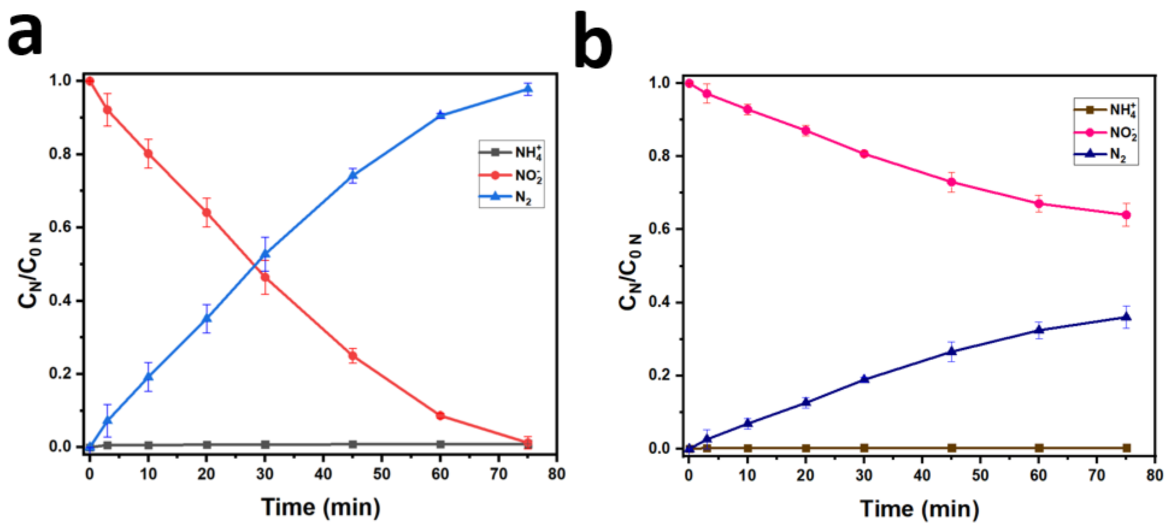

Fig. S4. Time evolution of nitrite, dinitrogen, and ammonium concentrations for a) 100 sc% Pd-on-Au catalyst and b) $Pd_{26}Au_{74}$ NPs. Dinitrogen selectivity was 98% and 96% for 100 sc% Pd-on-Au and $Pd_{26}Au_{74}$, respectively.

Comparison NP activities

Table S4. Comparison of various nanocatalysts for nitrite reduction

Entry	Catalyst	TOF	Ref.
1	$Pd_{53}Au_{47}$ NP	3.8 (min^{-1})	Seraj et al.[8]
2	Pd NP (2nm)	7.5 (min^{-1})	Zhang et al.[9]
3	$Pd_{80}Ag_{20}$ NP	2.8 (min^{-1})	Troutman et al.[4]
4	Fe_3O_4@SiO_2/Pd	1.75 (s^{-1})	Sun et al.[10]
5	Pd on Fe_3O_4@SiO_2	1.2 (s^{-1})	Sun et al.[11]
6	Peptide-mediated Pd-on-Au NP	5.33 (min^{-1})	This work
7	Peptide-mediated $Pd_{59}Au_{41}$ NP	2.27 (min^{-1})	This work

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