Supporting Information

Simultaneous chemical and refractive index sensing in 1-2.5 μm near-infrared wavelength range on nanoporous gold disks

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Fabrication of nanoporous gold disk nanoparticle array

The NPG disks (350/600 nm in diameter, ~75 nm thickness, and ~10 nm average pore size) were fabricated according to methods in recent studies published.[1, 2] The fabrication of substrate-bound NPG disk arrays initiates with DC sputtering of a 80 nm thick film of Au: Ag (30 : 70) alloy over the glass coverslip (~165 μm thick). A monolayer of 460/800 nm polystyrene (PS) beads was then deposited on the surface of the alloy film. To shrink and isolate the PS beads, oxygen plasma-etching was employed, followed by Ar plasma-etching to induce alloy disk formation on the glass surface. The remaining PS beads on top of the alloy disks were removed by dissolution in chloroform. The disks were dealloyed in 70% nitric acid for 1 min, followed by DI water wash for 2 min.

Infrared absorption measurements

The instruments used for the transmission-mode infrared absorption measurement are Jasco V-570 (dispersive scanning UV-Vis-NIR spectrometer) and Nicolet 6700 FT-IR inteferometric spectrometer. Each FT-IR spectrum was an average of 256 scans acquired from the hydrocarbon film sandwich sample configuration with a resolution of 4 cm^{-1}. The reported SENIRA spectra (I_{SENIRA}) were the results after directly subtracting the bulk spectra (I_{bulk}).

Table S1. Enhancement calculations for the ODT self-assembled monolayers on NPG disks

NIR assignment	NPG disk diameter	Hydrocarbon	Enhancement factor
1st C-H overtone (1725 nm)	600 nm	octadecanethiol	9100
	350 nm		4700
1st C-H combination (2400 nm)	600 nm		23100
	350 nm		11300

Enhancement factor parameters for the ODT monolayer for 2 mm irradiated spot:
~$2x10^{16}$ molecules in ODT solution for 10 um thickness
~5 $x10^{12}$ monolayer molecules on 350 nm NPG disk array
~6 $x10^{12}$ monolayer molecules on 600 nm NPG disk array

Table S2. Relative intensities of surface-enhanced near-infrared absorption of bulk hydrocarbons

NIR assignment	NPG disk diameter	Hydrocarbon	I_{bulk}	I_{enh}	I_{SENIRA}	I_{SENIRA}/I_{bulk}	I_{bulk} (per nm)	I_{SENIRA} (per nm)
2nd C-H overtone (1200 nm)	600 nm	hexadecane	0.031	0.12	0.09	2.9	3.10E-06	8.18E-04
	350 nm			0.35	0.32	10.3		2.91E-03
	600 nm	dodecane	0.062	0.13	0.07	1.1	6.20E-06	6.36E-04
	350 nm			0.22	0.16	2.7		1.45E-03
	600 nm	siloxane	0.053	0.11	0.06	0.1	5.30E-06	5.45E-04
	350 nm			0.31	0.26	5.2		2.36E-03
1st C-H overtone (1725 nm)	600 nm	hexadecane	0.18	0.296	0.12	0.7	1.80E-05	1.09E-03
	350 nm			0.183	0.003	0.02		2.73E-05
	600 nm	dodecane	0.3	0.64	0.33	1.1	3.00E-05	3.00E-03
	350 nm			0.32	0.02	0.07		1.82E-04
	600 nm	siloxane	0.29	0.63	0.34	1.2	2.90E-05	3.09E-03
	350 nm			0.36	0.07	0.2		6.36E-04
1st C-H overtone (1725 nm)	600 nm	octadecanethiol	0.002	0.008	0.006	3	2.00E-07	5.45E-05
	350 nm			0.0045	0.0025	1.25		2.27E-05
1st C-H combination (2400 nm)	600 nm		0.0034	0.0294	0.026	7.647	3.40E-07	2.36E-04
	350 nm			0.0135	0.0101	2.971		9.18E-05
1st O-H overtone (1925 nm)	600 nm	water	0.016	0.3211	0.3051	19.069	1.60E-06	2.77E-03
	350 nm			0.0282	0.122	0.763		1.11E-03
1st C-H overtone (1725 nm)	600 nm	pyrene	0.00345	0.00609	0.00264	0.765	3.45E-07	2.40E-05
	350 nm			0.00383	0.00038	0.11		3.45E-06
	600 nm	crude oil	0.378	0.667	0.289	0.765	3.78E-05	2.63E-03
	350 nm			0.438	0.06	0.159		5.45E-04

Table S3. Relative intensities of surface-enhanced near-infrared absorption for PMMA films at varying thickness

PMMA thickness (nm)	I_{bulk}	I_{enh}		I_{SENIRA}		I_{bulk} (per nm)	I_{SENIRA} (per nm)	
		350 nm NPGD	600 nm NPGD	350 nm NPGD	600 nm NPGD		350 nm NPGD	600 nm NPGD
50	1.70E-04	1.20E-03	4.90E-03	1.03E-03	4.73E-03	3.40E-06	2.06E-05	9.46E-05
60	2.10E-04	1.96E-03	8.26E-03	1.75E-03	8.05E-03	3.50E-06	2.92E-05	1.34E-04
70	2.40E-04	2.60E-03	1.45E-02	2.36E-03	1.42E-02	3.43E-06	3.38E-05	2.03E-04
80	2.90E-04	3.53E-03	1.73E-02	3.24E-03	1.70E-02	3.63E-06	4.05E-05	2.12E-04
90	3.10E-04	4.24E-03	2.50E-02	3.93E-03	2.47E-02	3.44E-06	4.37E-05	2.75E-04
100	3.30E-04	6.82E-03	2.62E-02	6.49E-03	2.59E-02	3.30E-06	6.49E-05	2.59E-04
110	3.35E-04	1.02E-02	3.68E-02	9.85E-03	3.65E-02	3.05E-06	8.95E-05	3.32E-04
120	3.40E-04	1.00E-02	3.61E-02	9.69E-03	3.58E-02	2.83E-06	8.81E-05	3.25E-04
130	3.45E-04	8.69E-03	3.43E-02	8.35E-03	3.39E-02	2.65E-06	7.59E-05	3.08E-04
140	3.55E-04	9.66E-03	3.51E-02	9.30E-03	3.48E-02	2.54E-06	8.46E-05	3.16E-04
150	3.65E-04	8.88E-03	3.43E-02	8.51E-03	3.39E-02	2.43E-06	7.74E-05	3.08E-04

References

1. Qi, J.; Motwani, P.; Gheewala, M.; Brennan, C.; Wolfe, J. C.; Shih, W.-C. *Nanoscale* **2013,** 5, (10), 4105-4109.
2. Zhao, F.; Zeng, J.; Parvez Arnob, M. M.; Sun, P.; Qi, J.; Motwani, P.; Gheewala, M.; Li, C.-H.; Paterson, A.; Strych, U.; Raja, B.; Willson, R. C.; Wolfe, J. C.; Lee, T. R.; Shih, W.-C. *Nanoscale* **2014,** 6, (14), 8199-8207.