Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplemental Information

Sunlight driven atmospheric water capture capacity is enhanced by nano-enabled photothermal desiccants

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Gold nanoparticle synthesis methods

Gold nanocubes and nanorods were synthesized using a seeded-growth technique according to Loeb et al. (2018).[1] The gold nanocube seed was synthesized by mixing 0.1 M CTAB (7.5 mL) with 0.01 M $HAuCl_4$ (0.25 mL), and ice-cold, freshly prepared 0.01 M $NaBH_4$ (0.6 mL), and it was then kept in an oven at 27°C for 1 hour. To make the growth solution, 0.1 M CTAB (524.8 mL), 0.01 M $HAuCl_4$ (65.6 mL), and 0.1 M ascorbic acid (311.6 mL) were added to 3280 mL of ultrapure water. The seed was diluted 1:10 in water, then 1.64 mL of the diluted seed solution was added to the growth mixture.

Gold nanorod seed solution consisted of 0.1 M CTAB (9.75 mL) mixed with 0.01 M $HAuCl_4$ (0.25 mL), and ice-cold, freshly prepared 0.01 M $NaBH_4$ (0.6 mL), and it was then kept in an oven at 27°C for 2 hours. To make the growth solution, 0.12 mL of the gold nanorod seed was added to 0.1 M CTAB (3800 mL), 0.01 M $HAuCl_4$ (190 mL), 0.01 M $AgNO_3$ (38 mL), 0.1 M HCl (76 mL), and 0.1 M ascorbic acid (30.4 mL).

The nanocube and nanorod solutions were stirred on a magnetic stir plate for 5 minutes, then stored overnight at 27°C. Finally, the growth solutions were centrifuged washed (13,000 RPM for 2 hours) two times with ultrapure water to isolate the nanoparticles and remove unincorporated solvents. The final gold nanocube solution is a bright red color (at 25 mg/L) and surface plasmonic resonance (SPR) peak at 534 nm. The final gold nanorod solution is a deep purple color (at 82 mg/L) and has two SPR peaks at 520 nm and 790 nm.

(1) Loeb, S.; Li, C.; Kim, J. H. Solar Photothermal Disinfection Using Broadband-Light Absorbing Gold Nanoparticles and Carbon Black. *Environ. Sci. Technol.* **2018**, *52* (1), 205–213. https://doi.org/10.1021/acs.est.7b04442.

Statistical analysis

Two-tailed t-tests were performed on adsorption and desorption data obtained by triplicates of desiccant samples to determine statistical similarity. Triplicate results of 2 independent samples (e.g., bare SiO_2 desiccant vs 5w/w%CB-SiO_2) were compared, with the null hypothesis stating that the results were statistically different. The analysis had 4 degrees of freedom, α=0.05 and t_{crit} = 2.132. Equation SI.1 was used to calculate t-value (t_{obs}) of the data set, where X_1 is the average of triplicate data from Sample 1, X_2 is the average of triplicate data from Sample 2, var_1 is the variance of data from Sample 1, var_2 is the variance of data from sample 2, n_1 is the number of data points obtained for sample 1 (i.e., 3), and n_2 is the number of data points obtained for sample 2. If $t_{obs} > t_{crit}$ (i.e., p-value <0.05), the null hypothesis was valid and the samples were determined to be statistically different, while if p-value was >0.05, the t-test failed and results were deemed statistically similar.

$$t_{obs} = \frac{X_1 - X_2}{\sqrt{\left(\frac{var_1}{n_1}\right) + \left(\frac{var_2}{n_2}\right)}} \qquad (SI.1)$$

Table S1: Desiccant adsorption and desorption capacities and rates over 1 cycle
(*Surface temperature achieved by all saturated desiccants under 1-sun irradiation is 10–15°C higher than temperatures achieved by dry desiccants, shown in Table 1. These differences can be attributed to differences in experimental setup.)

	40% RH				60% RH				80% RH			
	SiO_2	5wt% CB-SiO_2	5wt% AuNC-SiO_2	5wt% AuNR-SiO_2	SiO_2	5wt% CB-SiO_2	5wt% AuNC-SiO_2	5wt% AuNR-SiO_2	SiO_2	5wt% CB-SiO_2	5wt% AuNC-SiO_2	5wt% AuNR-SiO_2
ADSORPTION AT SPECIFIED RELATIVE HUMIDITY												
Maximum capacity (gH_2O/g)	0.067 ± 0.0033	0.049 ± 0.0084	0.045 ± 0.0036	0.049 ± 0.0039	0.201 ± 0.0152	0.119 ± 0.0083	0.116 ± 0.0156	0.101 ± 0.0059	0.495 ± 0.0284	0.421 ± 0.0643	0.352 ± 0.0250	0.212 ± 0.0341
Rate (mgH_2O/min)	5 ± 0.7	4 ± 0.4	4 ± 0.2	3 ± 0.8	9 ± 0.4	5 ± 0.1	5 ± 0.1	4 ± 0.4	8 ± 0.5	6 ± 0.6	6 ± 0.6	5 ± 0.6
Time to Equilibrium (hrs)	0.75	0.75	0.75	0.75	1	1	1	1	8	8	8	6
DESORPTION UNDER 1-SUN												
Harvested water (gH_2O/g)	0.041 ± 0.0056	0.045 ± 0.0052	0.043 ± 0.0054	0.046 ± 0.0016	0.165 ± 0.0052	0.116 ± 0.0110	0.096 ± 0.0212	0.086 ± 0.0095	0.458 ± 0.0237	0.401 ± 0.0630	0.343 ± 0.0290	0.202 ± 0.0309
Residual water (gH_2O/g)	0.026 ± 0.0027	0.004 ± 0.0034	0.002 ± 0.0018	0.003 ± 0.0025	0.036 ± 0.0119	0.003 ± 0.0028	0.020 ± 0.0102	0.015 ± 0.0096	0.037 ± 0.0075	0.020 ± 0.0027	0.009 ± 0.0063	0.010 ± 0.0035
Rate (gH_2O/min)	-0.003 ± 0.0001	-0.005 ± 0.0004	-0.004 ± 0.0006	-0.004 ± 0.0005	-0.007 ± 0.0000	-0.014 ± 0.0008	-0.011 ± 0.0030	-0.009 ± 0.0014	-0.013 ± 0.0015	-0.023 ± 0.0036	-0.021 ± 0.0032	-0.015 ± 0.0015
Time to equilibrium (min)	30 ± 5	23 ± 2.8	27 ± 2.9	27 ± 2.9	45 ± 0	17 ± 2.9	20 ± 0	20 ± 0	60 ± 0	27 ± 2.9	25 ± 0	25 ± 0
Surface Temperature (°C)	40 ± 6.9	66 ± 2.1	58 ± 3.3	55 ± 2.1	38 ±0.7	58 ± 2.5	50 ± 1.2	49 ± 1.7	43 ± 1.2	66 ± 2.9	57 ± 4.4	59 ± 2.9

Table S2: Brunauer-Emmett-Teller (BET) surface area of desiccants

Desiccant	BET Surface Area (m^2/g)
SiO_2	459.2
SiO_2-APTES	289.2
5wt%CB-SiO_2	297.2
5wt%AuNC-SiO_2	281.3
5wt%AuNR-SiO_2	248.6

Specific surface area of desiccants was measured using a Micromeritics Tristar II 3020 instrument. First, 0.2 g of sample was dried at 110°C to evacuate water vapor from the pores. Samples were placed in the instrument to obtain nitrogen physisorption data at 77 K. The Brunauer-Emmett-Teller (BET) equation was used to calculate the BET specific surface area.

Table S3: Time required per 1 adsorption- desorption cycle by desiccant under controlled humidity condition and theoretical number of adsorption-desorption cycles that could be performed in a 12-hour period

RH (%)	Material	Time per cycle (hr)	Number of cycles in 12 hours
40	SiO_2	1.3	9
	5wt%CB-SiO_2	1.1	10
	5wt%AuNC-SiO_2	1.2	10
	5wt%AuNR-SiO_2	1.2	10
60	SiO_2	1.8	6
	5wt%CB-SiO_2	1.3	9
	5wt%AuNC-SiO_2	1.3	9
	5wt%AuNR-SiO_2	1.3	9
80	SiO_2	8.7	1
	5wt%CB-SiO_2	8.4	1
	5wt%AuNC-SiO_2	8.4	1
	5wt%AuNR-SiO_2	6.4	1

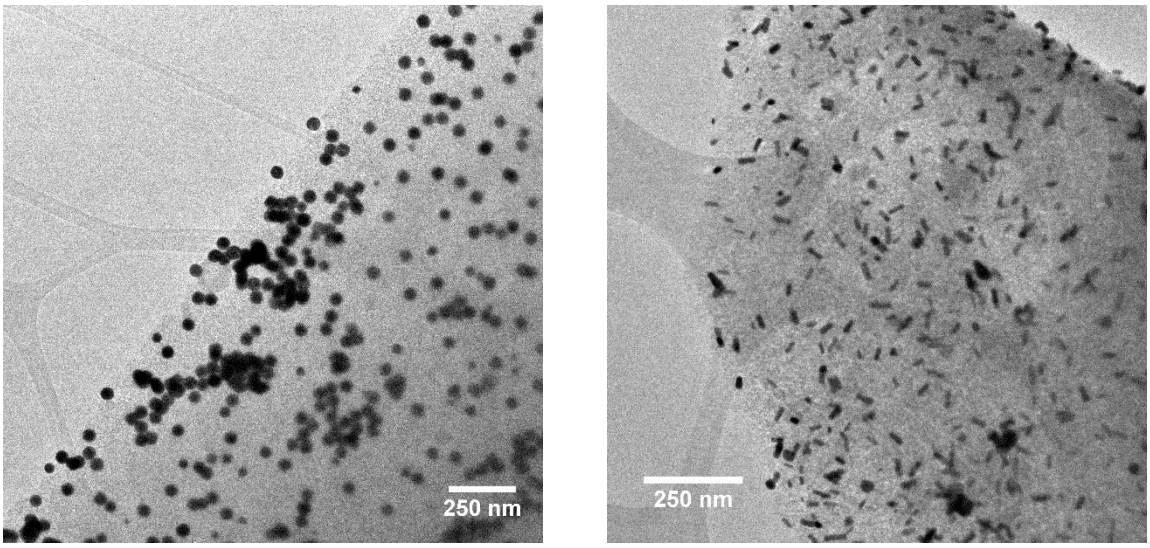

Figure S1: **A)** TEM image of AuNC attached to SiO_2. **B)** TEM image of AuNR attached to SiO_2. Images acquired using Philips CM200-FEG high resolution TEM.

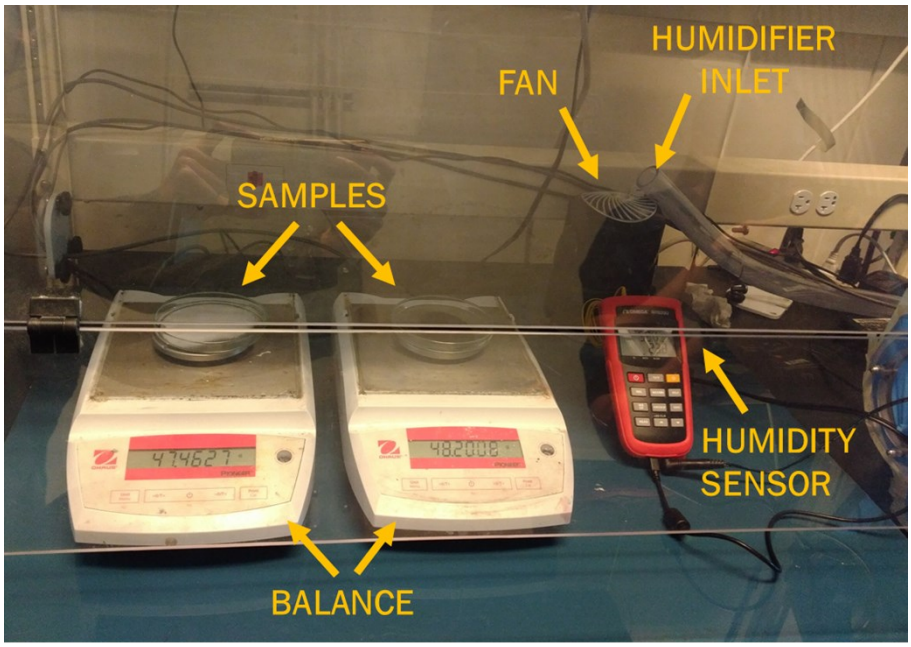

Figure S2: Testing setup for water vapor adsorption. Hood contains two balances with data loggers, desiccant samples in open glass petri dishes, humidity sensor, fan, and humidifier with setpoint either RH 40%, 60%, or 80%.

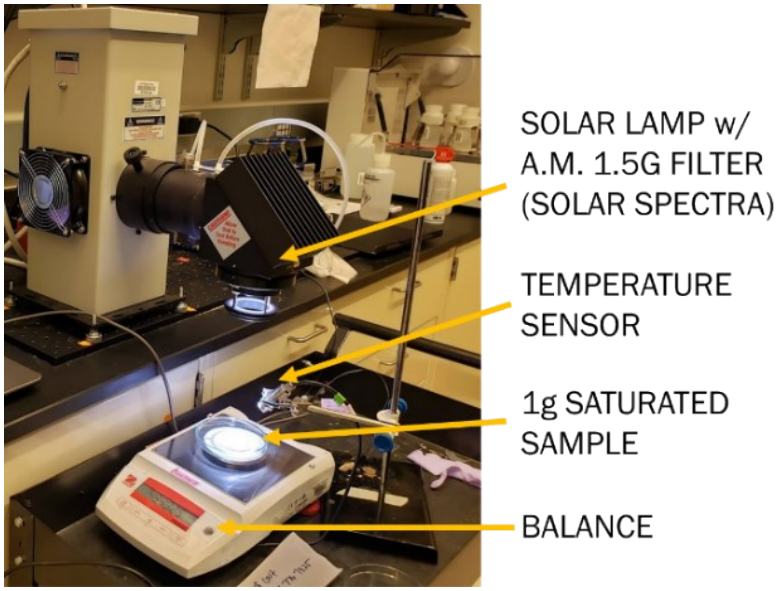

Figure S3: Testing setup for photothermal water vapor desorption. Petri dish containing saturated desiccant sample placed on balance with data logger underneath 1-sun simulated solar irradiation.

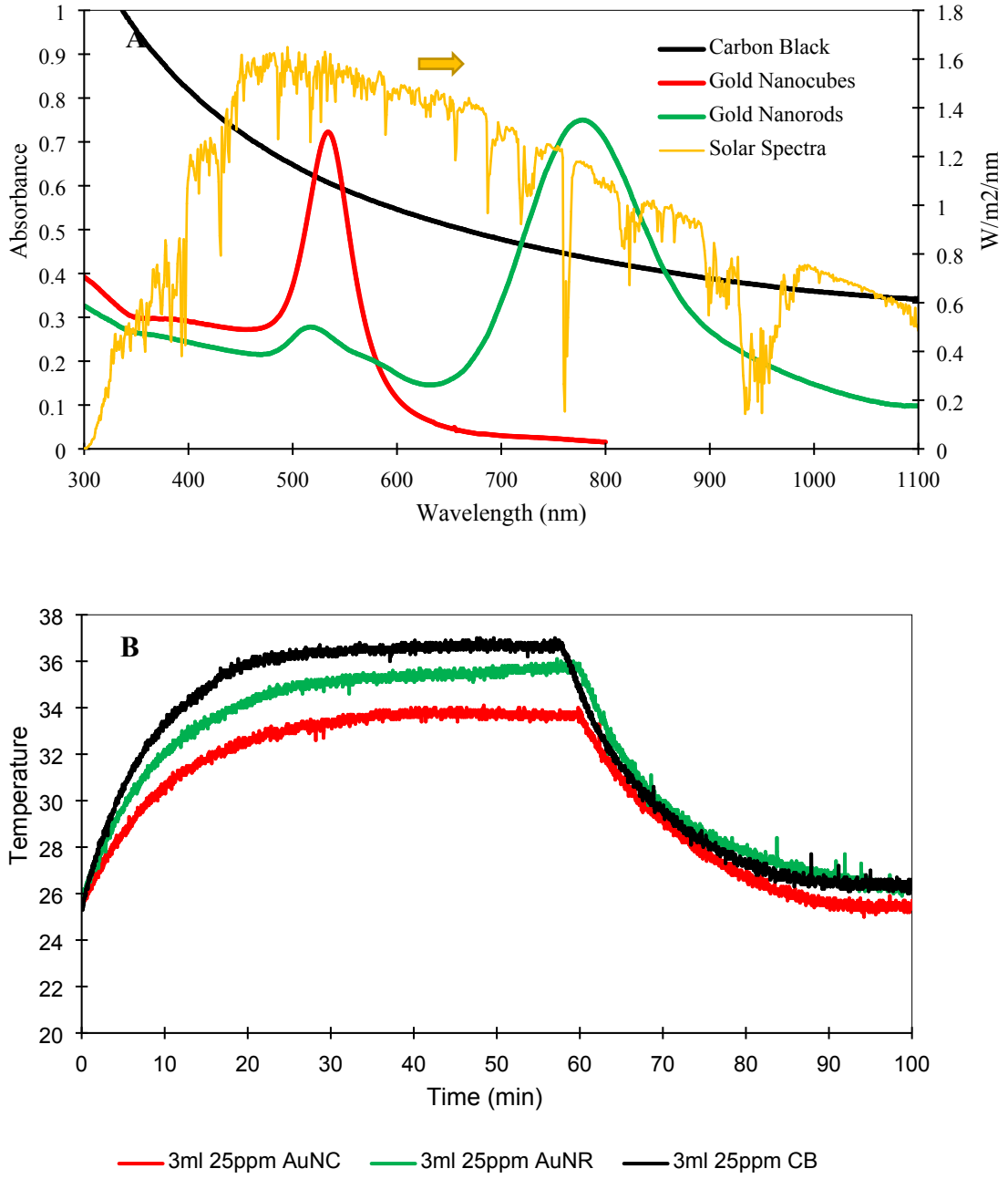

Figure S4: A) UV-Vis absorption spectra of photothermal nanoparticles (primary y-axis) superimposed over solar irradiation spectrum (secondary y-axis). **B)** Rate of heating and cooling of 3mL of 25 mg/L nanoparticles in water in quartz cuvette exposed to 1-sun solar irradiation. Sample temperature at time=0s was 25.7°C (ambient).

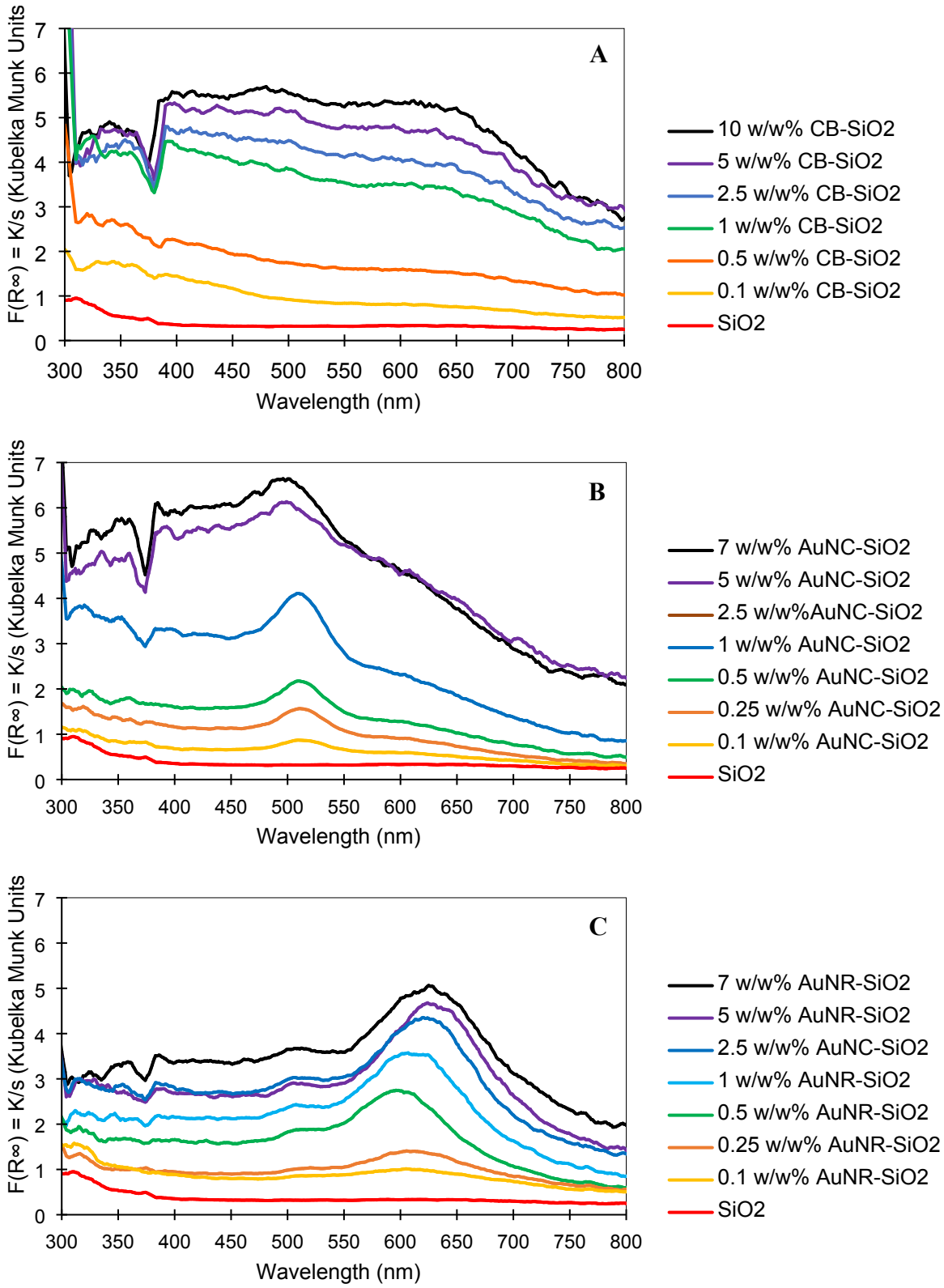

Figure S5: Kubelka-Munk transformation of diffuse reflectance on **A)** CB-SiO_2, **B)** AuNC-SiO_2, **C)** AuNR-SiO_2.

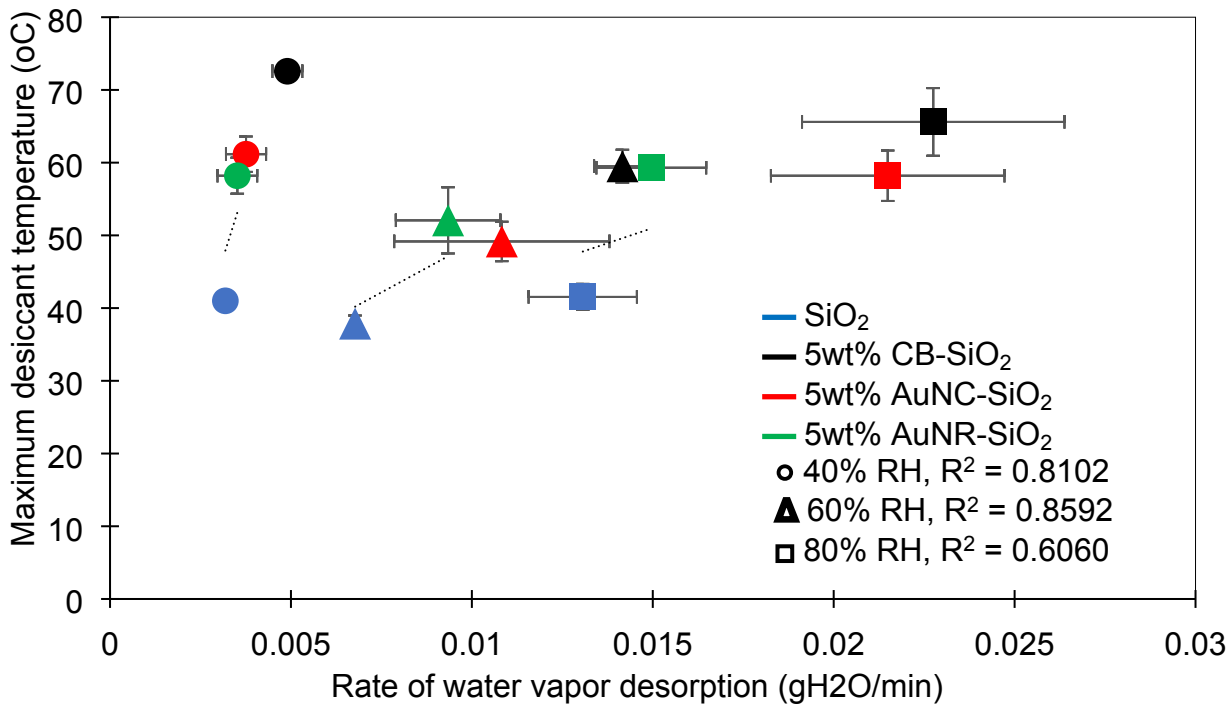

Figure S6: Linear regression fit of maximum desiccant temperature versus water vapor desorption rate for samples saturated at 40%, 60% and 80% RH.