Supplementary Information

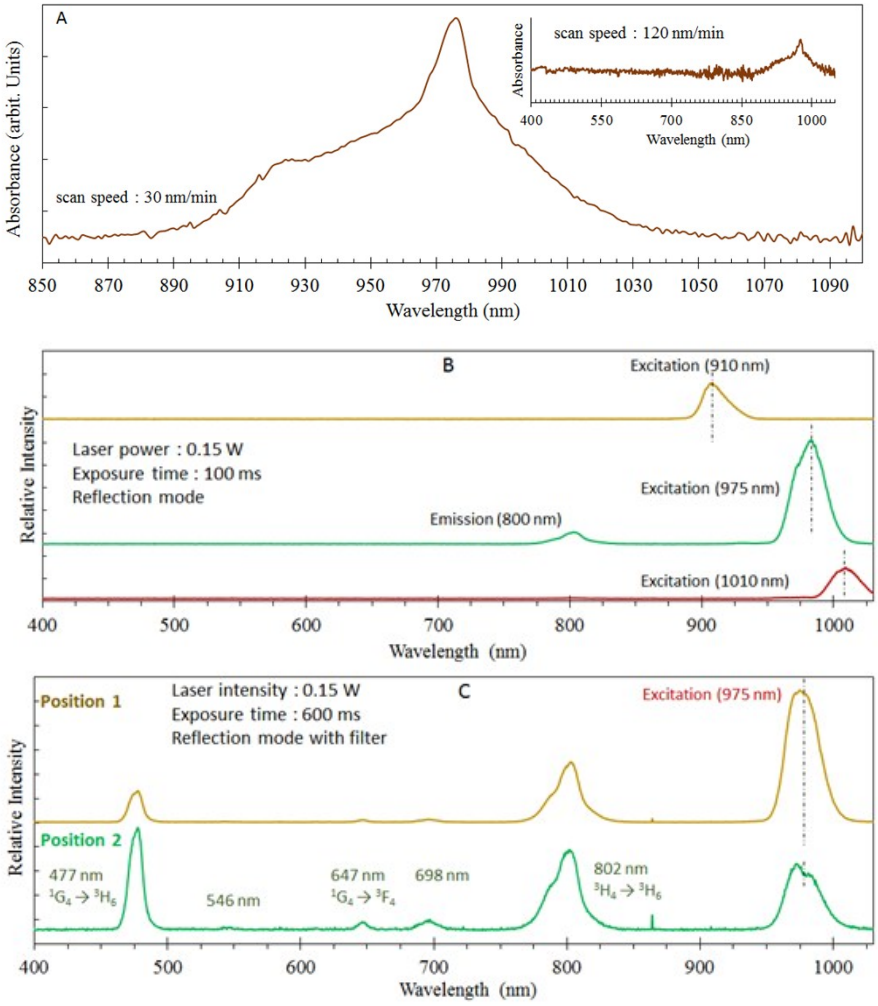


Figure S1A
UV-Vis absorbance of NaY(Yb)F_4:Tm showing absorbance in the 910-1010 nm. Inset: full range scan.

Figure S1B
Effect of Laser excitation wavelength on emission of NaY(Yb)F_4:Tm.

Top: excitation with higher energy than absorbance. The absence of emission at 800nm indicates that the material does not absorb this energy.

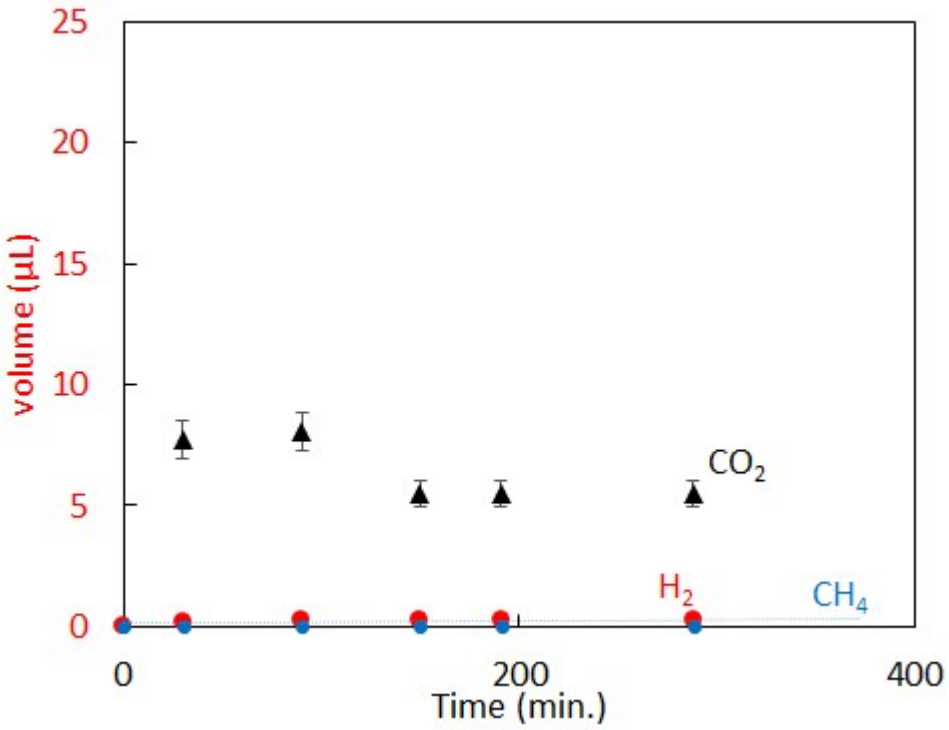
Middle, excitation at the absorbance edge and the simultaneous emission of the upconversion luminescence at 800nm.

Bottom: excitation with higher wavelength (lower energy) showing no emission. *Therefore, u*p-conversion occurs since an 800 nm emission is only observed when exciting the material in the absorbance range. A red filter # KC19 (see methodology section), is used to cut-off any residual light from the excitation below 700 nm. The lines at 546 and 698 cm-1 might be due to other rate earth impurities in Thulium (III) and Yittrium (III) nitrates.

Figure S*1C*
Optimization of the set up for upconversion emissions of NaY(Yb)F_4:Tm with excitation at 975nm (+/-5nm). A fraction of light is converted to the visible (477nm) and IR (802nm) light. KC19 (red filter) is used to cut-off any residual light from the excitation source below 700 nm. A blue filter # C3C23 is used to attenuate light above 700 nm. In the figure both excited and emitted lights are collected.

Figure *S2*

Products during the gas phase photoreaction, in the absence of methanol, under 980 nm excitation on (0.25 wt. % Au/CdS)-($NaYF_4$-Yb-Tm) with a 1 to 1 ratio. Methane was not observed during the experimental run, traces of hydrogen were observed and some adventitious CO_2 (did not increase with time) indicating its non-catalytic origin.



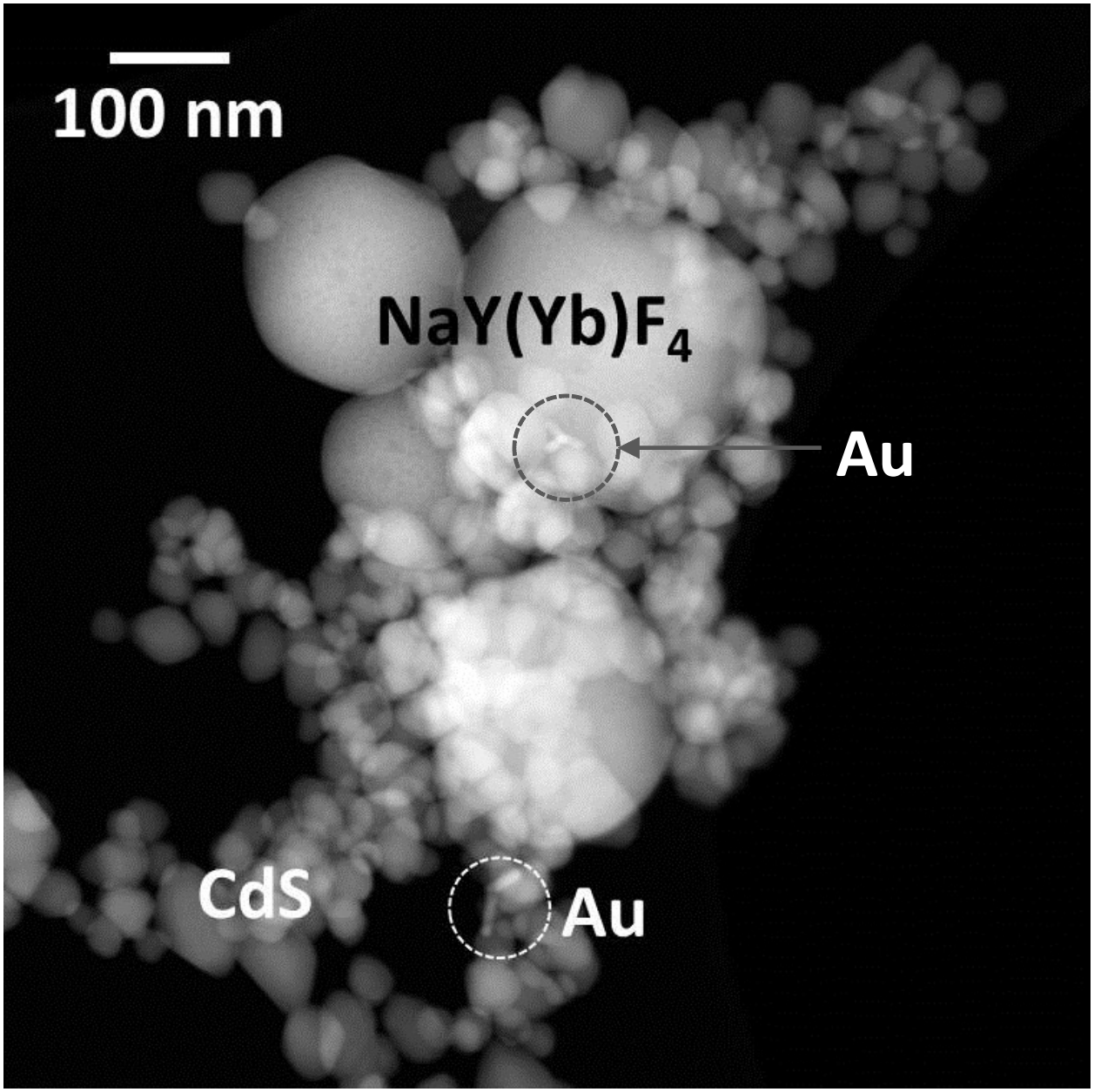


Figure SF3 A. STEM-HAADF of $NaYF_4$ (Yb):Tm

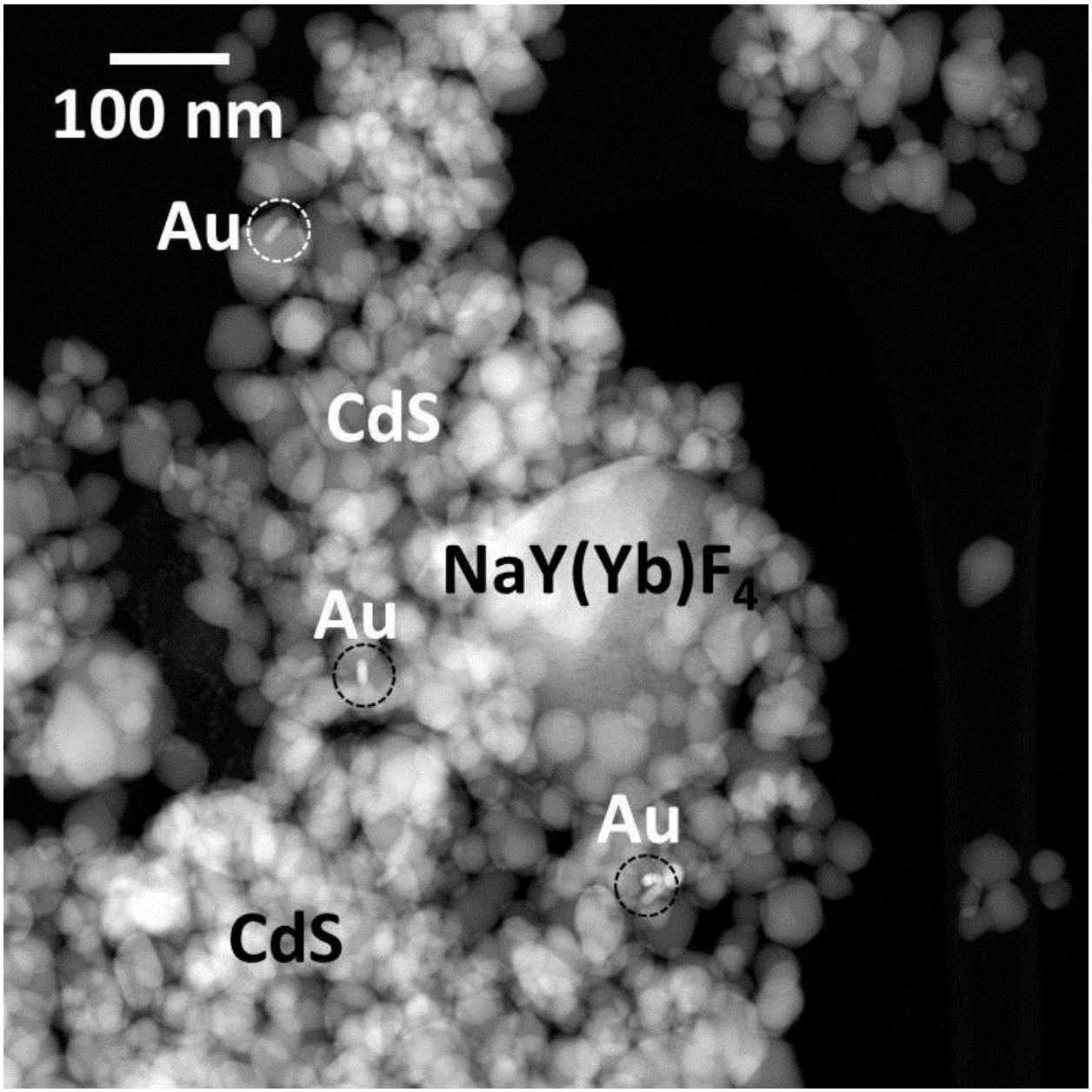


Figure SF3 B. STEM-HAADF of $NaYF_4$ (Yb):Tm

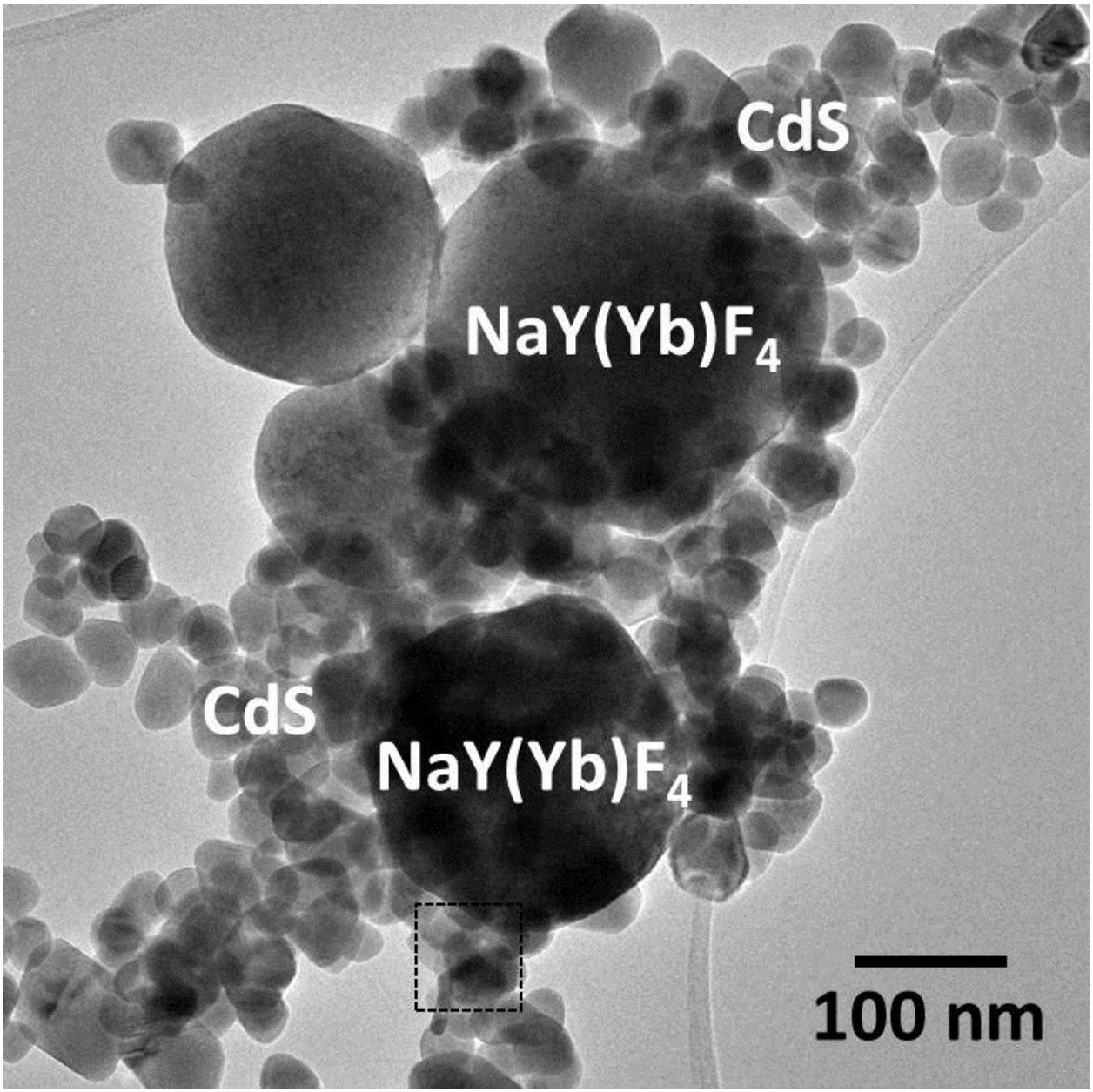


Figure SF3 C. HRTEM of $NaYF_4$ (Yb):Tm

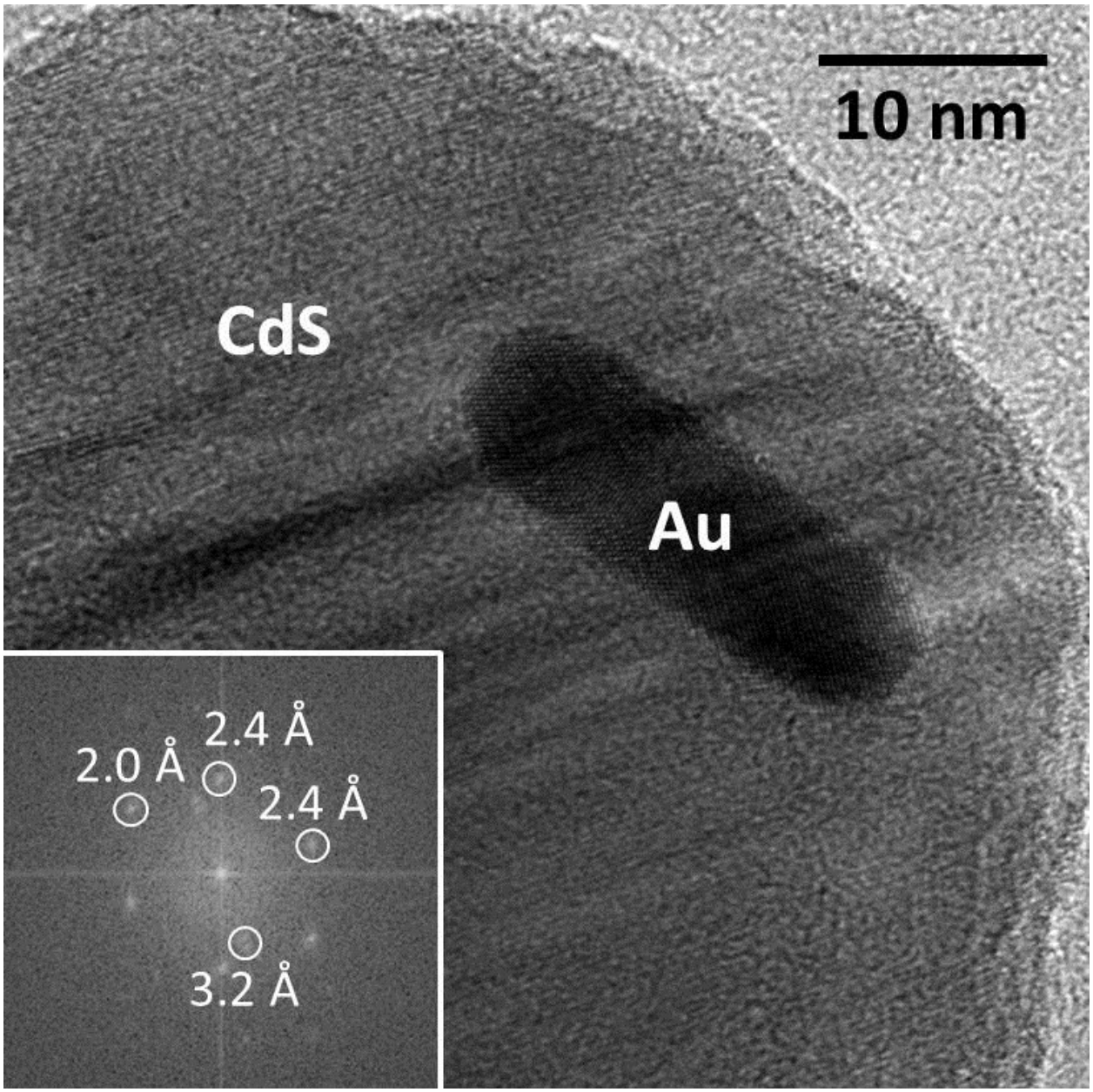
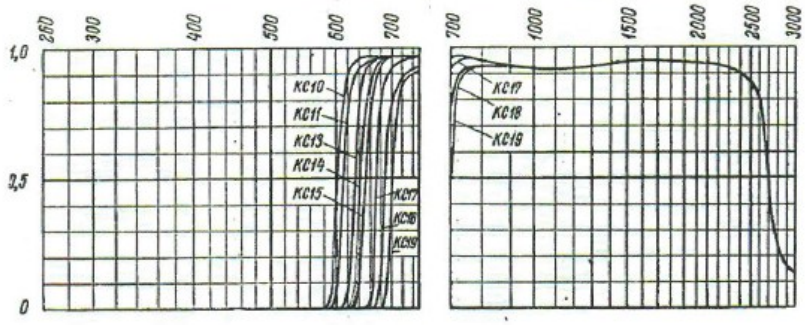


Figure SF3 D. HRTEM and FFT of Au/CdS nanoparticles

RED FILTERS

Transmission versus wavelength (nm)



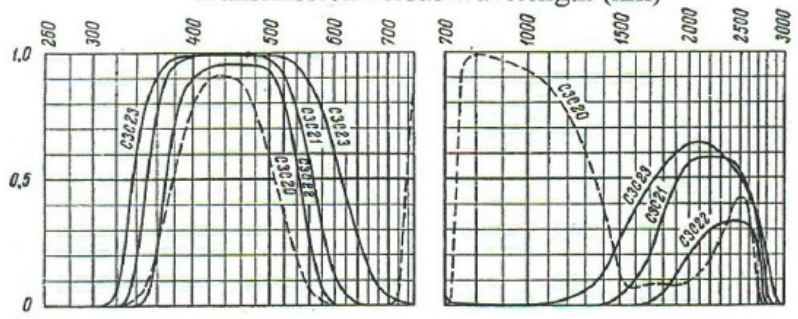
Optical density D

λ, нм	KC10	KC11	KC13	KC14	KC15	KC17	KC18	KC19
500								
510								
520								
530				>10				
540	>10	>10		10,0	>10			
550	9,7	10,0		8,5	9,7			
560	8,6	8,9		6,9	8,5			
570	6,7	7,7		6,5	7,2		>10	
580	3,9	6,3		6,4	6,5		9,5	>10
590	1,36	4,0	>10	6,7	6,3		8,9	9,9
600	0,32	1,21	8,9	7,3	6,4		8,5	9,2
610	0,110	0,32	5,0	6,5	6,8		7,9	8,9
620	0,050	0,115	1,20	3,3	6,7	>10	7,3	8,0
630	0,028	0,050	0,31	1,12	3,3	9,2	6,5	7,5
640	0,021	0,035	0,095	0,32	0,95	7,5	5,8	7,1
650	0,018	0,030	0,040	0,130	0,32	4,8	5,2	6,5
660	0,017	0,025	0,027	0,070	0,120	1,65	4,4	5,6
670	0,016	0,020	0,020	0,040	0,050	0,32	2,40	4,5
680	0,016	0,018	0,018	0,025	0,025	0,100	0,78	2,70
690	0,016	0,016	0,016	0,020	0,020	0,050	0,20	1,00
700	0,015	0,016	0,016	0,017	0,016	0,035	0,110	0,32
710			0,015			0,030	0,070	0,125
720						0,025	0,055	0,070
730						0,020	0,045	0,050
740			0,015			0,018	0,040	0,045
750						0,017	0,037	0,040
760			0,017			0,017	0,035	0,038
770						0,018	0,035	0,037
780			0,019			0,019	0,035	0,036
790						0,021	0,035	0,036
800			0,023			0,023	0,034	0,035
850			0,026			0,026	0,033	0,034
900				0,033				
950				0,035				
1000				0,038				
1200				0,037				
1400				0,030				
1600				0,025				
1800				0,025				
2000				0,027				
2200				0,032				
2400				0,047				
2600				0,100				
2800				0,60				
3000				0,86				

Figure SF4 A. Optical density of the ref filter used during the UC experiments.

BLUE - GREEN FILTERS

Transmission versus wavelength (nm)



Extinction coefficients K

λ нм	C3C23	C3C21	C3C22	C3C20	λ нм	C3C23	C3C21	C3C22	C3C20
240				4,4	700	0,47	1,32	4,0	1,30
250				3,7	710	0,53	1,48	4,5	0,79
260				3,2	720	0,58	1,65	5,0	0,40
270				2,70	730	0,64	1,75	5,4	0,160
280	>6			2,35	740	0,70	1,90	5,8	0,068
290	5,5			1,95	750	0,75	2,10	>6	0,024
					760	0,80	2,20	>6	0,009
300	2,00	>6		1,55	780	0,90	2,45	>6	0,002
310	0,93	2,89		1,24					
320	0,40	1,34	>6	0,96	800	0,98	2,65	>6	0,002
330	0,170	0,57	2,50	0,70	820	1,04	2,75	>6	0,002
340	0,072	0,23	1,10	0,49	840	1,08	2,90	>6	0,003
350	0,031	0,093	0,49	0,34	860	1,11	2,95	>6	0,003
360	0,015	0,038	0,21	0,22	880	1,13	3,00	>6	0,004
370	0,008	0,016	0,094	0,140					
380	0,004	0,007	0,046	0,087	900	1,13	2,95	>6	0,005
390	0,004	0,004	0,025	0,053	920	1,11	2,90	>6	0,006
					940	1,07	2,75	>6	0,007
400	0,003	0,003	0,017	0,033	960	1,03	2,70	>6	0,008
410	0,003	0,002	0,011	0,022	980	0,97	2,55	>6	0,009
420	0,002	0,001	0,009	0,016					
430	0,002	0,001	0,008	0,013	1000	0,93	2,50	6,1	0,011
440	0,002	0,001	0,007	0,015	1050	0,82	2,20	5,5	0,016
450	0,002	0,001	0,007	0,017	1100	0,72	1,90	5,0	0,021
460	0,001	0,001	0,007	0,018	1150	0,63	1,65	4,3	0,028
470	0,001	0,001	0,007	0,025	1200	0,55	1,40	3,9	0,038
480	0,001	0,001	0,007	0,036	1250	0,47	1,25	3,4	0,055
490	0,001	0,002	0,008	0,054	1300	0,42	1,11	3,00	0,070
					1350	0,36	0,93	2,50	0,100
500	0,001	0,003	0,011	0,077	1400	0,30	0,77	2,05	0,15
510	0,002	0,005	0,018	0,110	1450	0,23	0,59	1,70	0,20
520	0,003	0,008	0,028	0,147					
530	0,005	0,015	0,048	0,20					
540	0,008	0,023	0,076	0,24	1500	0,19	0,48	1,39	0,32
550	0,013	0,036	0,116	0,32	1600	0,15	0,33	0,92	0,39
560	0,019	0,056	0,180	0,41	1700	0,11	0,22	0,62	0,36
570	0,028	0,081	0,26	0,52	1800	0,090	0,14	0,44	0,36
580	0,038	0,117	0,37	0,61	1900	0,074	0,090	0,32	0,37
590	0,054	0,165	0,50	0,75					
					2000	0,067	0,080	0,24	0,34
600	0,070	0,21	0,67	0,97	2100	0,065	0,080	0,20	0,30
610	0,095	0,28	0,86	1,29	2200	0,068	0,080	0,17	0,25
620	0,120	0,34	1,09	1,46	2300	0,073	0,080	0,16	0,20
630	0,150	0,44	1,34	1,50	2400	0,083	0,080	0,15	0,15
640	0,185	0,54	1,65	1,52	2500	0,100	0,090	0,15	0,12
650	0,22	0,62	2,00	1,70	2600	0,12	0,12	0,16	0,15
660	0,27	0,76	2,40	1,85	2700	0,15	0,16	0,21	0,38
670	0,31	0,90	2,80	1,80	2800	0,22	0,35	0,42	0,75
680	0,36	1,02	3,3	1,75	2900	0,45	1,15	1,15	1,30
690	0,42	1,19	3,6	1,70	3000	1,20	2,10	1,90	2,10

Figure SF4 B. Extension coefficient of the blue filter used during the UC experiment.

Methodology

0.538 g of Yttrium (III) nitrate hexahydrate (Sigma Aldrich 99+; rare earth impurities is < 0.25%), 0.260 g of Ytterbium (III) nitrate pentahydrate (Sigma Aldrich 99.999 %) and 0.015 g of Thulium (III) nitrate pentahydrate (Sigma Aldrich 99.9 %; rare earth impurities < 0.15%) were dissolved in 75 mL de-ionized water. 5.777 g of citric acid was dissolved into the pre-mentioned mixture to obtain a concentration of 0.4 M and citric acid to rare earth metal ratio of 4. In a separate flask, 3.78 g of NaF were dissolved in 75 mL of de-ionized water to obtain a 1.2 M concentration. The two mixtures were left under stirring for 1 hour after which, the NaF solution was added to the rare earth metal solution dropwise. After mixing the two solutions, they were left stirring for 30 minutes then transferred into a Teflon-lined autoclave (where only ¾ of the autoclave was filled with solution). The solution was then treated hydrothermally at 180°C for 24 hours. After completion, the product was washed three times with de-ionized water and once with ethanol.

Gold nanorods colloidal suspension is acquired from Sigma Aldrich with a 10 nm diameter and 41 nm in length. Au concentration is estimated to be greater than 30 µg/mL in H_2O. The amount of cetyl trimethylammonium bromide, $C_{19}H_{42}NBr$ (CTAB) ligand on the metal (used to stabilize the nanorods) is estimated to be < 0.1 wt. %. CdS is prepared by precipitation of Na_2S and $CdNO_3$ followed by calcination under inert atmosphere at 600°C for four hours. 0.25 wt. % Au/CdS is made by mixing 120 mg of CdS with 10 mL of gold colloidal suspension and drying at 90°C overnight under stirring.

15 mg of 0.25 wt. % Au nanorods/CdS are mixed with 15 mg of ($NaYF_4$ – 28mol% Yb – 0.75mol% Tm) and sonicated in ethanol for several minutes. The mixture is then deposited on glass and the solvent dried at 70°C. Inside a 6 mL reactor, one drop of methanol (ca. 0.05 mL) is added along with the coated slide and the reactor is sealed. The catalyst is then excited with ≈ 0.15W at 980 nm (spot size ≈ to 3 mm) light provided from a 100 fs pulsed laser (Coherent), filters were provided from Concept Design Production (CDP) Systems Corp (SF4 contains information related to the filers usTCD and a Hysep Q column under N_2 carrier gas. The blank experiment (Figure S2) is conducted in the same manner with the exclusion of methanol to eliminate the possibility of ligand (CTAB) contribution.

Raman analysis were performed using a Thermo Scientific™ DXR™. Catalyst samples were analysed from 50 to 3400 cm^{-1} with multiple scans (16scans) with exposure time of 0.5 seconds, the wavelength of the laser used for the analysis was 532 nm, with the power of 8mW and the spot size was 2.1µm. The aperture opening was 50µm and grating had 900 lines per mm. High-Resolution Transmission Electron Microscopy (HRTEM) was carried out at 200 kV with a JEOL JEM 2100 instrument equipped with a LaB_6 source. The point-to-point resolution of the microscope was 0.19 nm. Samples were deposited on holey-C-coated Cu grids from alcohol suspensions.