Supplementary Material

Plasmon induced ultrafast injection of hot electrons in Au nanoislands grown on CdS film

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1. Description of ultrafast (femto-pico second) time resolved absorption Visible/NIR pump-probe spectroscopic system (UTRPPS).

To investigate the charge carrier excitation and relaxation dynamics of the device, UFTRPPS is best non contact technique. The ultrafast time resolved absorption spectroscopy is pump–probe method in which sample is excited /pumped at a given wavelength (UV/Vis/NIR) for different delay time period. In our experiment, UFTRPPS measurement has been performed at room temperature using experimental setup consists of an oscillator (micra), regenerative amplifier (coherent legend) coupled with an operational parametric amplifier (OPA). Figure S1 shows a simplified block diagram of the ultrafast (femto-pico second) time resolved absorption visible/NIR pump-probe spectroscopic system. The oscillator is basically a verdi pumped micra system whose output (350mW power with 800nm pulses) is seeded to an amplified Ti: sapphire laser system which produces a pulse with 800nm, 45fs pulse width with 1 KHz repetition rate and 4mJ average energy output. The output of the laser system further divides into 2 portions: one is fed into OPA (TOPAS) to produce a desired wavelength to excite the sample. The OPA produces a spectrally tunable (240-2600 nm) femto second (fs) pulses with an output pulse duration of 80fs to excite/pump the sample while other is fed into spectrometer (HELIOS, Ultrafast system) passing through a delay stage of 0-8ns which further falls on sapphire crystal producing white light continuum as a probe pulse.

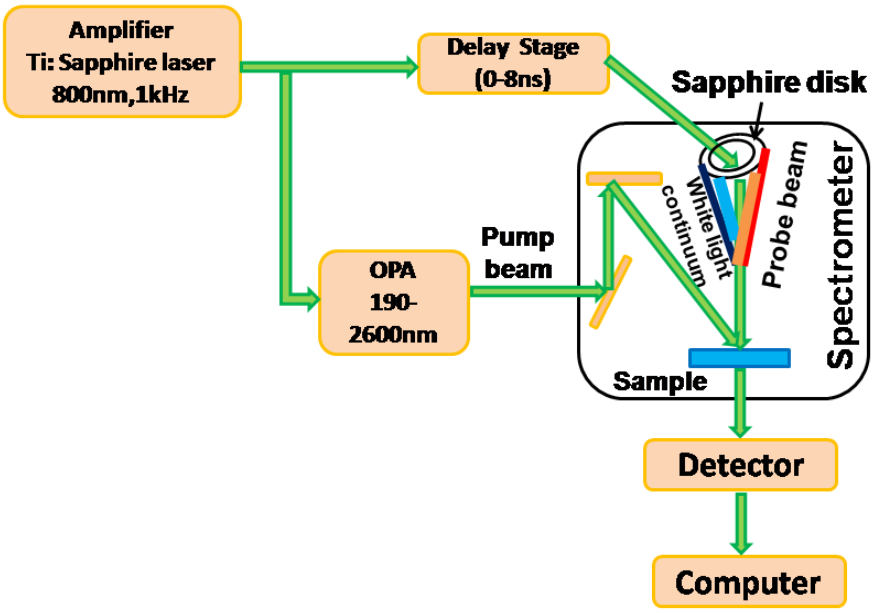


Fig.S1 Block diagram of the Ultrafast (femto-pico second) time resolved absorption Visible/NIR pump-probe spectroscopic system (UTRPPS).

2. Energy dispersive spectroscopy (EDS) spectra of Au-CdS film.

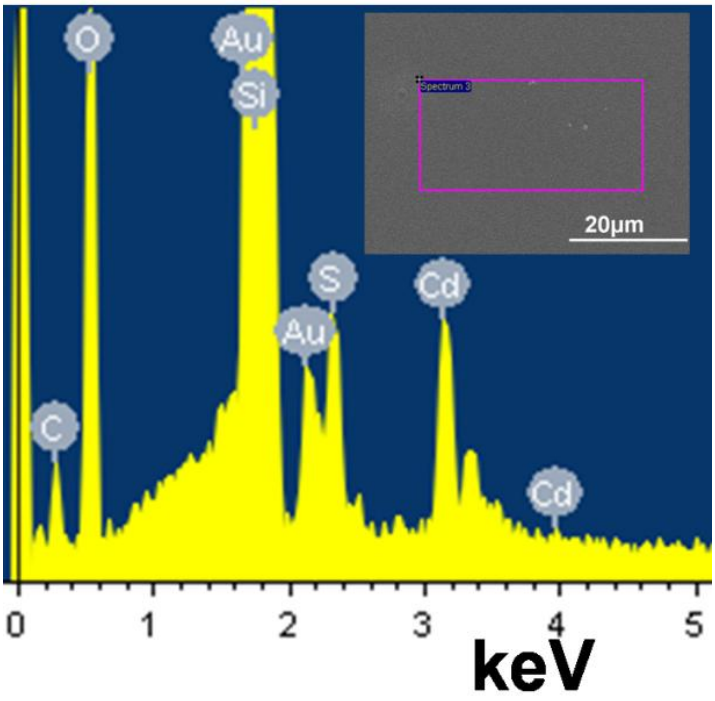


Fig. S2 EDS spectra of Au-CdS film. The characterized FESEM image is shown in inset.

3. Three dimensional schematic diagram of Au-CdS film

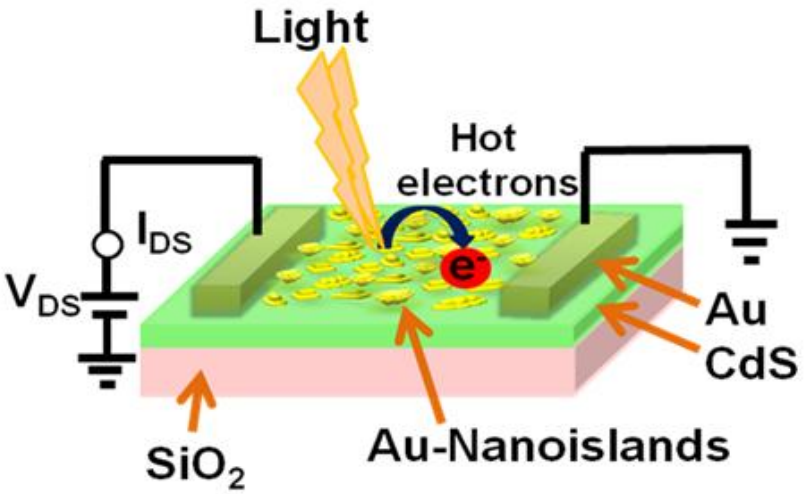


Fig.S3 Schematic diagram of the Au-CdS film based devices used for the experiments during research work. The channel of the device consist Au-nanoislands on top of CdS thin film. A laser light (halogen source act as Visible light Source, power density P_d =22mW/cm^2, continuous wave laser-1064nm as near infrared light source with tunable power meter (P_d from 0.04mW/cm^2 to 29mW/cm^2) assisted with Al coated fiber incident on the surface of Au-CdS film. This schematic of the device geometry helps to explain the generation of hot electron at the surface of metal nanoislands due to enhanced absorption of light with localized surface plasmon resonance. The black curved arrow in schematic indicates the transfer of generated (highly energetic) hot electron from Au (metal) nanoislands to CdS thin film (semiconductor).

4. Bias voltage dependent photocurrent measurement and stability of device under 400nm illumination and white light respectively.

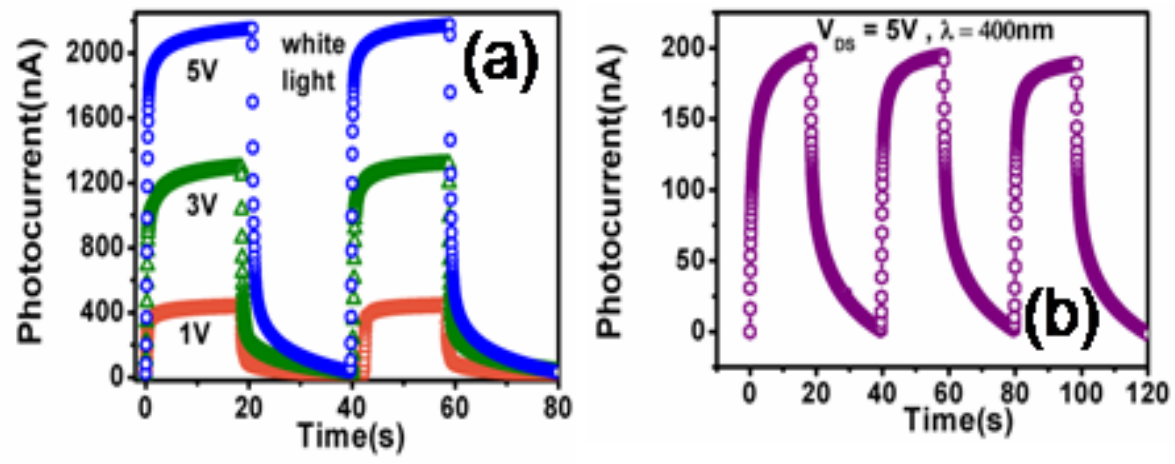


Fig.S4 (a) Bias voltage dependent photocurrent of Au-CdS film with halogen light as white light source (b) stability of the Au-CdS film at 5V under 400nm light illumination.

5. Power dependent photocurrent measurement and bias voltage dependent rise time measurement under NIR 1064nm illumination (power density; P_d= 29mW/cm^2).

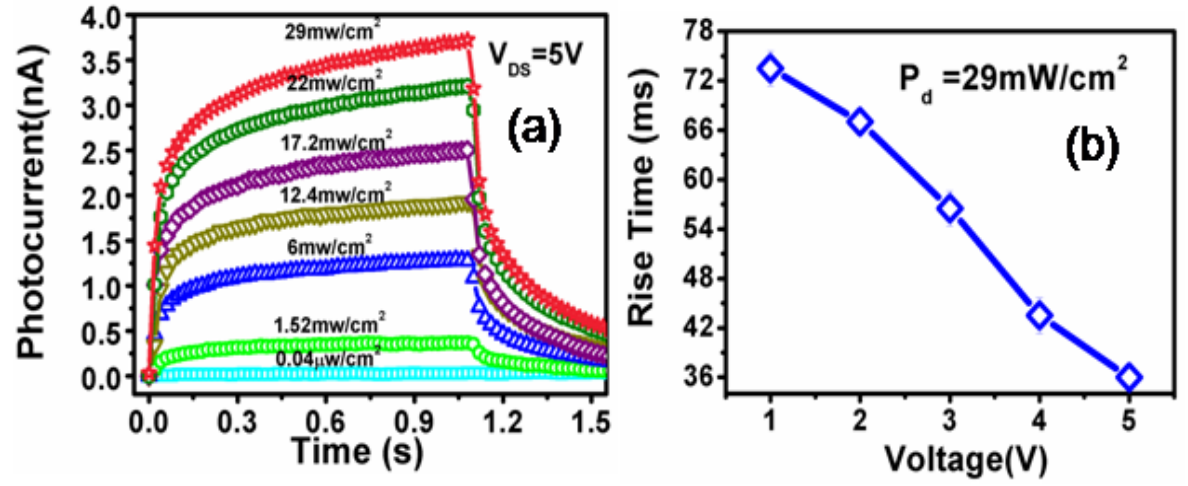


Fig.S5 (a) Transient photocurrent measurement Au-CdS film at different power densities ranges from (0.04mW/cm^2 to 29mW/cm^2). This figure shows Au-CdS film is sensitive for lower power densities P_d. The photocurrent amplitude~20pAfor 0.04mW/cm^2 increases to 3.7nA for 29mW/cm^2. This significant increase in photocurrent is may be due to enhancement in field at the near the surface of nanoislands. (b) Response time Vs voltage characteristics of epitaxial grown Au-CdS at fixed NIR (1064nm) P_d =29mW/cm^2. The rise time (defined as time of photocurrent to reach from 10% to maximum value 90%) dependence at different bias voltage of epitaxial grown Au-CdS. Rise time decreases with increase in voltage at fixed NIR (1064nm) P_d =29mW/cm^2. At 1V rise time was 73ms which decreases up to 39ms at 5V.

6. Step wise rise of current & photocurrent dependence on power density.

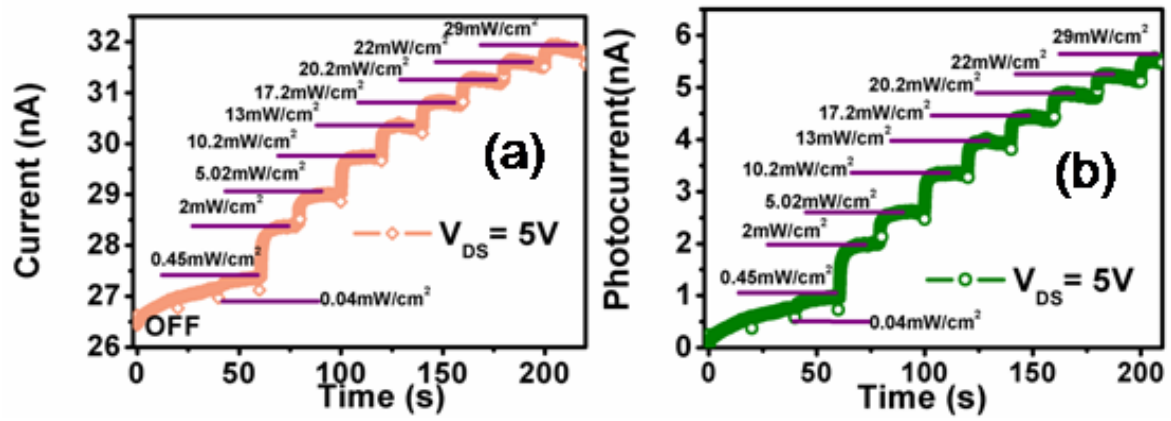


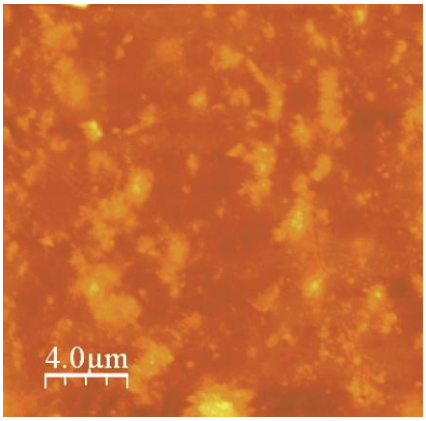
Fig. S6 (a) Step wise dependence of current on power w.r.t time at 5V bias voltage. (b) Step photocurrent dependent on power density w.r.t to time at 5V bias voltage of Au-CdS.

7. Description of topographic (2D) NSOM imaging.

The plasmonic enhancement in the visible range, of gold nanoislands having height up to several hundred nanometers has been investigated using, integrated near-field scanning optical microscope (Nanonics MultiView 2000) – atomic force microscope- Raman system has been used.

NSOM

NSOM has a cantilevered aperture probe (~100 nm in diameter) pulled from single-mode fiber with gold coating, operating in illumination mode with laser source at 532 nm. The near-field experiments were performed using reflection modewith illumination through a fiber aperture probe produced by Nanonics. The NSOM tip is positioned above the sample. When the probe is close to the illuminated surface of the sample, it scatters the evanescent waves of the near field. The resulting radiated waves are reflected and detected in reflection mode by a photomultiplier tube (PMT) through a microscope objective (x50, N.A. 0.45). An image is formed by raster scanning the sample (20 µm X 20 µm) and recording the collected light intensity as a function of the scan position



8. FDTD simulation results of Au-CdS film.

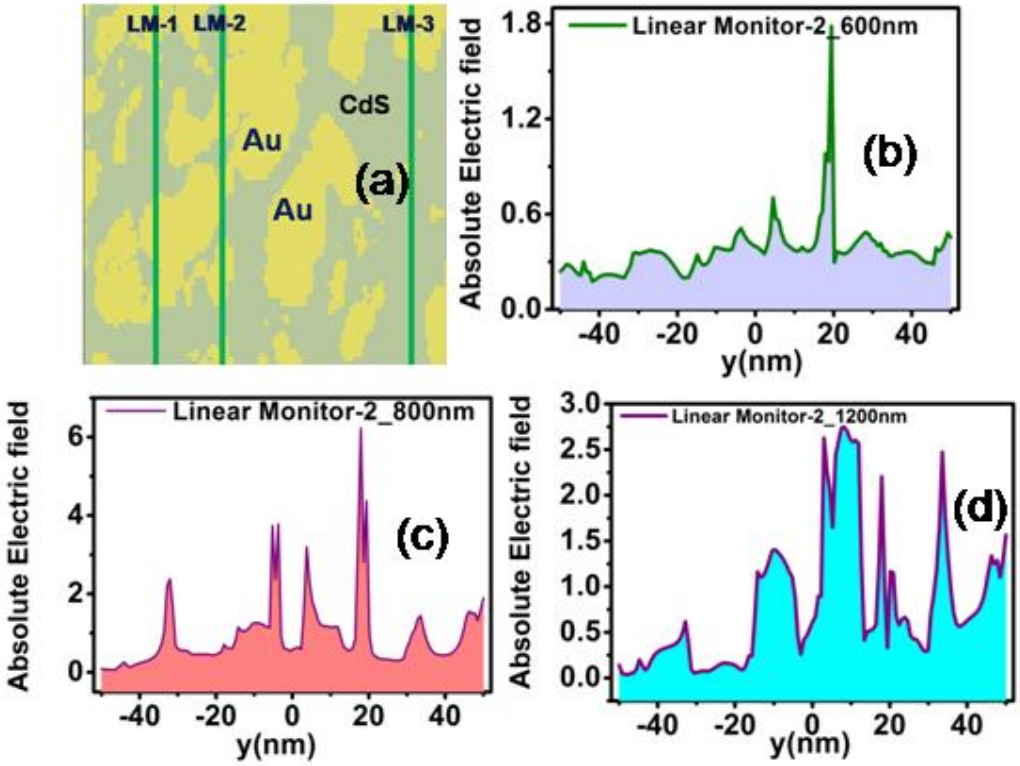


Fig.S8 (a) 2D false image (top view) of Au- CdS film used during simulation. To show the electric field enhancement at Au-CdS interface along y-z plane, we cropped the image and use three linear monitors (LM-1, LM-2, and LM-3). (b) Electric field enhancement of Au-CdS at 600,800,1200nm. The electric field intensity enhancement was calculated using formula; enhancement (%) = 100* (E-E0)/E0, Where E = Electric field intensity of Au nanoislands grown on CdS film and E0 = Electric field intensity of only CdS film. The strong enhancement in electric field is observed between two close located Au-nanoislands.

9. Simulated absorption spectra of Au-CdS and experimental result of transmission spectra of Au-CdS.

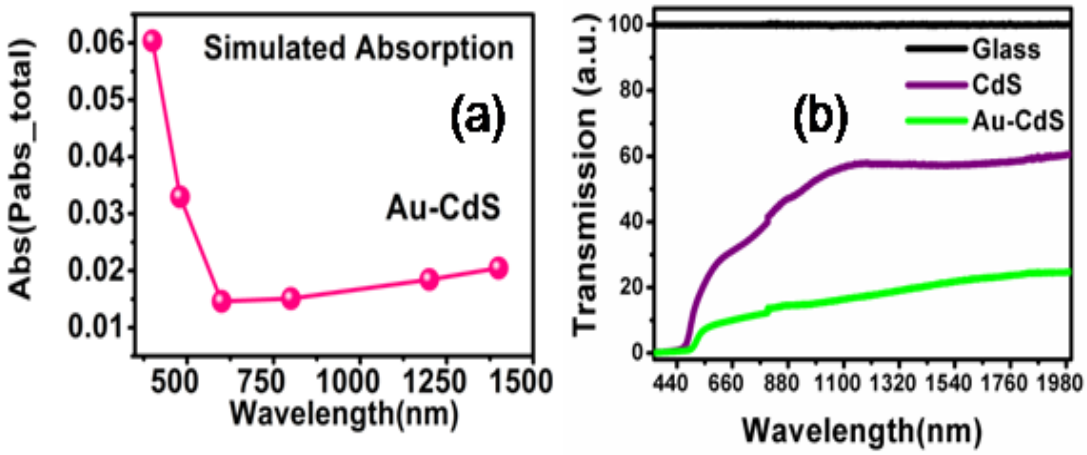


Fig.S9 (a) simulated absorption spectra of Au-CdS film. It can observe absorption increases at higher wavelength. (b) Experimental comparison of transmission spectra of only glass, CdS film on glass and Au nanoislands decorated CdS Film. It indicates that 100% transmission in case of glass where as transmission decreases for CdS and very small transmission of light for Au-CdS.

10. Expanded spectra of CdS and Au-CdS pumped at 480nm.

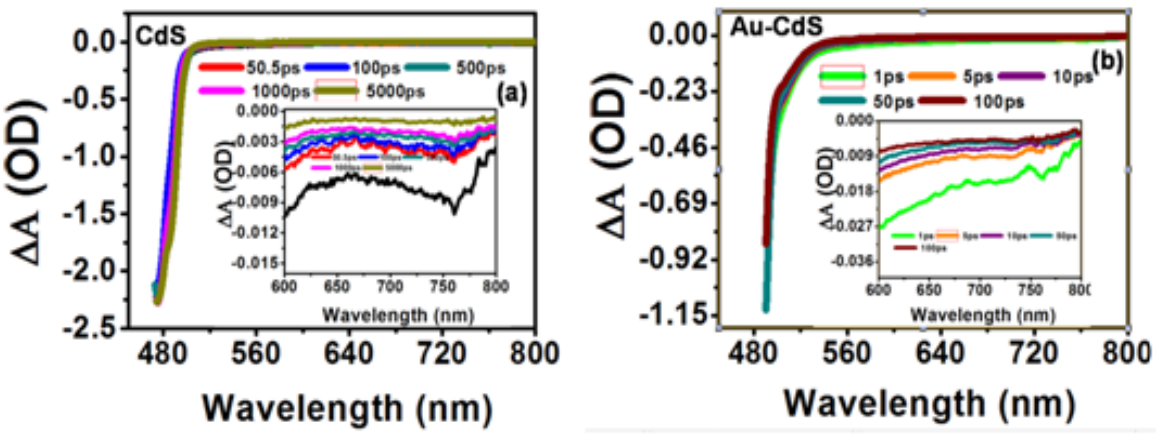


Fig.S10 depicts the absorption spectra for only CdS film probed from 450nm to 800nm for 10ps to 5000ps; Inset indicates the zoomed view of absorption spectra from 600nm to 800nm. It clearly shows that with increase in delay time period, absorption reaches close to zero. (b) indicates the absorption spectra of Au nanoislands grown on CdS film from 450nm to 800nm for 1ps to 100ps; Inset shows enlarged view of absorption spectra for respective time period. It clearly shows that absorption decreases with increase in delay time period

11. Transient absorption spectrum of only gold nanoislands at 1250nm pumping.

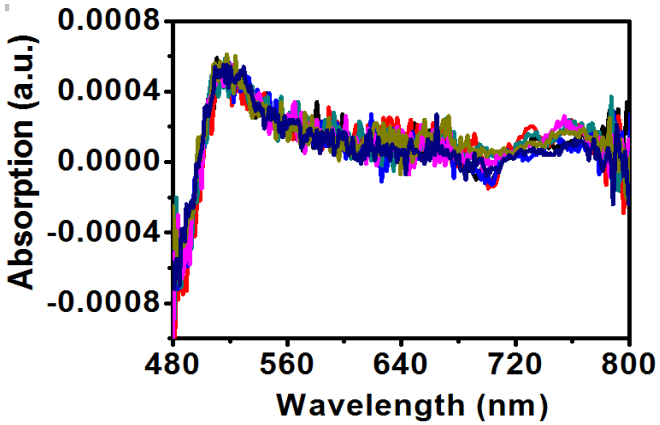
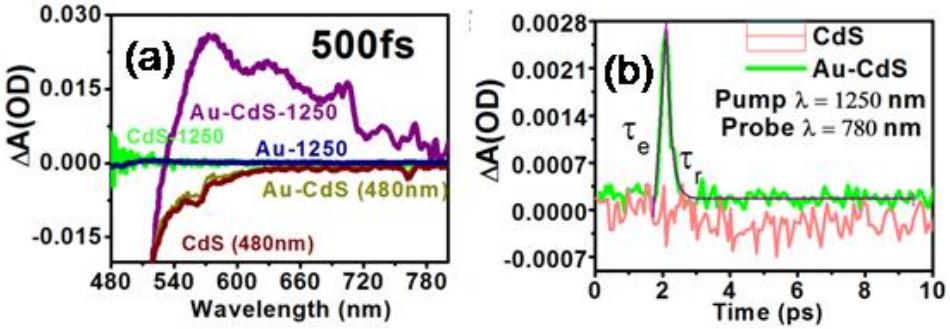


Fig. S11 Transient absorption of only gold film pumped at 1250nm. We observed the expected absorption signal of gold at 540nm which is consistent with the published articles.

12. Comparison between CdS and Au-CdS in transient absorption and transient kinetic spectrum.



13. Table 1: Transient kinetic analysis of CdS film pumped at 1250nm.

S.NO.	λ nm	IRF (ps)	τ_0 (ps)	τ_1 (ps)	A_1	τ_2 (ps)	A_2	τ_3 (ps)	A_3
1.	486	0.218 ±1.29	0.2784 ±0.103	0.109 ±0.11	-0.185 ±1.100	271.9 ±3100	-0.0035 ±0.21	401.8 ±205	-0.0012 ±0.0088
2.	508	0.237 ±0.07	0.2883 ±0.0414	0.199 ±0.77	0.0253 ±0.02	250.9± 148	-0.0139 ±0.009	1534 ±11700	-0.00031 ±0.0009
3.	550	0.208 ±2.91	0.2936 ±0.0238	0.1043 ±0.021	0.109± 15000	121 ±364	-0.00023 ±0.003	1534 ±17200	0.00008 ±0.0003
4.	600	0.191 ±2.74	0.2763 ±0.0091	0.0958± 0.001	0.0852 ±12000	112.5 ±387	-0.00013 ±0.0023	1533 ±1700	-0.00005 ±0.0019
5.	650	0.179 ±3.41	0.2690 ±0.0150	0.0897 ±0.010	0.0458 ±87000	81.32 ±121	-0.00043 ±0.0003	9739 ±243	-0.00005 17±0.00 048
6.	700	0.165 ±2.01	0.2098 ±0.0012	0.1209± 0.005	0.0104 ±6	24.04 ±0.05	-0.00000 984±1	288900 00±0.01	-515±1
7.	720	0.013 ±1.09	0.1633± 0.09	0.1335± 0.001	0.0040 ±5	24.74 ±0.01	-0.00245 ±1	288900 00±0.00 2	-358±1
8.	750	0.085 ±0.09	0.205 ±0.100	0.0857 ±0.05	0.00924 ±1	150.08 ±0.001	-0.00010 4±1	288900 00±0.00 4	-255±1
9.	800	0.162 ±0.05	0.04186 ±0.025	0.0813± 0.001	0.00677 ±1	235.2 ±0.002	-0.00006 79±1	288900 00±0.00 6	-380±2

Table 2: Transient kinetic analysis of Au-CdS pumped at 1250nm.

S.NO.	λ nm	IRF (ps)	τ_0 (ps)	τ_1 (ps)	A_1	τ_2 (ps)	A_2	τ_3 (ps)	A_3
1.	486	0.205 ±0.1	0.1285 ±0.121	0.7108 ±0.065	-0.164 ±0.440	243.4 ±99.1	-0.0014 ±0.0013	3720 ±5690	-0.0056 ±0.0012
2.	508	0.237 ±0.06	0.1677 ±0.066	0.7902 ±0.037	0.0599 ±0.058	224.3 ±37.5	-0.000506 ±0.00017	29220 ±82800	-0.0018 ±0.0009
3.	532	0.226 ±1.61	0.1133 ±0.031	0.8205 ±0.0309	0.168 ±1200	225 ±59	-0.00004±0.00096	29220 ±60500	-0.000094 ±0.0003
4.	600	0.167 ±1.51	0.0837 ±0.013	0.0.8928 ±0.124	0.138 ±1300	226 ±129	-0.00018±0.000045	29220 ±965000	-0.0000203 ±0.00027
5.	650	0.176 ±2.17	0.0800 ±0.020	0.9215 ±0.02015	0.0624 ±7700	227.9 ±118	-0.000445±0.00002	29220 ±145000	-0.0000127 ±0.00048
6.	700	0.139 ±1.41	0.0609 ±0.020	0.9509 ±0.0366	0.0409 ±4100	191.2 ± 137	-0.0004±0.00027	29130 ±16500	-0.000173 ±0.0043
7.	750	0.013 ±0.09	0.0066 ±26.5	0.9789 ±39.15	7.37 ±6300	172.4 ±187	-0.0000263±0.0009	32200 ±872000	-0.000186 ±0.0093
8.	800	0.013 ±0.05	0.0060±18.3	0.9818 ± 23.1	2.35± 530000	141.4 ±76.2	-0.000157±0.00002	32200 ±46300	-0.000125 ±0.000034

Table 3: Comparison between recovery dynamics of CdS and Au-CdS pumped at 1250nm.

Probe Wavelength	**CdS** **Decay time**	**Au-CdS** **Decay time**
535nm	980fs	180fs
600nm	184fs	90fs
650nm	160fs	103fs

Table 4: Reported mechanism for metal and semiconductor.

S.No	System	Pump Wavelength	Probe wavelength	Formation Time/ Excitation Time	Decay Time/ Recovery Time	Relaxation Time	Mechanism	Ref
1.	Au-CdSe	800nm	3000nm	20±10fs	~1.45±0.15 ps	---	PICTT	1
2.	Au-CdS Colloidal Nanocomposite	400nm	-----	300fs	11ps	100ps	PCT	2
3.	CdS-Au Nanorods	400nm	3000nm	97fs	1.83±0.22 ps	--	PIHET	3
4.	Ag@Cu_2O	600-750nm	800nm	---------	----------		PIRET+DET	4
5.	Au-TiO2	550nm	---------	<240fs	----------	--	PCT	5
6.	Au@Cu2O	650nm	----------	<100fs	2ps	--	DET+RET	6
7.	**Au-CdS**	**1140nm** **1250nm** **1440nm**	**550nm**	**150fs** **104fs** **125fs**	**220ps** **120ps** **180ps**	**3.5ns** **1.53ns** **2.12ns**	**PICTT/ DET/PIHET**	**Our Work**

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6. S. K. Cushing, J. Li, F. Meng, T. R. Senty, S. Suri, M. Zhi, M. Li, A. D. Bristow and N. Wu, *Journal of the American Chemical Society*, 2012, 134, 15033-15041.

Table 5: Detail kinetic study at different pumping wavelength.

S.No.	Pump Wavelength	Probe Wavelength	τ_1 excitation time (ps)	τ_2 recovery time (ps)	τ_3 relaxation time (ps)
1.	1140nm	500nm	0.2068±0.0712	3.946±1.6	328.6±26.2
		650nm	0.1111±0.0243	5.596±0.254	486.9±43.2
		780nm	0.3182±0.02582	4.493±0.292	485.2±81.8
2.	1250nm	480nm	0.109±0.11	273±3100	401.8±205
		650nm	0.0897±0.001	81.32±121	9739±243
		780nm	0.0857±0.05	150.08±0.001	28890000±0.0004
3.	1400nm	480nm	0.114±0.0392	361.8±71.4	±2690
		650nm	0.1115±0.0194	5.00±0.215	6853±1440
		780nm	0.629±0.0245	2.67±0.324	6848±1630