NanoTBTech

Nanoparticles-based 2D thermal bioimaging technologies

H2020-FETOPEN-1-2016-2017
Grant Agreement: 801305

Standardization of light-to-heat conversion efficiency of colloidal nanoheaters

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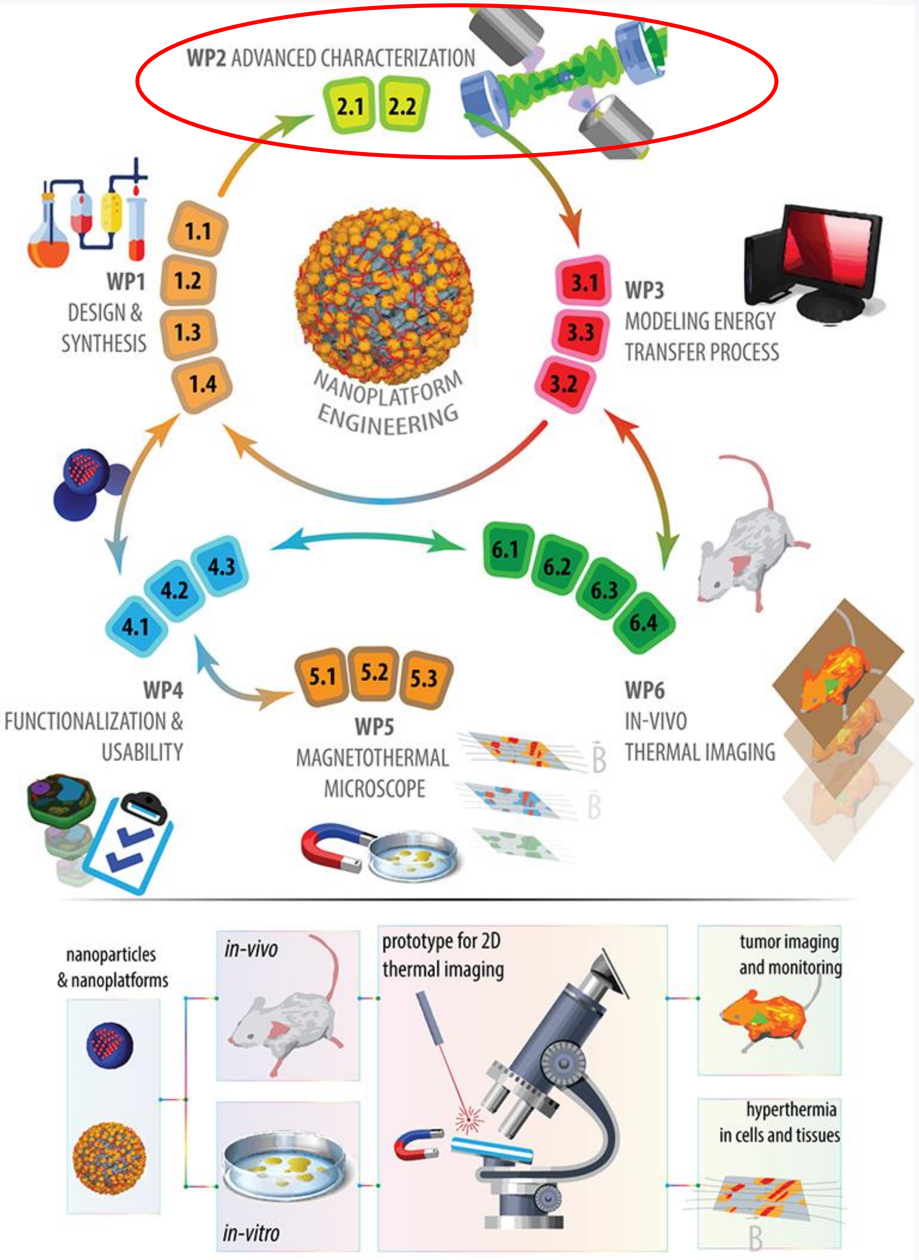
Luminescent Nanoparticle Assisted Sensing and Imaging



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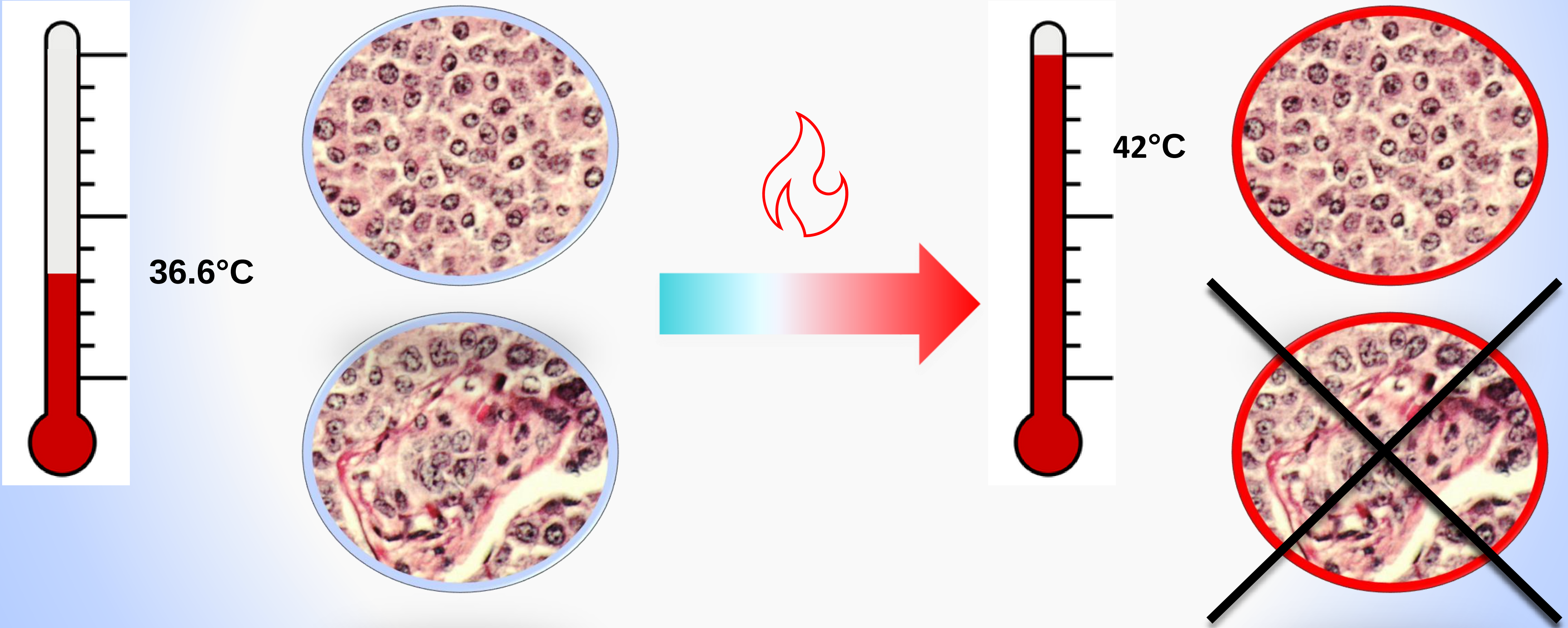
Standardization of light-to-heat conversion efficiency - presentation plan

1. Aim of studies
2. Examples of nanoheaters
3. Methods of η determining
4. Need of standardization
5. Results
6. A receipt

Why to measure light-to-heat conversion efficiency of nanoparticles?

Motivation of study the light-to-heat conversion efficiency - hyperthermia



Motivation of study the light-to-heat conversion efficiency - hyperthermia

Hippocrates: "*What medicines to not heal, the lance will; what the lance does not heal, fire will*"

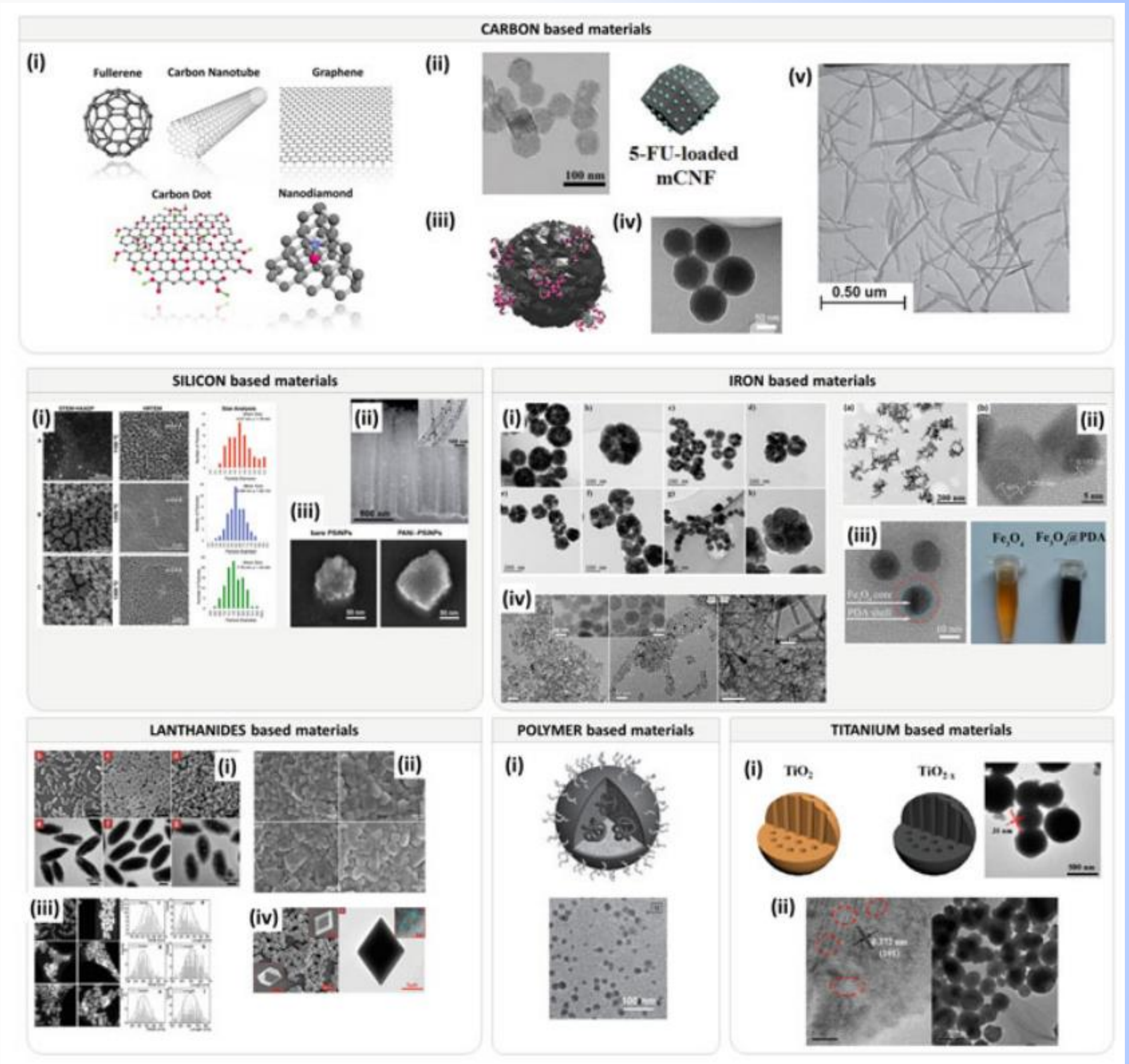
How to make hyperthermia more localized?

Whole body hyperthermia

Nanoparticles for hyperthermia treatment - requirements

- Nontoxicity, biocompatibility
- Chemical and photostability
- Nanoparticle size – fitting in circulatory/vascular system
- Irradiation wavelength fit in the biological window
- High absorption and **light-to-heat conversion efficiency**
- Multifunctionality

Hyperthermia nanomaterials



L. Marciniak, K. Kniec, K. Elzbieciak, A. Bednarkiewicz *Non-plasmonic NIR-Activated Photothermal Agents for Photothermal Therapy*. In: Benayas A., Hemmer E., Hong G., Jaque D. (eds) *Near Infrared-Emitting Nanoparticles for Biomedical Applications. Springer*

Other examples of light-to-heat conversion application

- Solar thermal energy

Z. Wang *et al.*, "Dynamic tuning of optical absorbers for accelerated solar-thermal energy storage," *Nat. Commun.*, vol. 8, no. 1, 2017.

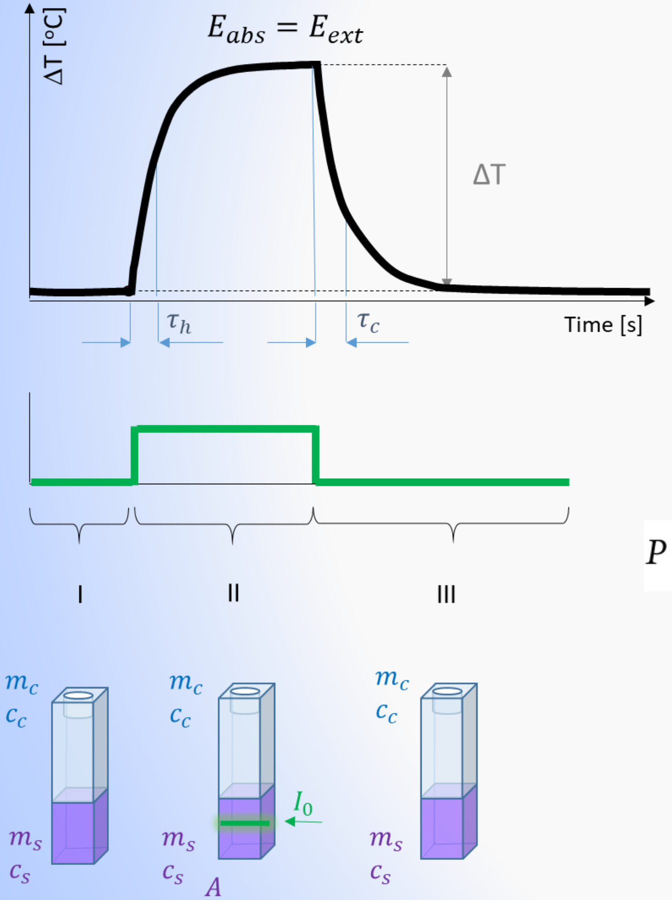
- Steam generation after solar illumination – possibility of sterillisation

O. Neumann, A. S. Urban, J. Day, S. Lal, P. Nordlander, and N. J. Halas, "Solar vapor generation enabled by nanoparticles," *ACS Nano*, vol. 7, no. 1, pp. 42–49, 2013.

- Photoactuators

Y. Yamamoto, K. Kanao, T. Arie, S. Akita, and K. Takei, "Air Ambient-Operated pNIPAM-Based Flexible Actuators Stimulated by Human Body Temperature and Sunlight," *ACS Appl. Mater. Interfaces*, vol. 7, no. 20, pp. 11002–11006, 2015

How to measure the light-to-heat conversion efficiency - methodology



Irradiated sample

$$P\eta = \frac{dQ_i}{dt} = mC_p\frac{dT}{dt} + \frac{dQ_{ext}}{dt}$$

Energy absorbed by sample

Light-to-heat conversion efficiency

Heat accumulated in the sample

Heat released to environment

$$P = P_{in} - P_{out} = P_{in}(1 - 10^{-A_\lambda})$$

Equilibrium condition

$$\boxed{P\eta = \frac{dQ_i}{dt} = \frac{dQ_{ext}}{dt}}$$

Laser turned off

$$mC_p\frac{dT}{dt} + \frac{dQ_{ext}}{dt} = 0$$

P – light power that is adsorbed by the sample
P_{in} – power of the incident laser beam
P_{out} – outgoing light power
A_λ – absorbance of the sample
Q_i – heat energy gained from the absorbed light energy
m – mass of sample
C_p – specific heat capacity
T – temperature
ΔT – temperature increase
Q_{ext} – heat dissipated into the environment
t – time

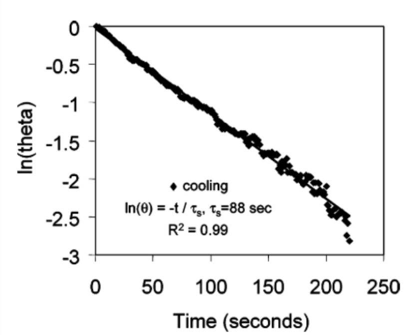
R. Li, L. Zhang, L. Shi, and P. Wang, “MXene Ti3C2: An Effective 2D Light-to-Heat Conversion Material,” *ACS Nano*, vol. 11, no. 4, pp. 3752–3759, 2017

Light-to-heat conversion efficiency of nanomaterials - models

Temperature probing?
mass of all system components

Roper's model

- $Q_L + Q_0 = Q_{ext}$
- $Q_{ext} = hA\Delta T \equiv \frac{\sum_i m_i C_{p,i}}{\tau_C} \Delta T$
- $\tau_C = -\ln\left(\frac{T - T_{amb}}{T_{max} - T_{amb}}\right)$

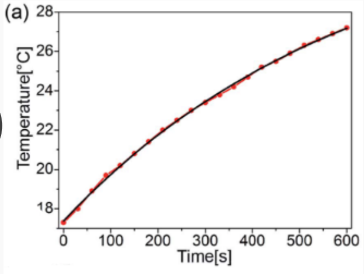


$$\eta = \frac{\frac{\sum_i m_i C_{p,i} \Delta T}{\tau_C} - Q_0}{I\left(1 - 10^{-A}\right)}$$

„effective mass" of the setup

Wang's model

- $\frac{d(T - T_{amb})}{dt} = a - b\,(T - T_{amb})$
- $T(t) = T_{amb} + \frac{a}{b}\left(1 - e^{-bt}\right)$



$$\eta = \frac{a \sum_i m_i C_{p,i}}{I\left(1 - 10^{-A}\right)}$$

$$1 = \frac{a \sum_i m_i C_{p,i}}{P_{in}}$$

D. K. Roper, W. Ahn, and M. Hoepfner, "Microscale heat transfer transduced by surface plasmon resonant gold nanoparticles," J. Phys. Chem. C, vol. 111, no. 9, pp. 3636–3641, 2007.
X. Wang, G. Li, Y. Ding, and S. Sun, "Understanding the photothermal effect of gold nanostars and nanorods for biomedical applications," RSC Adv., vol. 4, no. 57, pp. 30375–30383, 2014

Light-to-heat conversion efficiency of nanomaterials – Chen's model

$$Q_{\mathrm{laser}} = I\,(1-\xi)\left(1-10^{-E_\lambda}\right)\eta + I\xi \qquad Q_{\mathrm{loss}} = B\Delta T + C\,(\Delta T)^2$$

Energy balance

$$\left(\mathrm{m_s}c_{\mathrm{p,s}} + \mathrm{m_c}c_{\mathrm{p,c}}\right)\frac{\mathrm{d}\Delta T}{\mathrm{dt}} = I(1-\xi)\left(1-10^{-\mathrm{E}_\lambda}\right)\eta + I\,\xi - B\Delta T - C\,(\Delta T)^2$$

Efficiency

$$\eta = \frac{B\,(T_{\mathrm{end}} - T_0) + C\,(T_{\mathrm{end}} - T)^2 - I\xi}{I\,(1-\xi)\,(1-10^{-E_\lambda})}$$

I – power of the incident laser beam
ξ - the fraction of the laser energy absorbed by the cuvette walls and the solution
ms, cs - mass, heat capacity of the solution
mc cc mass and heat capacity of cuvette
ΔT difference between solution temperature at the time **t** ans starting solution temperature $\mathbf{T_0}$
$\mathbf{E_\lambda}$ - the extinction value at the illumination laser wavelength
η - the ratio of the absorption to extinction

H. Chen *et al.*, "Understanding the photothermal conversion efficiency of gold nanocrystals," *Small*, vol. 6, no. 20, pp. 2272–2280, 2010.

Literature approaches: Experimental setups

- Experimental cell in a vacuum – Roper
- Cuvette with/without stirrer – Chen
- Eppendorf
- Droplet - Richardson

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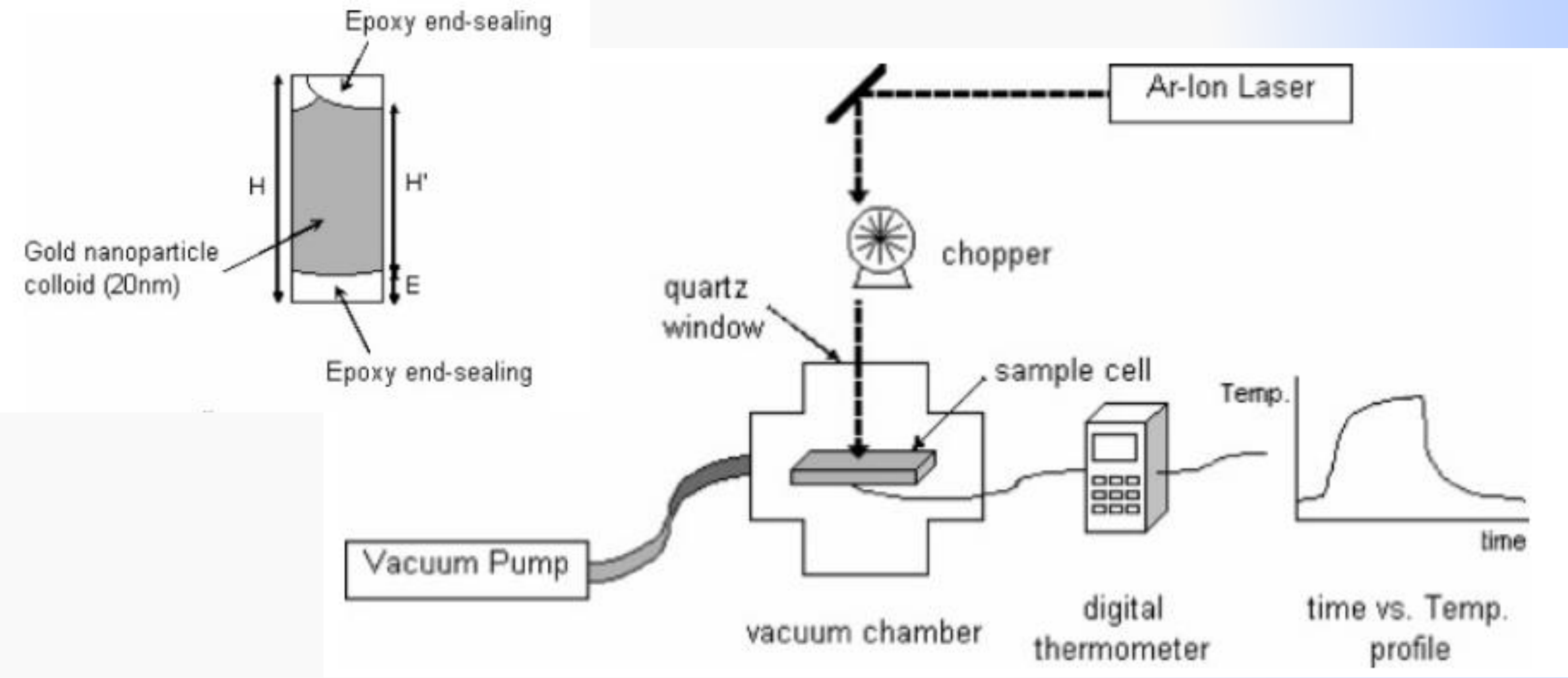

+ measurements in vacuum
+ sample cell is tight
- require dedicated sample cell
- thermocouple does not touch sample directly

D. K. Roper, W. Ahn, and M. Hoepfner, “Microscale heat transfer transduced by surface plasmon resonant gold nanoparticles,” *J. Phys. Chem. C*, vol. 111, no. 9, pp. 3636–3641, 2007.

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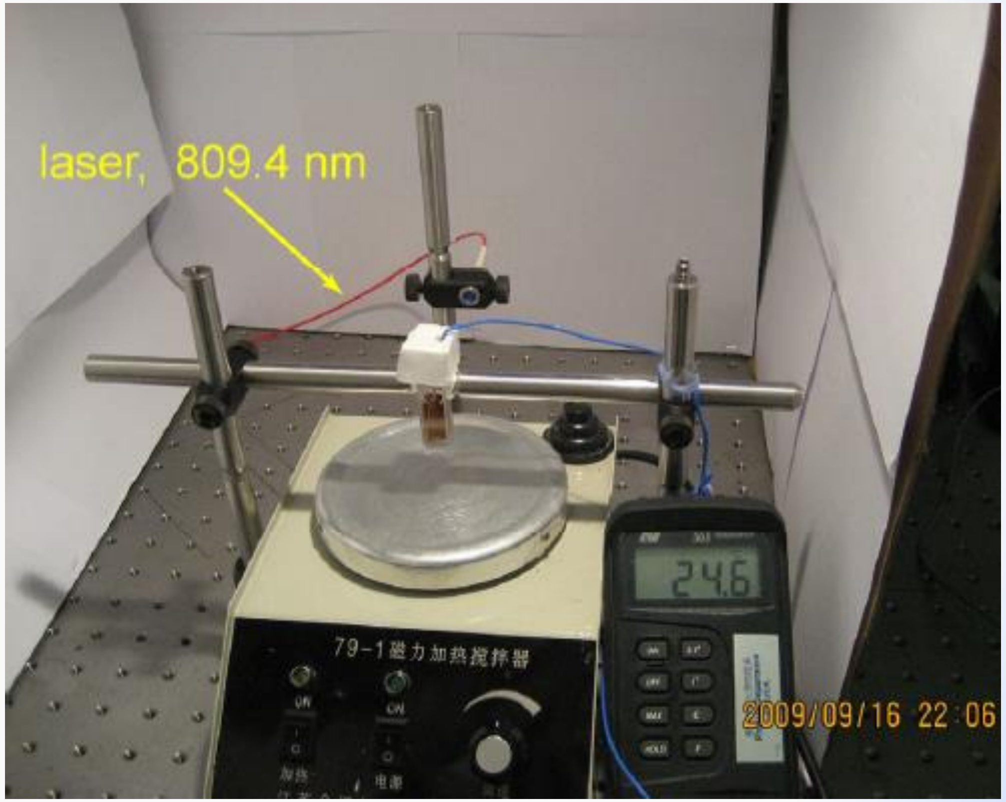
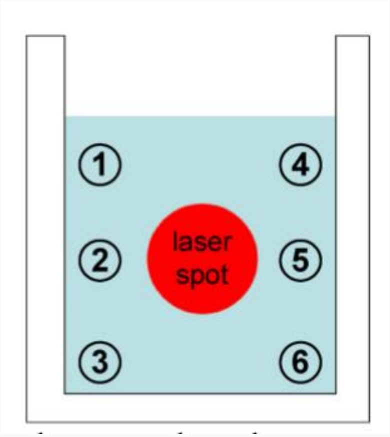


+ easy to implement
+ uniform temperature distrubution – magnetic stirrer
- large amount of sample required



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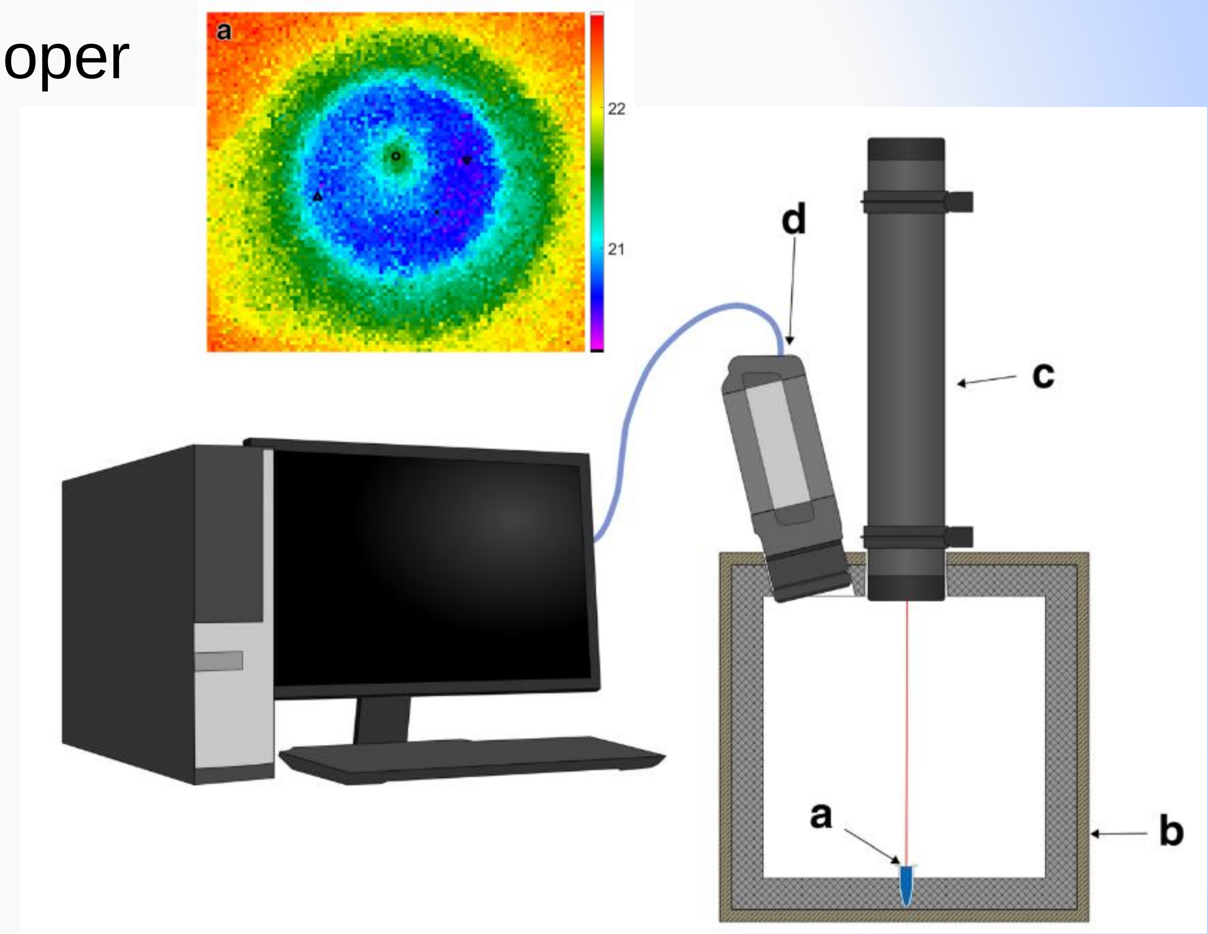

+ small amount of sample required
+ direct observation of sample temperature
- region of interest for temperature probing not specified

G. Chernov, J. L. Ibarra-Valdez, R. C. Carrillo-Torres, T. C. Medrano-Pesqueira, V. Chernov, and M. Barboza-Flores, “Improved Method of Study on the Photothermal Effect of Plasmonic Nanoparticles by Dynamic IR Thermography,” *Plasmonics*, pp. 935–944, 2018

Literature approaches: Experimental setups

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- Cuvette with a stirrer – Chen
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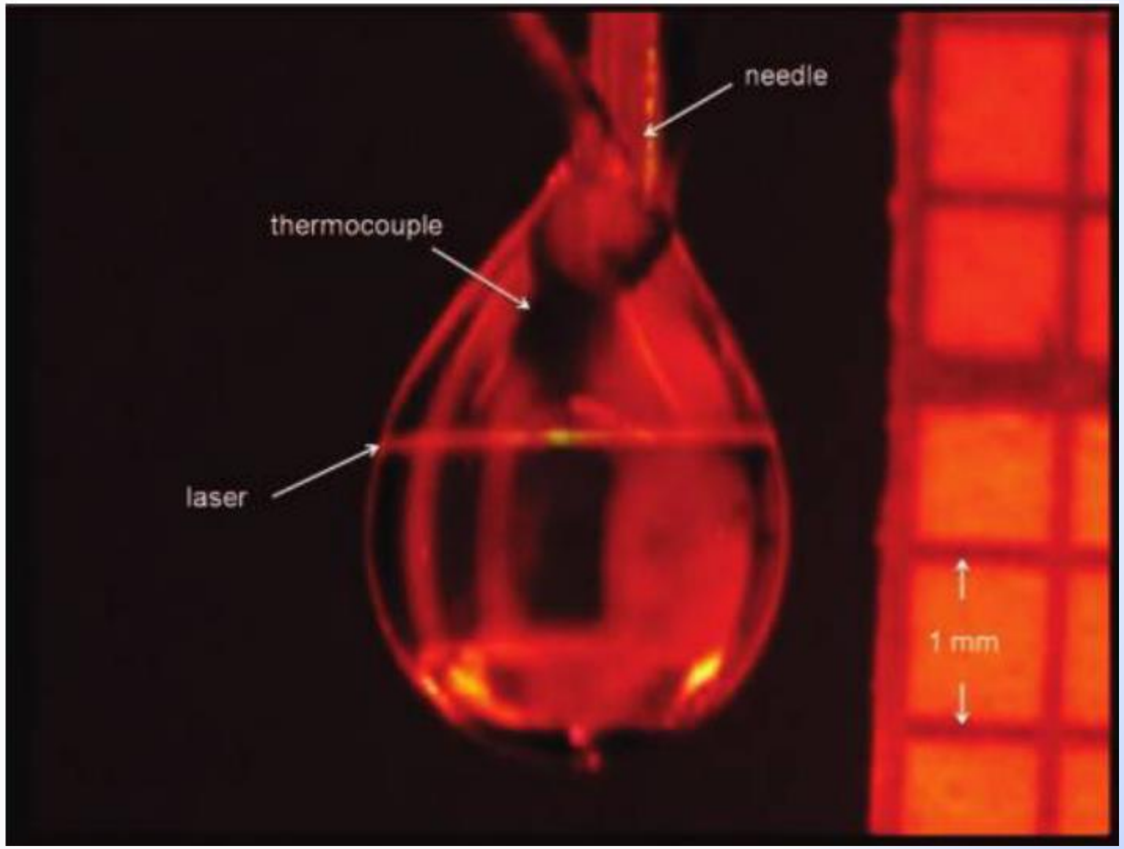
- **Droplet - Richardson**



+small amount of sample required
+direct observation of sample temperature
-positioning of the droplet against thermocouple/laser beam
-evaporation of the sample

H. H. Richardson, M. T. Carlson, P. J. Tandler, P. Hernandez, and A. O. Govorov, “Experimental and theoretical studies of light-to-heat conversion and collective heating effects in metal nanoparticle solutions,” *Nano Lett.*, vol. 9, no. 3, pp. 1139–1146, 2009.

Comparison of η for AuNPs

Material (Gold NPs)	Size [nm] (diameter)	Irradiation wavelength [nm]	LSPR wavelength [nm]	Part of mass of a cuvette	Experimental setup comments	Model	η_Q [%]	Reference (next slide)
nanocrystals	20	514	524 (broad: 475-575)	whole glass cell	small sample cell in a vacuum chamber	R*	**3.4-9.9**	[1]
$Au@SiO_2$ nanoshells	154	815	~815	all elements included	vacuum chamber, magnetic stirrer	R	30	[2]
nanorods	44x13	815	780	all elements included	vacuum chamber, magnetic stirrer	R	55	
nanocrystals	20	532	not mentioned?	no cuvette	sample is a droplet	R*	**100**	[3]
nanocrystals	16-100	809	809	whole cuvette	magnetic stirrer	C*	95-51%	[4]
nanospheres	5-50	532	not mentioned	solvent only	magnetic stirrer, open cuvette	R/C	80-65	[5]
nanostars	~20-120	785	684, 774, 829	"effective mass"	cuvette covered with foam plastic, magnetic stirrer	W*	79.5-65.2	[6]
nanorods	63.8x24.5, 70.1x19.0, 56.9x13.9	785	683, 774, 821	"effective mass"		W	94.2-69.7	
nanomatryoshkas	100	810	783	whole cuvette		R	63	[7]
nanoshells	150	810	796	whole cuvette		R	39	
nanoshells	15-100	532	520-565?	"effective mass"		W	100-55	[8]
nanorods	10x30-60	700-850	700-850?			W	~100	
nanorods@polymers: chitosan, alginate and poly(vinyl alcohol)	100x50, 150x100, 57x15	808	798, 807 (chitosan)	whole cuvette		R	47–51	[9]
spiky gold	54 - core 58 - spike	808	broad NIR	solvent only		R	78.8	[10]
Bumpy nanospheres	70-90	790	broad (NIR I)	The integral of the temperature gradient was used to determine the effective mass of the cuvette		C	96-97	[11]
Smooth nanospheres	56	790	790			C	99	
Nanospheres	20	808	524	solvent only	magnetic stirrer	R/C	7.7	[12]
Nanourchins	80		620				25.3	
Nanorods	25x60		650				17.8	
Nanorods	10x41		808				81	
Nanoconjugates (IR806 dye)	20 (Au) 250 (conjugate)		788				31.4	

References

- [1] D. K. Roper, W. Ahn, and M. Hoepfner, “Microscale heat transfer transduced by surface plasmon resonant gold nanoparticles,” J. Phys. Chem. C, vol. 111, no. 9, pp. 3636–3641, 2007.
- [2] J. R. Cole, N. A. Mirin, M. W. Knight, G. P. Goodrich, and N. J. Halas, “Photothermal efficiencies of nanoshells and nanorods for clinical therapeutic applications,” J. Phys. Chem. C, vol. 113, no. 28, pp. 12090–12094, 2009.
- [3] H. H. Richardson, M. T. Carlson, P. J. Tandler, P. Hernandez, and A. O. Govorov, “Experimental and theoretical studies of light-to-heat conversion and collective heating effects in metal nanoparticle solutions,” Nano Lett., vol. 9, no. 3, pp. 1139–1146, 2009.
- [4] H. Chen et al., “Understanding the photothermal conversion efficiency of gold nanocrystals,” Small, vol. 6, no. 20, pp. 2272–2280, 2010.
- [5] K. Jiang, D. A. Smith, and A. Pinchuk, “Size-Dependent Photothermal Conversion Efficiencies of Plasmonically Heated Gold Nanoparticles,” J. Phys. Chem. C, vol. 117, no. 51, pp. 27073–27080, Dec. 2013.
- [6] X. Wang, G. Li, Y. Ding, and S. Sun, “Understanding the photothermal effect of gold nanostars and nanorods for biomedical applications,” RSC Adv., vol. 4, no. 57, pp. 30375–30383, 2014.
- [7] C. Ayala-Orozco et al., “Au nanomatryoshkas as efficient near-infrared photothermal transducers for cancer treatment: Benchmarking against nanoshells,” ACS Nano, vol. 8, no. 6, pp. 6372–6381, 2014.
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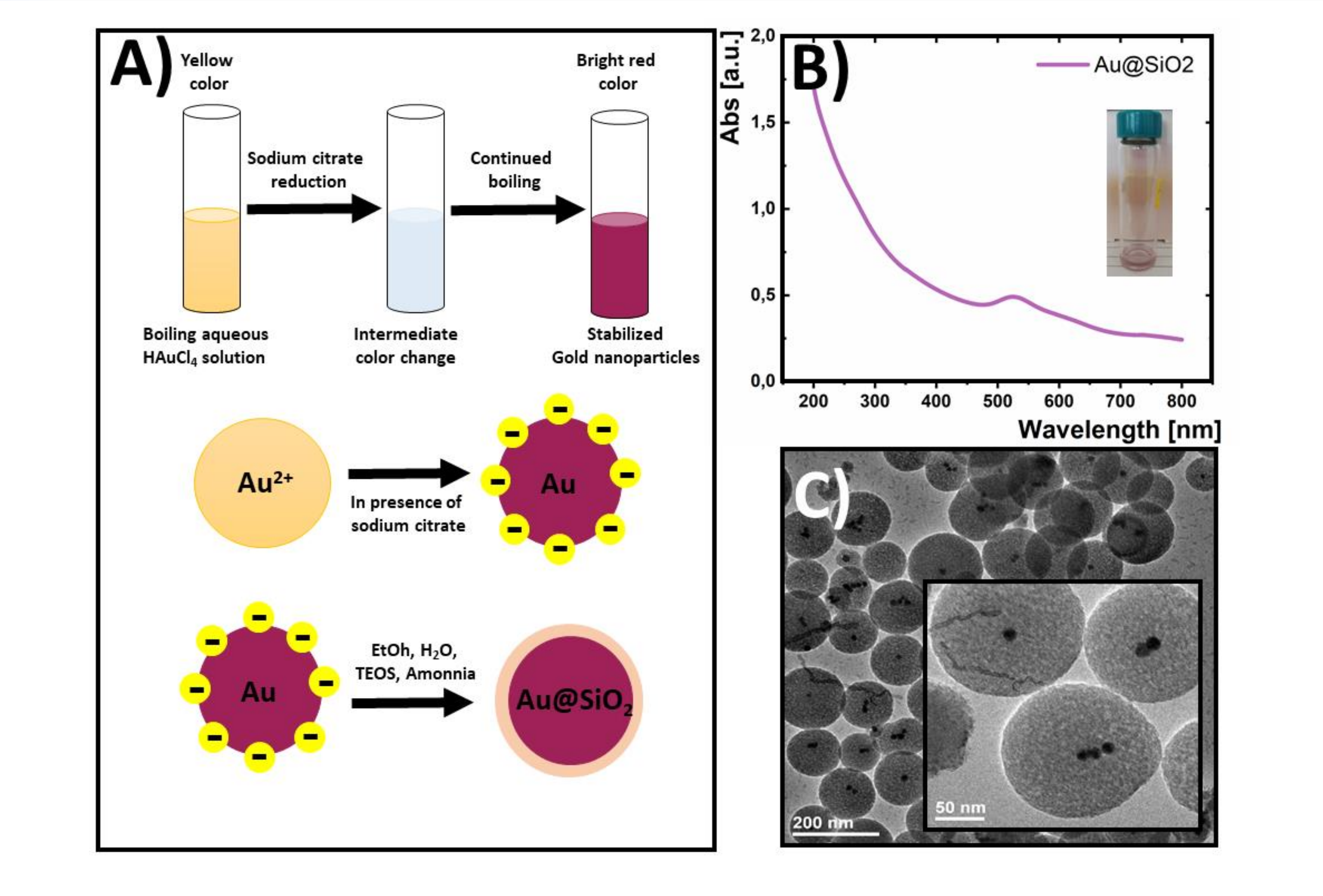
- [9] M. Almada et al., “Photothermal conversion efficiency and cytotoxic effect of gold nanorods stabilized with chitosan, alginate and poly(vinyl alcohol),” Mater. Sci. Eng. C, vol. 77, pp. 583–593, 2017.
- [10] C. Bi et al., “Realizing a Record Photothermal Conversion Efficiency of Spiky Gold Nanoparticles in the Second Near-Infrared Window by Structure-Based Rational Design,” Chem. Mater., vol. 30, no. 8, pp. 2709–2718, 2018.
- [11] S. A. Lindley and J. Z. Zhang, “Bumpy Hollow Gold Nanospheres for Theranostic Applications: Effect of Surface Morphology on Photothermal Conversion Efficiency,” ACS Appl. Nano Mater., vol. 2, no. 2, pp. 1072–1081, 2019.
- [12] M. Alrahili, R. Peroor, V. Savchuk, K. McNear, and A. Pinchuk, “Morphology Dependence in Photothermal Heating of Gold Nanomaterials with Near-Infrared Laser,” J. Phys. Chem. C, 2020.

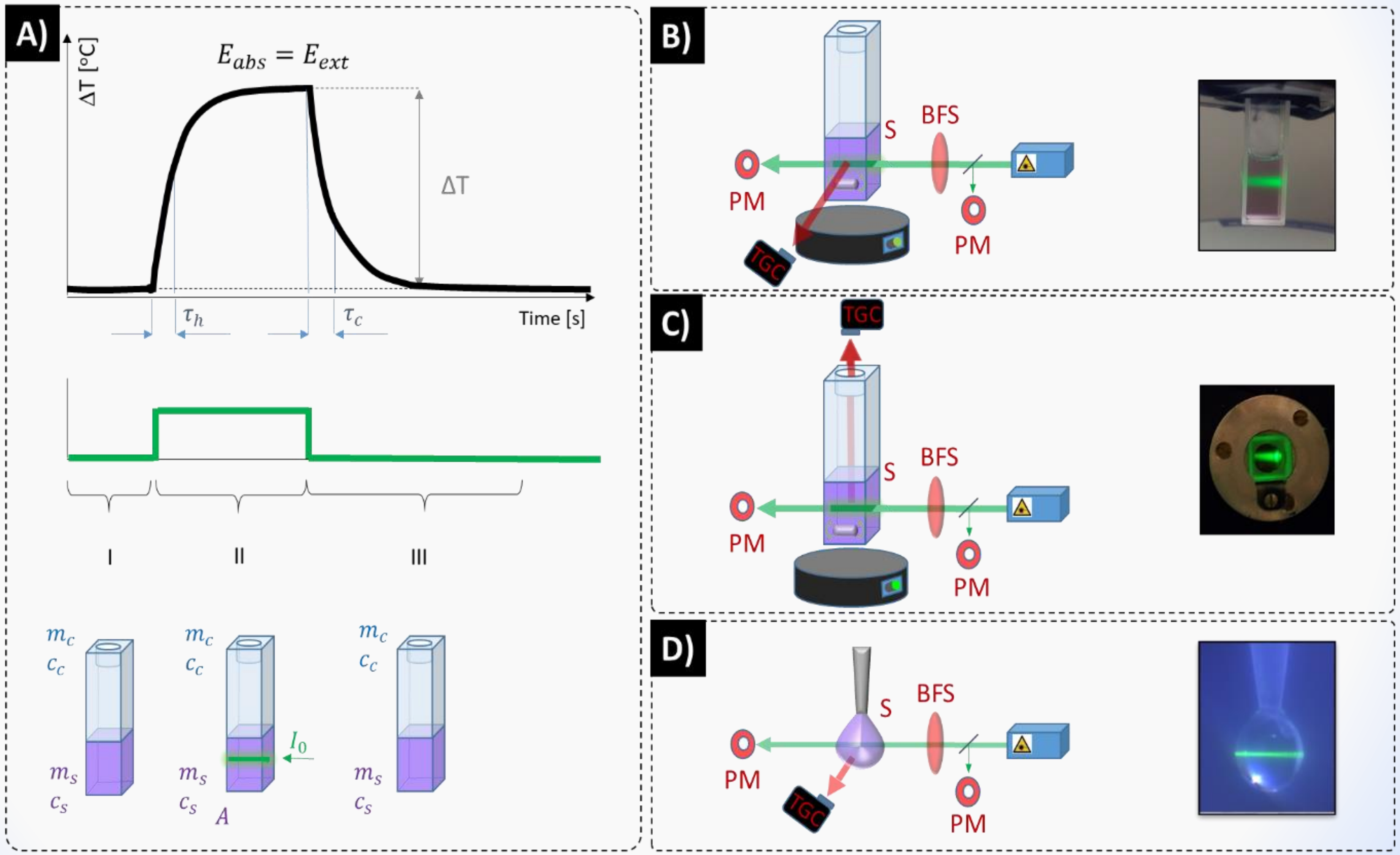
Standardization – why results obtained by different labs may differ?

- Efficiency depends on a wavelength
- Differences in existing models
- Effective mass of the sample and holder
- Stirring?
- Region of interest for temperature probing?

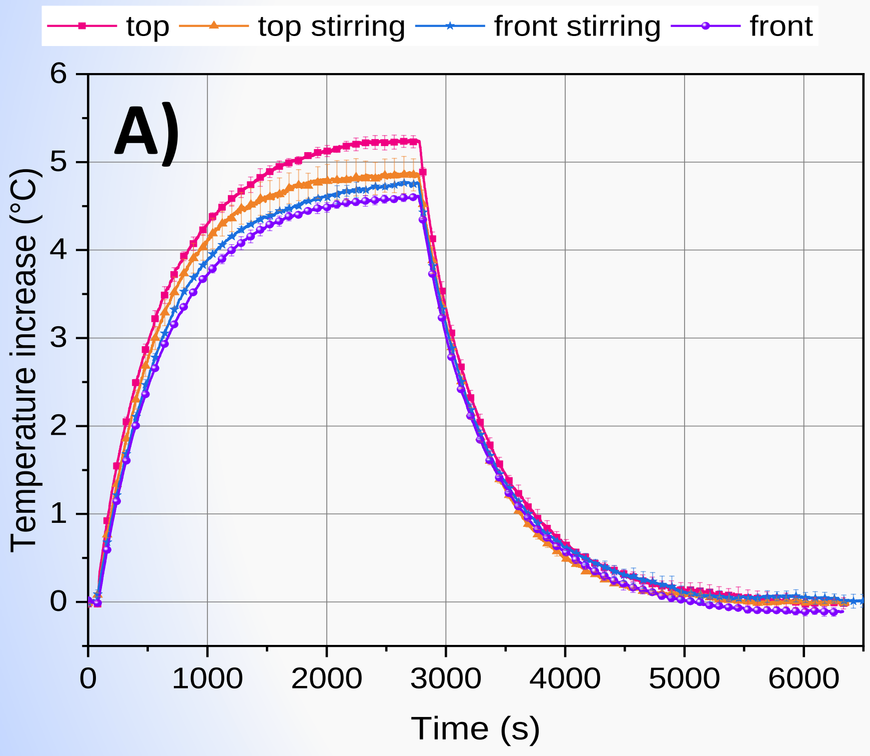
The same batch of Au@SiO_2 NPs were applied…

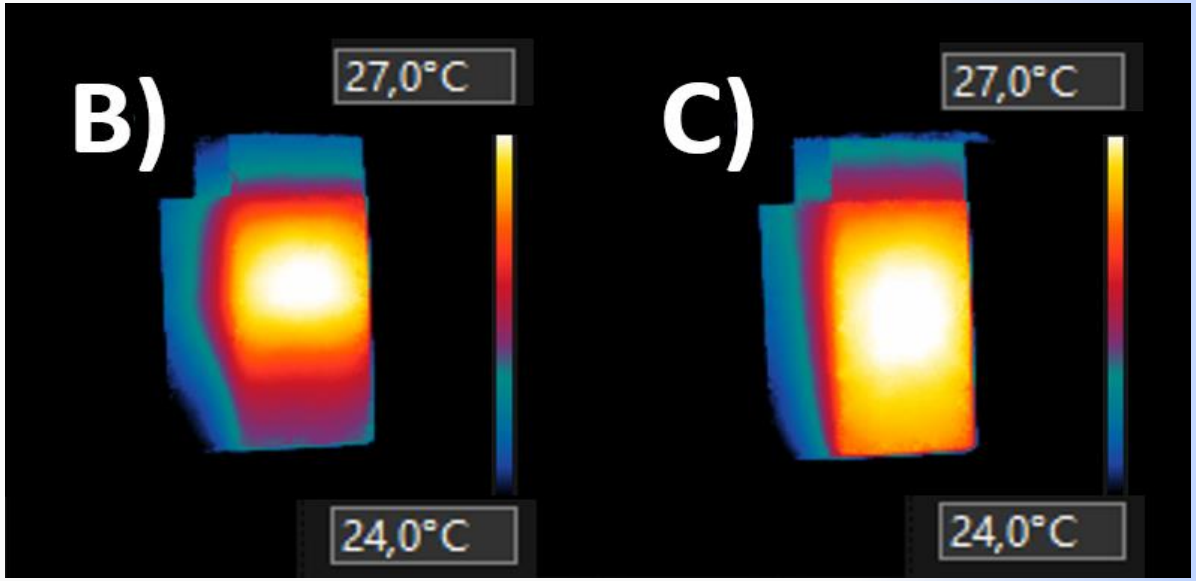


…and tested in different experimental conditions



Experimental setup comparison





Light-to-heat conversion efficiency

Material	Size [nm] (diameter)	λ_{EXC} [nm]	Part of mass of a cuvette	Temperature detector	Experimental setup comments	Model	η_Q [%]
Au NPs [1]	20	514	whole glass cell	TC outside the measurement cell	small sample cell in a vacuum chamber	R*	3.4-9.9
Au NPs [2]	20	532	no cuvette	TC inside the droplet	sample is a droplet	R*	100
Au NSp [3]	15	532	solvent only	TC inside the cuvette	magnetic stirrer, open cuvette	R/C	**78.4**
Au NSp [3]			-		theoretical value	-	**99.6**
Au@SiO$_2$ [4]	14 (Au), ~140 (Au@SiO$_2$)	532	solvent only	Measurement through glass	magnetic stirrer on/off	R	**57.5 / 50.8**
			solvent only	Measurement of sample surface temperature	magnetic stirrer on/off	R	**63.1 / 67.5**
			cuvette included	Measurement through glass	magnetic stirrer on/off	R	**90.5 / 80.8**
			cuvette included	Measurement of sample surface temperature	magnetic stirrer on/off	R	**98.4 / 106.7**
			"effective mass"	Measurement through glass	magnetic stirrer on	W	80.5
				Measurement of sample surface temperature		W	80.6
			no cuvette	Measurement of sample surface temperature	sample is a droplet	R	**66.8**
						W	81.1

1. D. K. Roper, W. Ahn, and M. Hoepfner, "Microscale heat transfer transduced by surface plasmon resonant gold nanoparticles," J. Phys. Chem. C, vol. 111, no. 9, pp. 3636–3641, 2007.
2. H. H. Richardson, M. T. Carlson, P. J. Tandler, P. Hernandez, and A. O. Govorov, "Experimental and theoretical studies of light-to-heat conversion and collective heating effects in metal nanoparticle solutions," *Nano Lett.*, vol. 9, no. 3, pp. 1139–1146, 2009.
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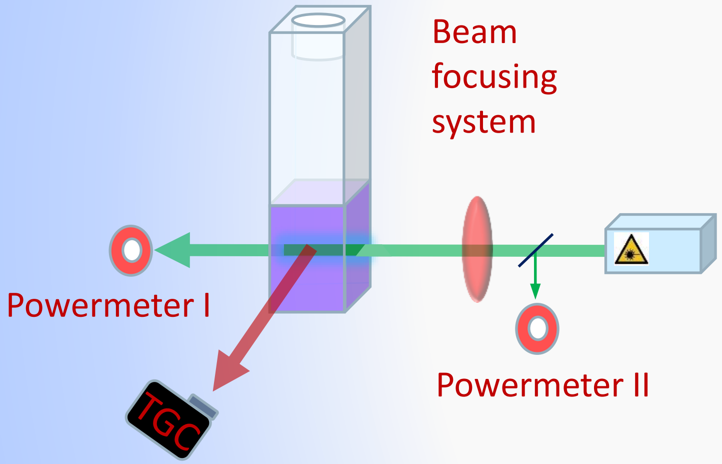
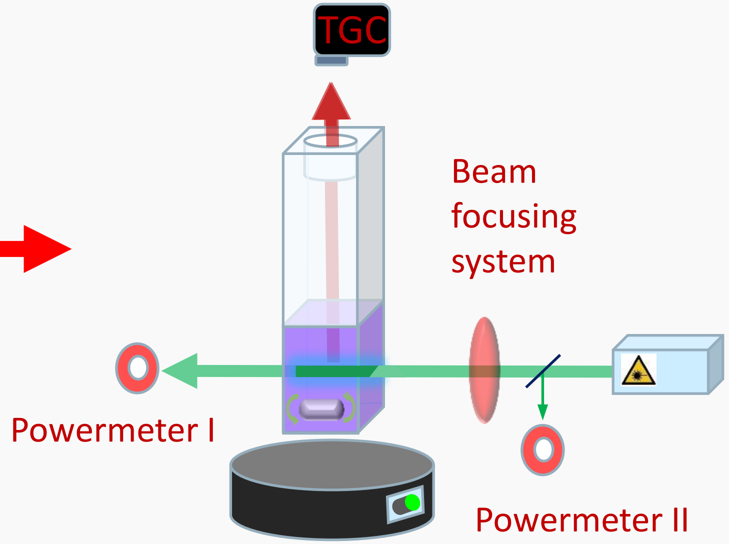
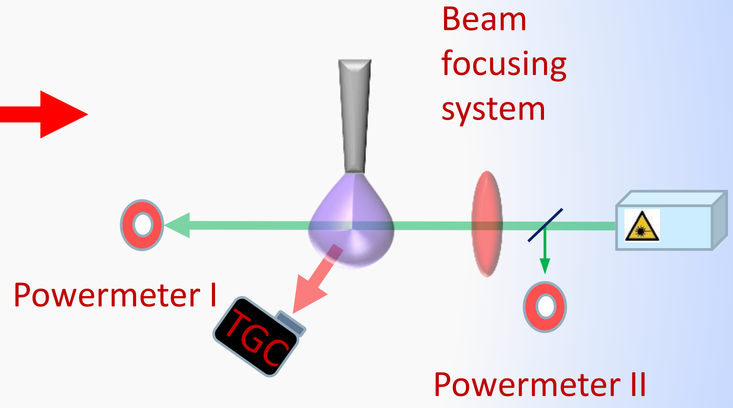
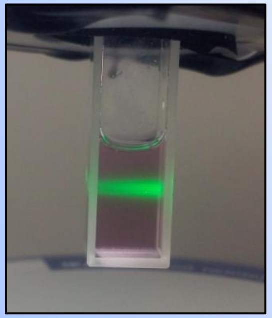
4. Standardization of light-to-heat conversion efficiency of colloidal nanoheaters, A. Paściak, A. Pilch-Wróbel, Ł. Marciniak, A. Bednarkiewicz (to be submitted)

Laboratory experience – evolution of experimental systems



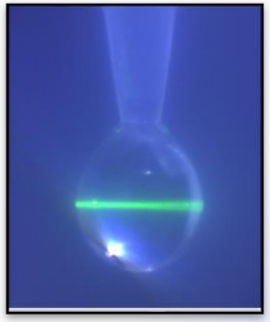






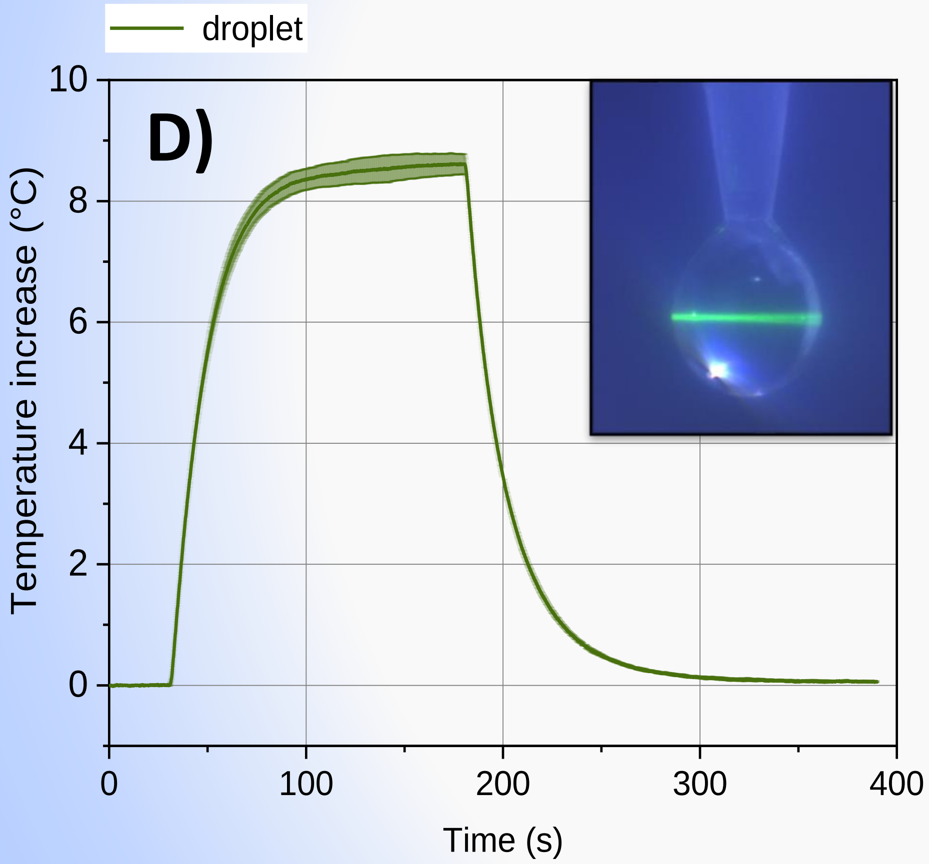
- Temperature gradients
- Heat receiver – glass
- Large volume of a sample
- Need for calibration

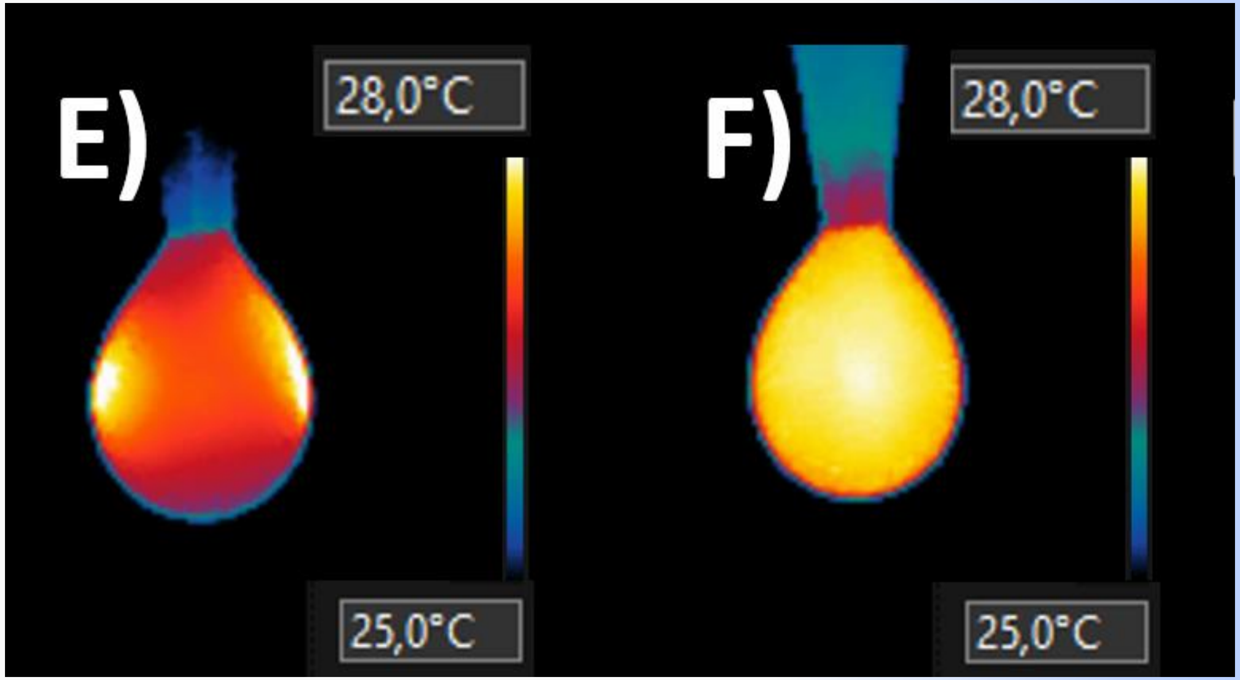
- No temperature gradients
- Heat receiver – glass – less important
- Large volume of a sample
- Need for calibration



- Natural convection only
- Heat receiver – tip – less important
- Small volume of a sample
- No need for calibration

Miniaturized system performance





A receipt for a correct measurement

- Stable colloidal sample required
- Reference measurement for solvent should be performed to evaluate Q_0
- Model – it is important to be sure what is the effective mass of the setup
- Impact of environment – ambient temperature should not change during measurement, evaporation should be minimized
- Use Wang's model rather than Roper's for calculations – it does not require full heating/cooling curves

Acknowledgements

Financial support from NanoTBTech-H2020-FETOPEN (801305) “Nanoparticle-based 2D thermal bioimaging technologies„ is greatly acknowledged.

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