Electronic Supplementary Material (ESI) for RSC Advances.

NIR Light Triggered Shrinkable Thermoresponsive PNVCL Nanoshells for Cancer Theranostics

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Calculation to determine photothermal efficiency:

According to Roper et. al [26], total energy balance of the system is expressed by the following equation (1)

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = Q_{NS} + Q_{Dis} - Q_{Surr} \quad (1)$$

Where, m = mass of water, C_p = heat capacity of water, T = solution temperature, Q_{NS} = energy input by the Au PNVCL NS, Q_{Dis} = baseline energy input by the sample cell and Q_{Surr} = heat conduction from the system surface by air.

Q_{NS} is the laser induced source term and represents the heat dissipated from the surface during irradiation of Au PNVCL NS by 750nm laser.

$$Q_{NS} = I\left(1 - 10^{-A_{750}}\right)\eta \quad (2)$$

Where, I is incident laser power, η is the conversion efficiency, and A_{750} is the absorbance of Au PNVCL NS at 750 nm.

Q_{Surr} is the outgoing thermal energy and is represented by following equation

$$Q_{Surr} = hS(T - T_{Surr}) \quad (3)$$

where h is heat transfer coefficient, S is the surface area of the well, T is the solution temperature, and T_{Surr} is temperature of the surrounding.

Since, heat output Q_{Surr} is increased along with the increase in temperature according to the equation (3), system temperature will rise to a maximum when the heat input is equal to heat output as shown in following equation (4):

$$Q_{NS} + Q_{Dis} = Q_{Surr-Max} = hS(T_{Max} - T_{Surr}) \quad (4)$$

Where $Q_{Surr\text{-}Max}$ is heat conduction away from the system when the sample cell reaches the equilibrium temperature, and T_{Max} is the equilibrium temperature. Photothermal transduction efficiency η can be calculated by substituting equation (2) for Q_{NS} into equation (4) and obtaining equation (5)

$$\eta = \frac{hS(T_{Max} - T_{Surr}) - Q_{Dis}}{I(1 - 10^{-A_{750}})} \quad (5)$$

Where Q_{Dis} was measured independently using water to be 8.1 mW for 750 nm laser, $T_{Max} - T_{Surr}$ was found to be 20.6 °C for Au PNVCL NS, I was 650 mW, A_{750} was determined to be 0.2544 at 750 nm. Thus, only the hS remains unknown for calculating η. To determine hS, a dimensionless driving force temperature, ϑ is introduced using the maximum system temperature $T_{Max.}$

$$\theta = \frac{T - T_{Surr}}{T_{Max} - T_{Surr}} \quad (6)$$

And a sample system time constant τ_s

$$\tau_s = \frac{\sum_i m_i C_{p,i}}{hS} \qquad (7)$$

which is substituted into equation (1) and rearranged to yield

$$\frac{d\theta}{dt} = \frac{1}{\tau_s}\left[\frac{Q_{NS} + Q_{Dis}}{hS(T_{Max} - T_{Surr})} - \theta\right] \qquad (8)$$

When the laser source is turned off, $Q_{NS} + Q_{Dis} = 0$, thereby reducing the equation (8) to

$$\frac{d\theta}{dt} = \frac{-\theta}{\tau_s} \qquad (9)$$

and after integration, giving the expression

$$t = -\tau_s ln\theta \qquad (10)$$

Hence, time constant (τ_s) was determined by plotting the time versus the negative logarithm of temperature in cooling period. Thus, with the help of equation (10) and (7), *hS* deduced to be 3.81 mW after taking *m* = 0.1 g and *C* = 4.2 J/g. Substituting these values in equation (5), the photothermal transduction efficiency (η) of Au PNVCL NS turned out to be 24.42 %.

Supporting Figures:

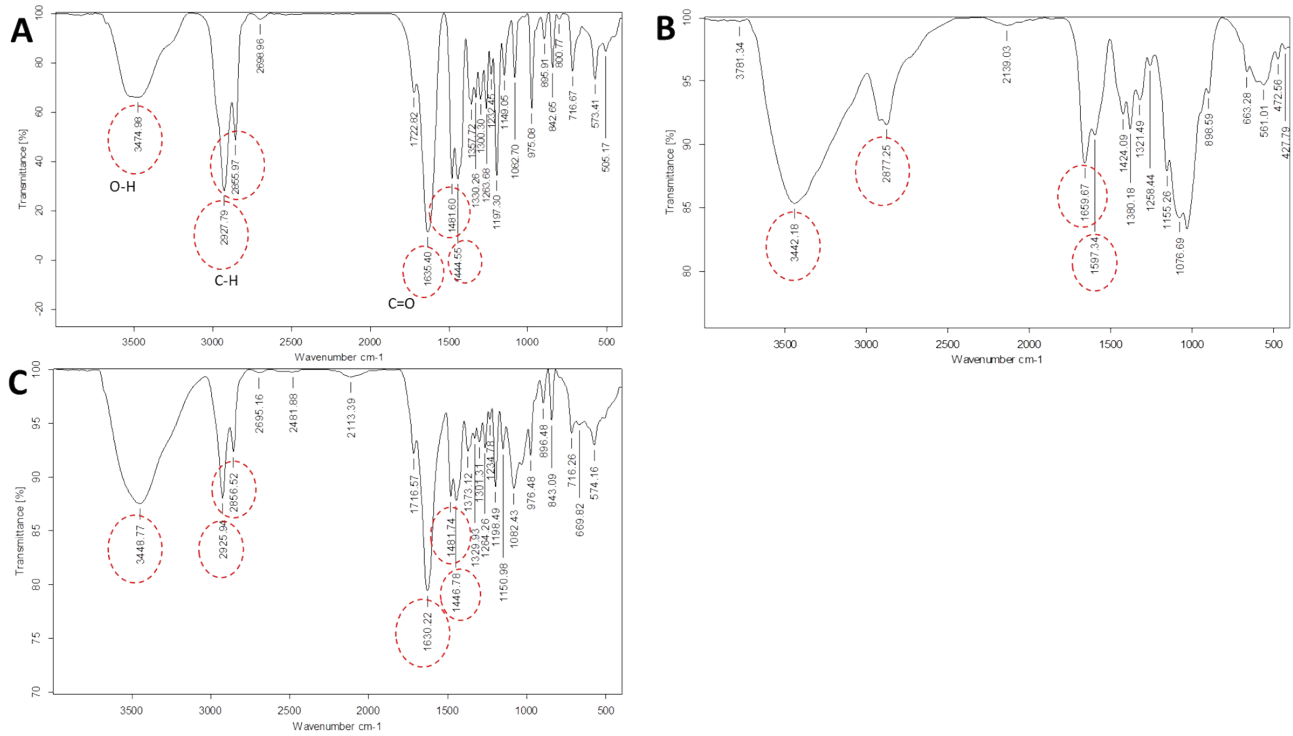

Fig. S1. FTIR spectrum of **(A)** PNVCL-COOH, **(B)** CHT, and **(C)** CHT-g-PNVCL. Red circles indicate relevant peaks

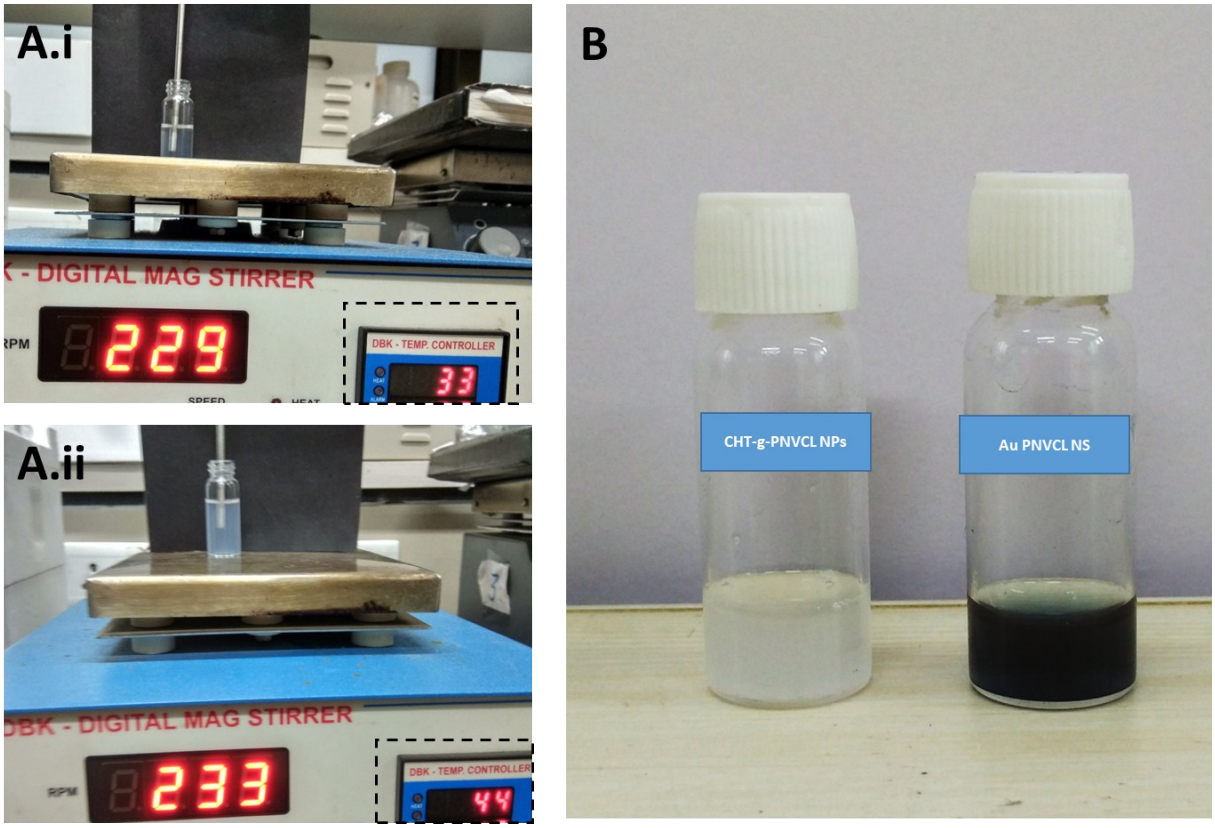

Fig. S2. Phase separation with increase in temperature and color change of CHT-g-PNVCL NPs after gold coating. **(A.i, ii)** CHT-g-PNVCL at physiological temperature i.e. 30-40 °C (i), and phase separated CHT-g-PNVCL at hyperthermic temperature i.e. 43-44 °C (ii); dashed rectangle shows the set temperature. **(B)** Change in color due to gold shell formation over the surface of CHT-g-PNVCL NPs.

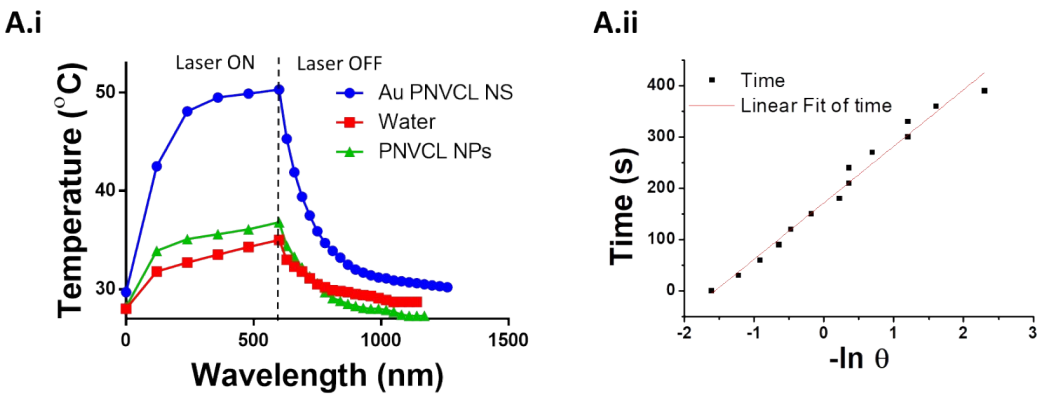

Fig.S3. Photothermal characterization of Au PNVCL NS. **(A.i, ii)** Temperature change corresponding to laser ON and OFF (i), and time versus negative logarithm of driving force temperature (*ϑ)* from the cooling stage of Au PNVCL NS (ii).

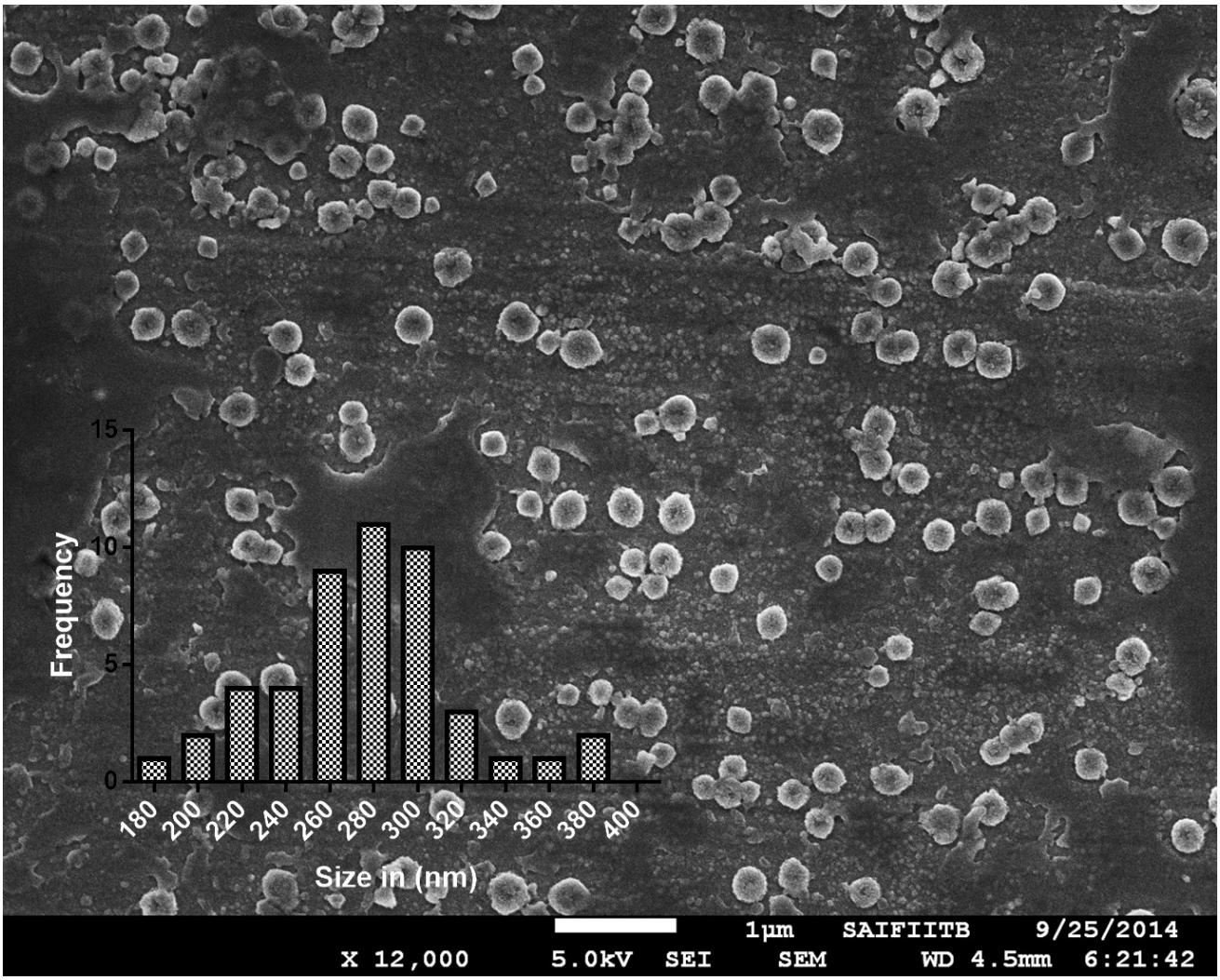

Fig. S4. FEG-SEM image of CHT-g-PNVCL NPs and size distribution.

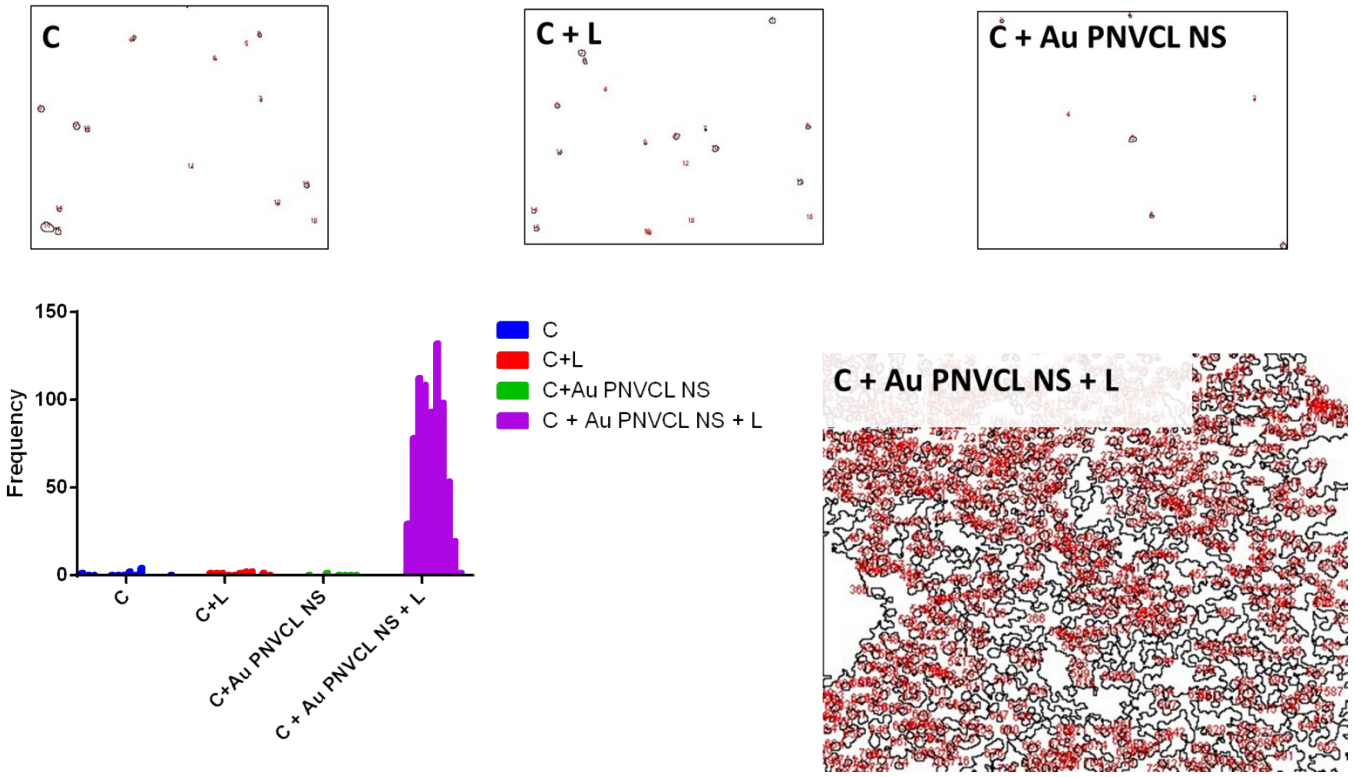

Fig. S5. Intensity drawing and percentage frequency of dead cells. Abbreviation C: Cells only, C+ L: Cells + Laser, C+ Au PNVCL NS: Cells incubated with Au PNVCL NS, and C + Au PNVCL NS + L: 4 min laser irradiation over cells incubated with Au PNVCL NS.

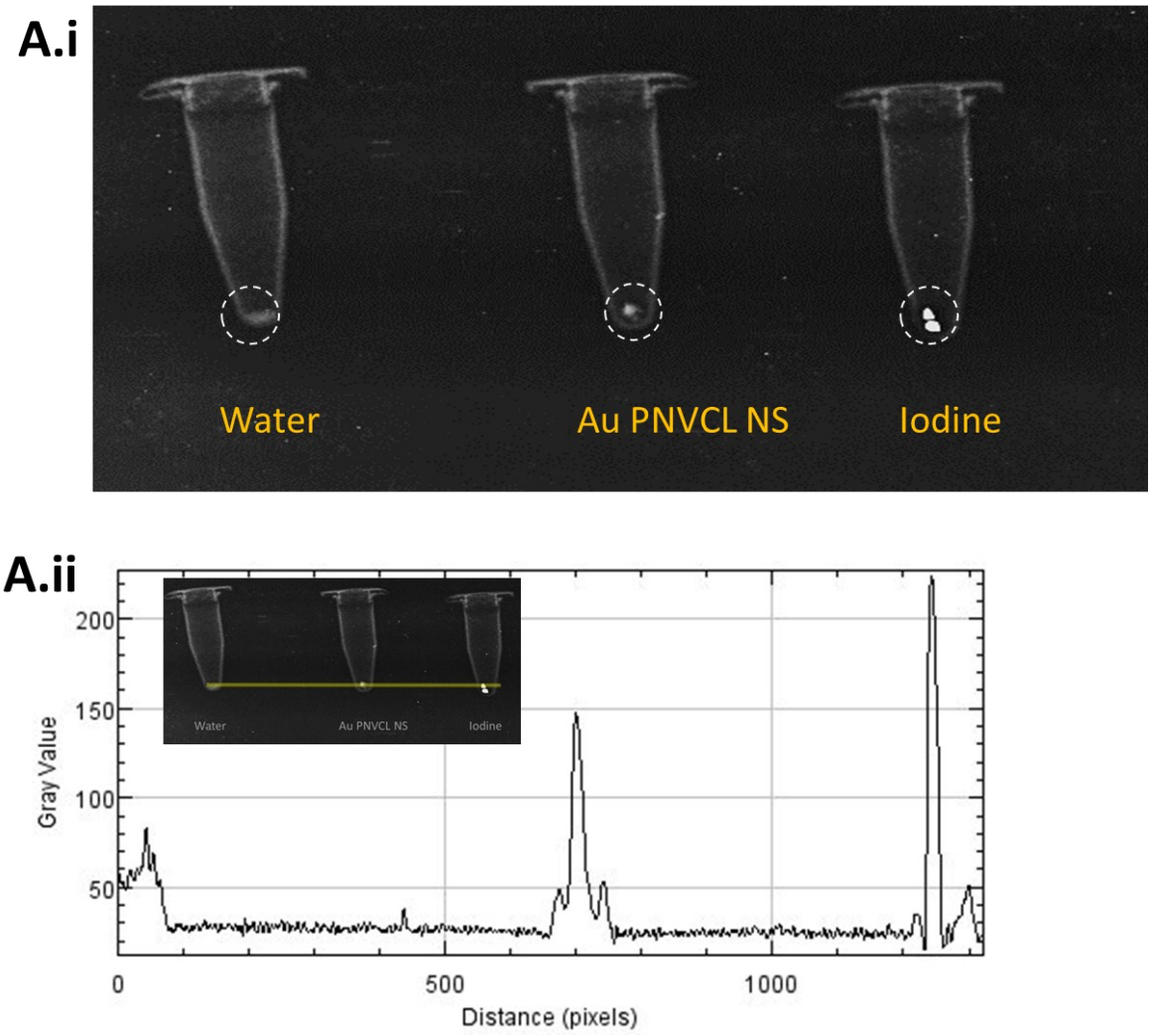

Fig. S6. Pilot X-ray imaging. **(A.i, ii)** X-ray imaging of water (left), Au PNVCL NS (centre), iodine (right) (i), and intensity plot profile showing exact gray values (ii).