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Supporting information

Thermosensitive Cu_2O-PNIPAM core-shell nanoreactors with tunable photocatalytic activity

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Theory for surface versus diffusion controlled reactions

We have stated in the main manuscript that the reaction is surface controlled. To reach to such conclusion we consider that the total reaction time, k^{-1}, is the sum of the time for the reactant methyl orange (MO) to diffuse to the Cu_2O nanocubes, k_D^{-1}, and the time to react once it is in the surface proximity, k_S^{-1}, i.e.,

$$k^{-1} = k_D^{-1} + k_S^{-1} \tag{s1}$$

The time to diffuse to the Cu_2O nanocubes is the sum of the time to diffuse from the bulk to the nanoreactor shell, k_{D0}^{-1}, and the time to diffuse from the nanoreactor shell to the nanocube, k_{Dg}^{-1}, i.e. $k_D^{-1} = k_{D0}^{-1} + k_{Dg}^{-1}$. As we find that MO has a two-orders of magnitude higher concentration (see below) in the hydrogel shell than in bulk, according to our theory for nanoreactors [R1], the rate limiting step in the diffusive approach (i.e. the slowest time) is the mean time of MO to reach the nanoreactor shell. Thus, the diffusion-controlled rate, k_D, is simply given by the Smoluchowski equation

$$k_D \approx k_{D0} = 4\pi D_0 R_g c_0 \tag{s2}$$

while we express the surface reaction, k_S, as

$$k_S = K_{vol} c_g \tag{s3}$$

where D_0 is the MO bulk diffusion coefficient, R_g is the radius of the core-shell nanoreactor, c_0 is the bulk MO concentration, c_g is the MO concentration in the hydrogel adjacent to the nanocube surface, and $K_{vol} = k_{vol} \Delta V$, being k_{vol} the fraction per unit time of the MO molecules arriving to the nanocubes that are allowed to react, and ΔV the volume of the shell next to the nanocubes where effectively the chemical reaction is happening. As a consequence, the surface reaction is directly proportional to the number of reactants within the reactive volume. This also holds naturally for the number of hydroxyl radicals in the reactive volume as well. In the main manuscript we explain that the changes in the reaction rate can be rationalized qualitatively by the changes in the production of OH radicals and by a local re-partitioning of the reactants. Hence, these two effects are included in Eq. (s3) through the local number of reactants and radicals in the reactive volume.

We estimate the diffusion time of the MO reactants to the nanoreactor and we find it to be much faster than the measured total reaction time, which means that the reaction is surface controlled (see Table s1). Note that the diffusion-controlled rate is many orders of magnitudes faster and details of the assumptions leading to eq. (s2) (e.g., the exact value of MO concentration in the hydrogel or which exact shell radius really to take) are negligible.

Table s1. Cu_2O@PNIPAM core-shell nanoreactors. Total measured reaction rate k, theoretical diffusion rate k_D from eq. (s2) and the finally calculated surface reaction rates k_S from using eq. (s1) at different temperatures. The total reaction rates shown here (in units of s^{-1}) have been obtained by multiplying the measured ones (in units of L min^{-1} m^{-2}) by the surface of the reacting nanocubes and dividing them by the suspension volume.

T (°C)	k (10^{-4} s^{-1})	k_D (10^7 s^{-1})	k_S (10^{-4} s^{-1})
15	2.4	9.5	2.4
40	0.19	1.1	0.19

Average concentration of MO from adsorption data in Fig. s10

The average MO concentration in the PNIPAM shell can be obtained from the adsorption data in Fig. s10 as

$$c_g = c_0 \frac{1}{\phi} \frac{m}{m_0} \tag{s4}$$

where ϕ is the nanoreactor volume fraction, and m and m_0 are the MO mass adsorbed by the nanoreactors and the total MO mass added to the suspension, respectively (see Fig. s10). The numerical values for our system are shown in Table s2. First, we observe that MO strongly adsorbs to the nanoreactors where a two-orders of magnitude higher concentration (on average) than in bulk is found. Thus, nanoreactors feature a large binding affinity of MO in both hydrophilic and hydrophobic cases. Although the amount of MO adsorbed by the nanoreactors is roughly three times larger at 15ºC than at 40ºC, the average MO concentration in the hydrogel is 1.75 times larger at 40ºC as the volume of the PNIPAM shell is approximately fives times smaller. While a larger c_g would give raise to a larger reaction rate, literature suggests that there is a non-trivial local re-partitioning of MO within the PNIPAM shell at 40ºC [R2], where the MO would be mostly situated in a thin shell at the outer surface (the hydrogel/water interface) of the core-shell nanoreactors, leading to a reduced concentration close to the nanoparticle and accordingly a diminished rate.

Table s2. Cu_2O@PNIPAM core-shell nanoreactors. Volume fraction of nanoreactors, mass of MO adsorbed by the nanoreactors, and ratio between the MO concentrations in the gel and in the bulk at different temperatures.

T (ºC)	ϕ	m/m_0	c_g/c_0
15	4×10^{-4}	0.075	204
40	8×10^{-4}	0.027	358

References:

[R1] S. Angioletti-Uberti, Y. Lu, M. Ballauff, J. Dzubiella, *J. Phys. Chem. C* 2015, **119**, 15723.

[R2] T. Fujieda, K. Ohta, N. Wakabayashi, S. Higuchi. *J. Colloid Interface Sci.* 1997, **185**, 332.

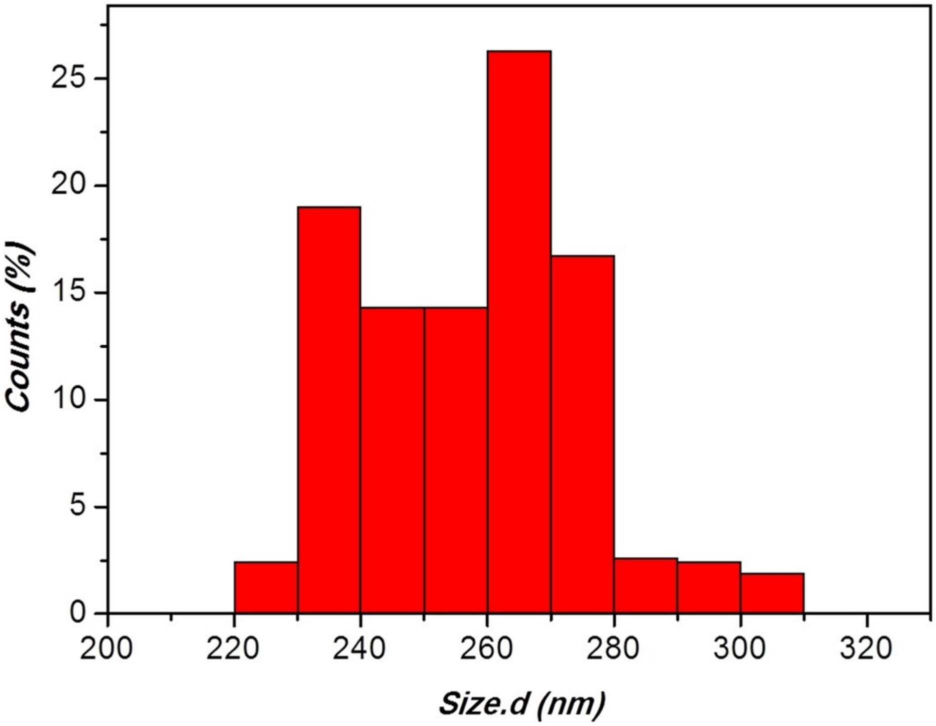

Figure s1. The size distribution of pure Cu_2O nanocubes.

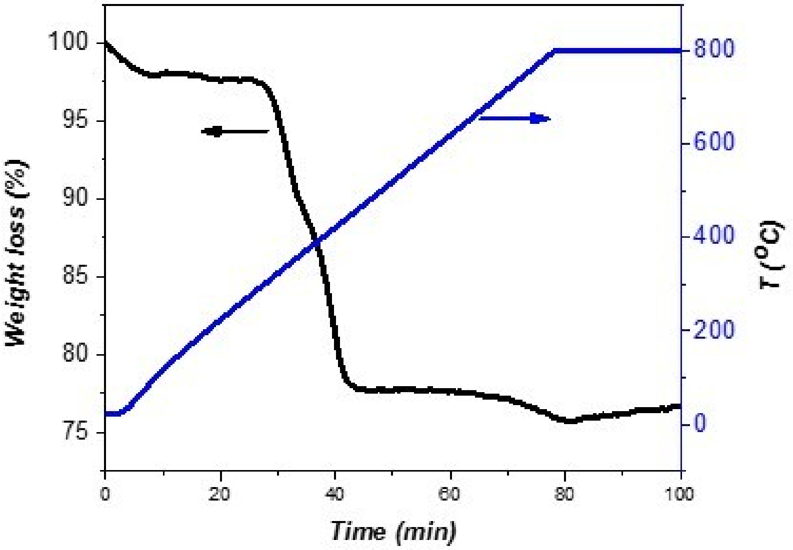

Figure s2. TGA spectra of Cu_2O@PNIPAM core-shell nanoparticles.

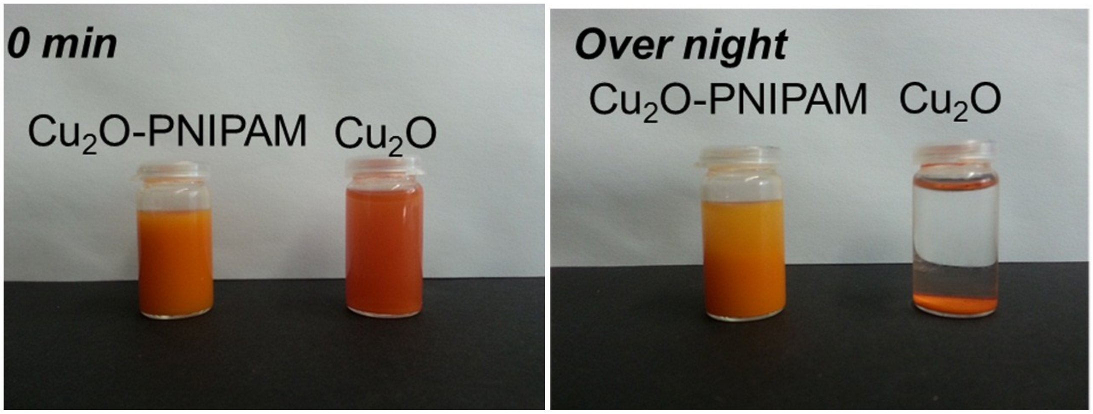

Figure s3. The photographs of solution of Cu_2O@PNIPAM core-shell nanoparticles (left) and Cu_2O nanocubes (right) after storing for different times.

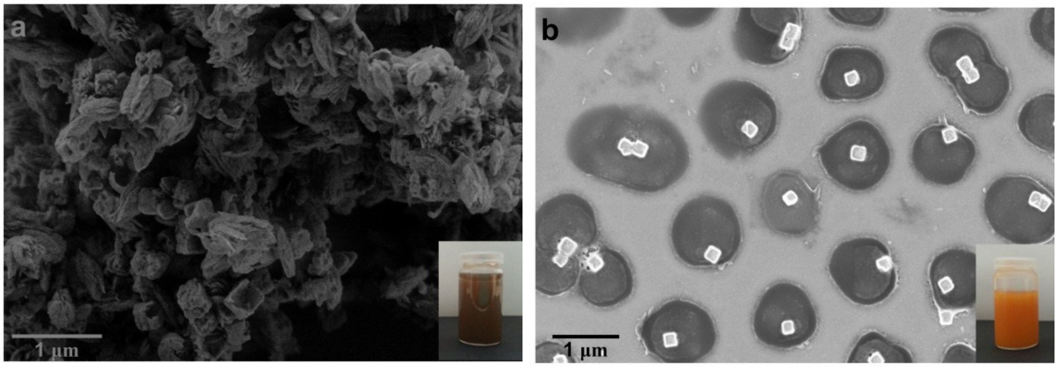

Figure s4. SEM images of (a) Cu_2O nanocubes without PNIPAM coating: kept in water at room temperature for 10 days, (b) Cu_2O@PNIPAM core-shell nanoparticles: kept in water at room temperature for 10 days.

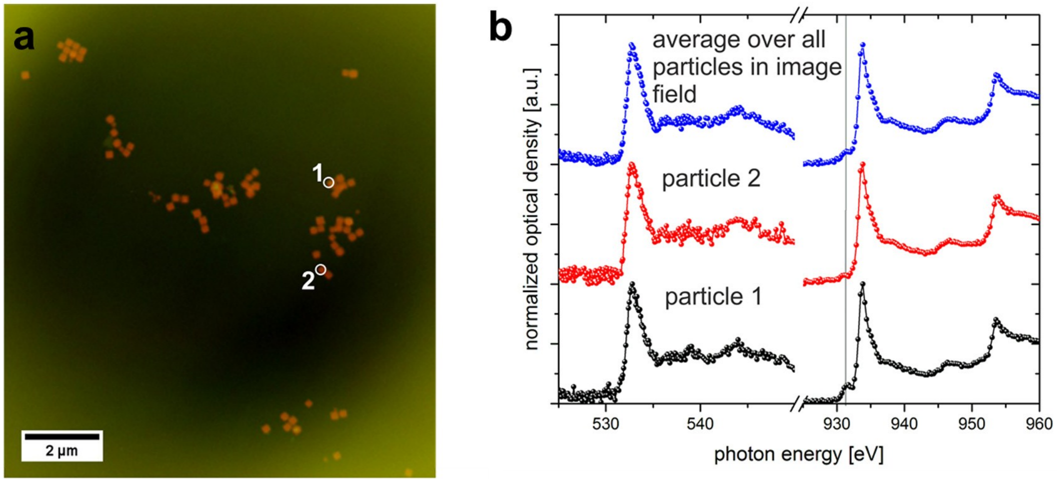

Figure s5. (a) TXM micrograph of bare Cu_2O nanocubes at two different photon energies: The red channel depicts the nanocubes with Cu_2O, and the green channel refers to CuO. (b) NEXAFS-spectra of the average signals over all Cu_2O nanocubes in field of view (blue line) and the marked particles in the inset of micrograph on the left hand side at the O-*K*-edge and the Cu-*L*$_{2,3}$-edge (red and black lines).

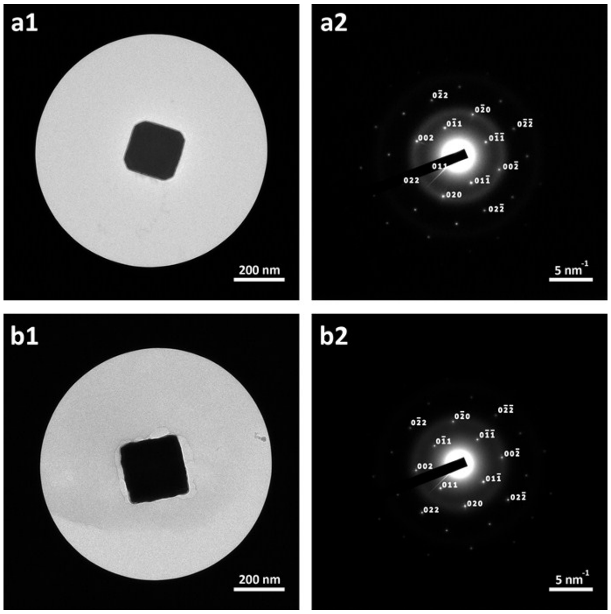

Figure s6. TEM images and their corresponding selected area electron diffraction (SAED) patterns of freshly prepared bare Cu_2O nanocubes (a1 and a2), and Cu_2O@PNIPAM core-shell nanoparticles (b1 and b2).

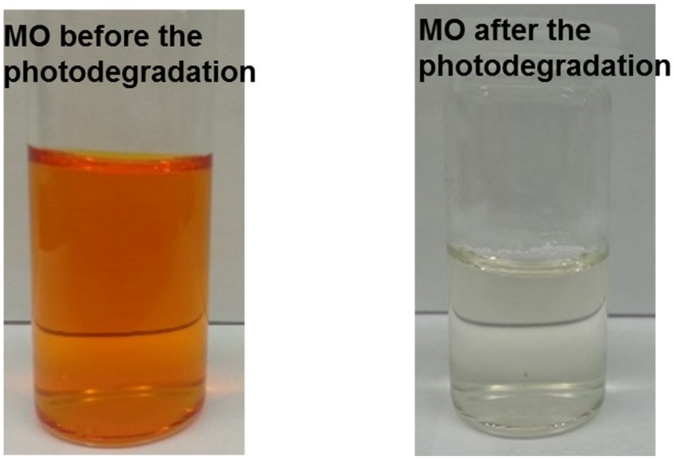

Figure s7. The color change of MO before and after photodegradation using Cu_2O@PNIPAM core-shell nanoparticles as the photocatalyst.

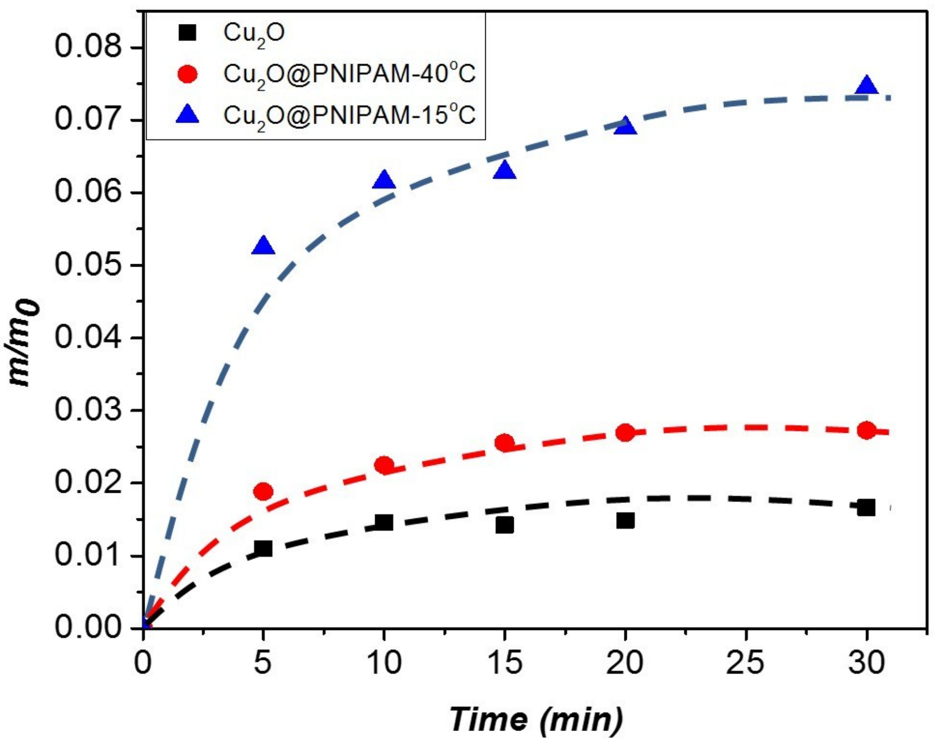

Figure s8. The Methyl Orange (MO) adsorption curve of pure Cu_2O nanocubes at 15^{o}C (squares), Cu_2O@PNIPAM core-shell nanoparticles at 40^{o}C (circles) and at 15^{o}C (triangles), respectively.

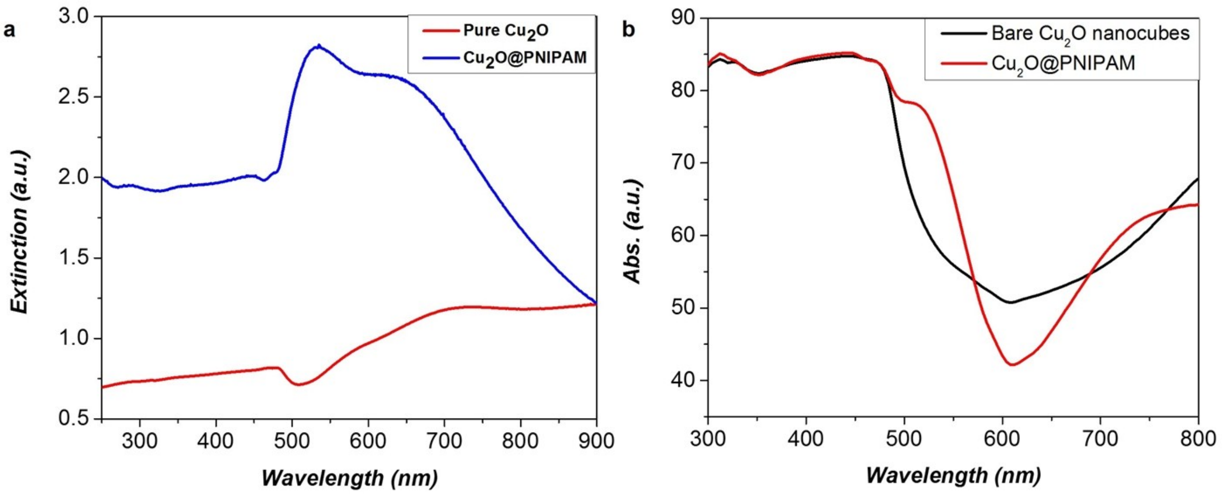

Figure s9. (a) UV-vis spectra of Cu_2O nanocubes (red) and Cu_2O@PNIPAM core-shell microgels solutions (blue) at room temperature with the solid content of 0.21mg/mL. (b) UV-vis spectra of Cu_2O nanocubes (black) and Cu_2O@PNIPAM (red) films prepared by drop casting.

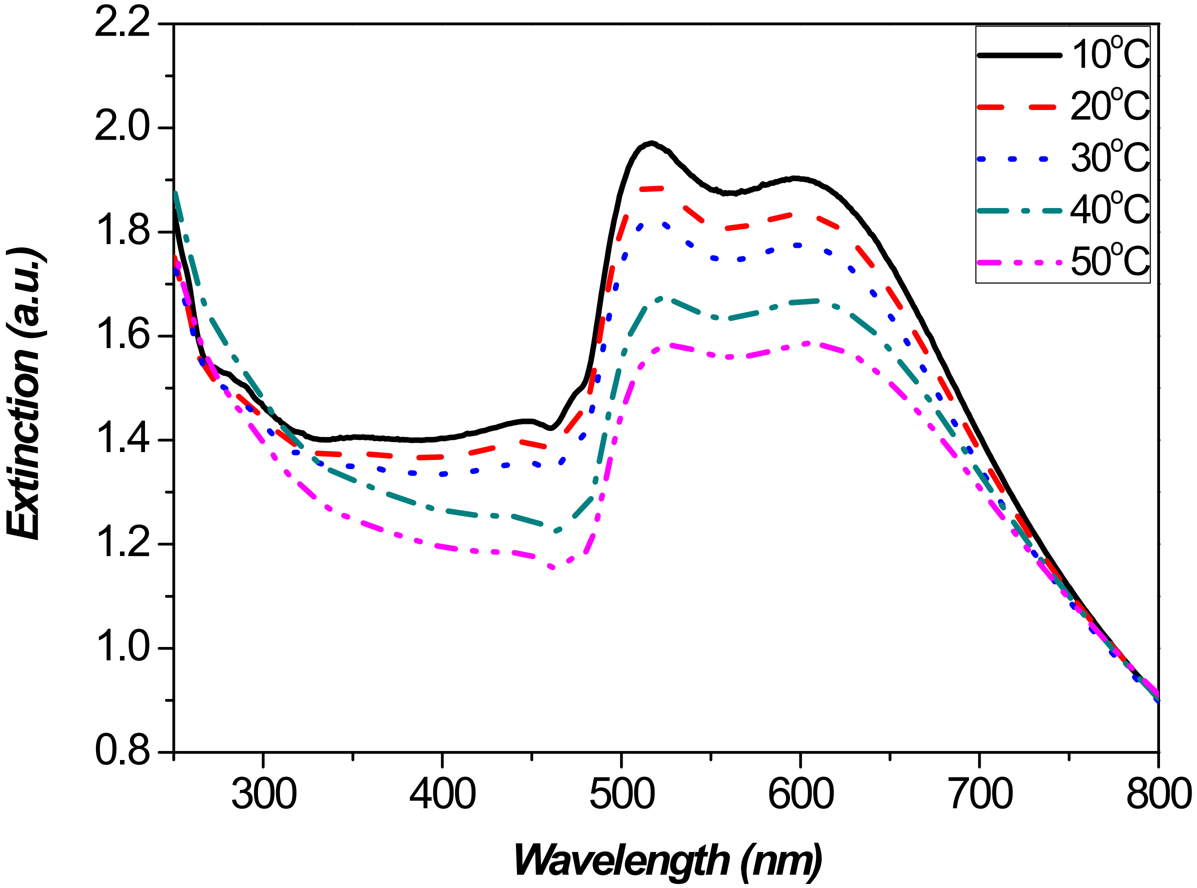

Figure s10. UV-vis spectra of Cu_2O@PNIPAM core-shell nanoparticles as a function of the temperature.