Supporting information

Thermosensitive Cu₂O-PNIPAM core-shell nanoreactors with tunable photocatalytic activity

He Jia,¹ Rafael Roa,¹ Stefano Angioletti-Uberti,²,¹ Katja Henzler,³ Andreas Ott,¹ Xianzhong Lin,⁴ Jannik Möser,⁵ Zdravko Kochovski,¹ Alexander Schnegg,⁵ Joachim Dzubiella,¹,⁶ Matthias Ballauff,¹,⁶ Yan Lu¹*

¹Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, Berlin (Germany), ²International Research Centre for Soft Matter, Beijing University of Chemical Technology, Beisanhuan East Road 19, 100099 Beijing (PR China), ³Paul Scherrer Institut, 5232 Villigen PSI (Switzerland), ⁴Heterogeneous Materialien und Energie, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, Berlin (Germany), ⁵Institute for Nanospectroscopy Helmholtz-Zentrum Berlin für Materialien und Energie, Kekulestr 5, Berlin (Germany), ⁶Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, Berlin (Germany).

*Correspondence and requests for materials should be addressed to Y. L. (email: yan.lu@helmholtz-berlin.de)
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 \( \text{Cu}_2\text{O} \) nanocubes, \( k_D^{-1} \), and the time to react once it is in the surface proximity, \( k_S^{-1} \), i.e.,

\[
k^{-1} = k_D^{-1} + k_S^{-1}
\]  

(s1)

The time to diffuse to the \( \text{Cu}_2\text{O} \) 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

\[
k_D \approx k_{D0} = 4\pi D_0 R_g c_0
\]  

(s2)

while we express the surface reaction, \( k_S \), as

\[
k_S = K_{vol} c_g
\]  

(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 \( \Delta V \) 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$_2$O@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.

| $T$ (ºC) | $k$ ($10^{-4}$ 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

\[ c_g = \frac{1}{\phi} \frac{m}{m_0} \]

where \( \phi \) 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 five 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$_2$O@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) | $\phi$     | $m/m_0$ | $c_s/c_0$ |
|---------|------------|---------|-----------|
| 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$_2$O nanocubes.

Figure s2. TGA spectra of Cu$_2$O@PNIPAM core-shell nanoparticles.
**Figure s3.** The photographs of solution of Cu$_2$O@PNIPAM core-shell nanoparticles (left) and Cu$_2$O nanocubes (right) after storing for different times.

**Figure s4.** SEM images of (a) Cu$_2$O nanocubes without PNIPAM coating: kept in water at room temperature for 10 days, (b) Cu$_2$O@PNIPAM core-shell nanoparticles: kept in water at room temperature for 10 days.
**Figure s5.** (a) TXM micrograph of bare Cu$_2$O nanocubes at two different photon energies: The red channel depicts the nanocubes with Cu$_2$O, and the green channel refers to CuO. (b) NEXAFS-spectra of the average signals over all Cu$_2$O 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$_2$O nanocubes (a1 and a2), and Cu$_2$O@PNIPAM core-shell nanoparticles (b1 and b2).

Figure s7. The color change of MO before and after photodegradation using Cu$_2$O@PNIPAM core-shell nanoparticles as the photocatalyst.
Figure s8. The Methyl Orange (MO) adsorption curve of pure Cu$_2$O nanocubes at 15°C (squares), Cu$_2$O@PNIPAM core-shell nanoparticles at 40°C (circles) and at 15°C (triangles), respectively.
**Figure s9.** (a) UV-vis spectra of Cu$_2$O nanocubes (red) and Cu$_2$O@PNIPAM core-shell microgels solutions (blue) at room temperature with the solid content of 0.21mg/mL. (b) UV-vis spectra of Cu$_2$O nanocubes (black) and Cu$_2$O@PNIPAM (red) films prepared by drop casting.
Figure s10. UV-vis spectra of Cu$_2$O@PNIPAM core-shell nanoparticles as a function of the temperature.