Localized Catalysis Driven by the Induction Heating of Magnetic Nanoparticles

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- *Optimization of the Catalytic Reaction*
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I-   *Synthesis of Iron Oxide Magnetic Nanoparticles (MNPs):*

Iron oxide magnetic nanoparticles (MNPs) were synthesized using a previously published procedure.[1] Briefly, equimolar masses of Iron (II) chloride $FeCl_2.4H_2O$ (1.2g) and Iron (III) chloride $FeCl_3.6H_2O$ (3.25g) were dissolved in 80 mL deionized water. Next, 10 mL of ammonium hydroxide solution (28% w/v) was added while mechanical stirring. Twenty minutes later, 4.4g of trisodium citrate dihydrate powder was dissolved and the whole mixture was stirred while the temperature was raised and maintained at 90 °C for 30 min. After cooling down to room temperature, the magnetic nanoparticles produced were collected by an external magnet and re-suspended in 10mL deionized water (Figure S1) yielding an estimated 139 mg/mL solution of particle size equal to *ca.* 257 nm (Table S1).

Figure S1: Iron oxide magnetic nanoparticles (MNPs) before and after applying an external magnetic field.

This resulted in the assembly of MNPs/AuNPs macro structures with the heat generating element and the catalytic surface closely positioned.

To further confirm the assembly, we resorted to compare the hydrodynamic radius of the MNPs/AuNPs mixture to that of MNPs and AuNPs solutions. The increase in the cumulant

diameter from 257 nm and 92 nm for MNP and AuNP respectively, to 3800 nm in the assembled

solution supports the suggested attachment (Table S1).

Sample	Cumulant Diameter (nm)	Polydispersity Index
MNP	257	0.19
AuNP	92	0.159
Mixture	3800	0.637

Table S1: Hydrodynamic radius for the prepared particles and assembled micro-catalytic structure measured using NanoPlus HD.

II-   Optimization of the Catalytic Reaction:

The optimization of the reaction conditions was done in a water bath maintained at 65°C.

Concentrations were varied, each at a time, and were analyzed based on the florescence intensities

of resorufin.

a) Optimization of Hydroxylamine- NH$_2$OH Concentration:

The concentration of the reducing agent NH$_2$OH was varied to check for its optimum amount

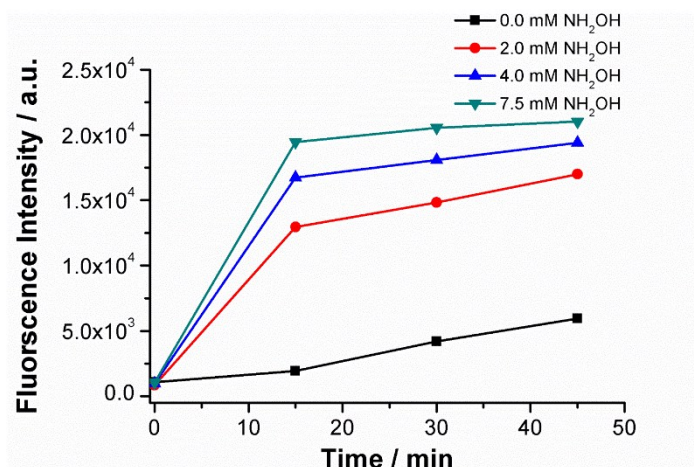needed for the reduction (Figure S2).

Figure S2: The maximum fluorescence intensities of resorufin acquired at different hydroxylamine concentrations. The results were obtained at 4 different time points: 0, 15, 30, and 45 min.

b) **Optimization of the PDDA Concentration:**

PDDA is used to assemble the catalytic micro-structure by electrostatically gluing the negatively charged magnetic and gold nanoparticles. Samples with different concentrations of PDDA were tested and the fluorescent signal of resorufin was measured (Figure S3).
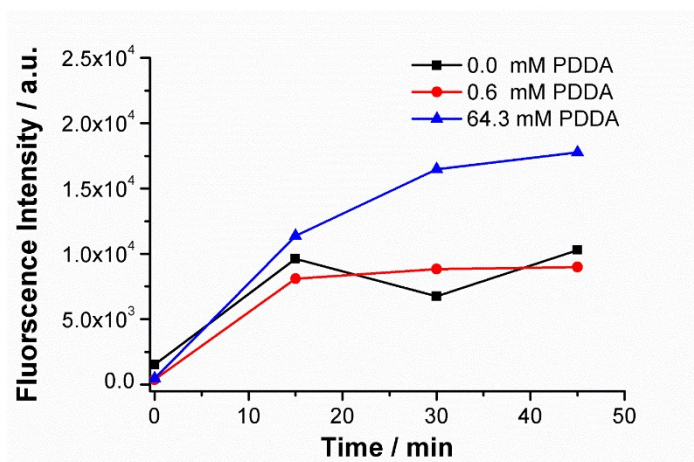

Figure S3: The maximum fluorescence intensities of resorufin acquired at different poly diallyl dimethyl ammonium chloride (PDDA) concentrations. The results were obtained at 4 different time points: 0, 15, 30, and 45 min.

c) Optimization of Temperature:

To check for the optimum temperature at which the reaction is neither saturated, nor sluggish, a series of experiments was done at different water bath temperatures ranging from 25 to 85 °C. All trials were performed using identical mixtures based on the aforementioned optimized standard conditions. To insure consistency with the MagneTherm trials and to account for the expected decrease in the reaction's rate in the MagneTherm due to the presence of magnetic nanoparticles, the temperature optimization in the water bath was done while mixing MNP with the reduction solution mixture (Figure S4). Above 55°C, the reaction starts to saturate, thus 45°C was chosen as a standard temperature for further trials.
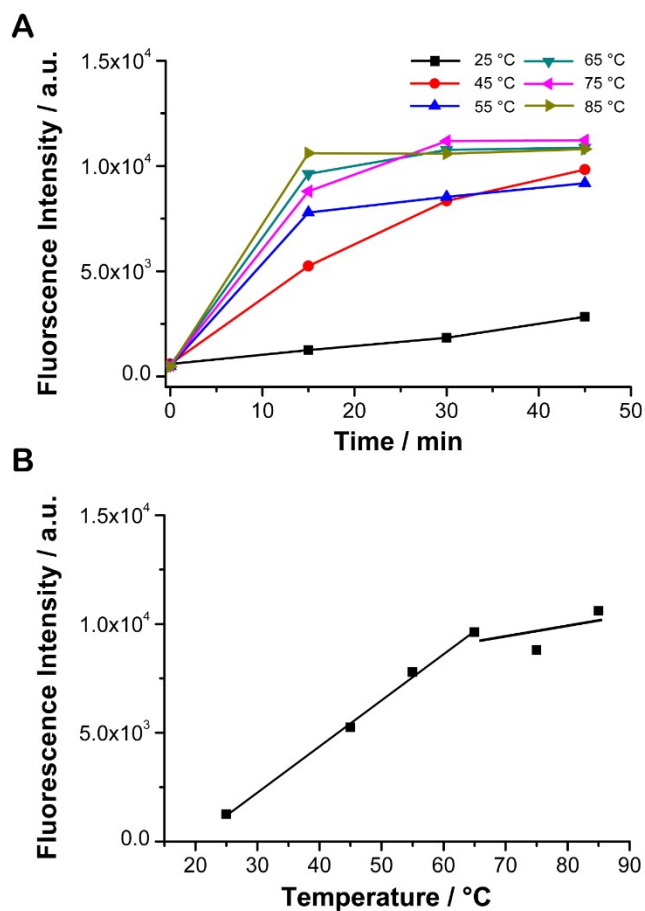

Figure S4: (A) The maximum fluorescence intensities of resorufin acquired at different temperatures between 25.0°C and 85.0°C with a step increment of 10.0°C in a water bath.

Measurements were obtained at 4 different time points: 0, 15, 30, and 45 min. (B) The maximum fluorescence intensities of resorufin at 15 min time point versus temperature.

III-   *Heating by Induction Versus Water Bath Trials:*

To insure comparable experimental conditions and maintain a stable temperature, the thermal variations were measured and tracked via a thermocouple dipped inside the solution tube and connected to a data logger machine. Adjustments were manually introduced, when needed, to maintain a constant value. Figure S5 shows an example of the thermal tracking. Both solutions reached steady values within the first few minutes and remained relatively constant throughout the experiment.
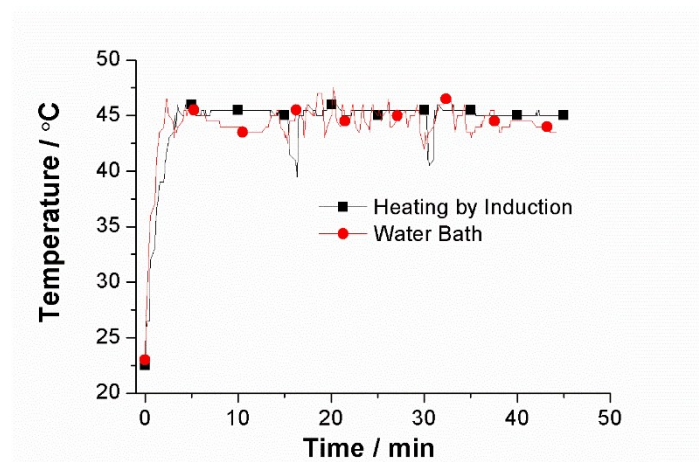

Figure S5: Plot tracking the increase in temperature of the solution as a function of time, recorded via a data logger. Solution 1 was inserted in the MagneTherm while the other in a water bath at 45°C.

IV-   Heat Induction by Gold Nanoparticles

Given that gold nanoparticles could have magnetic properties,[2] we measured the temperature of AuNPs solution overtime under the same experimental conditions. No changes in the temperature was observed (Figure S6).
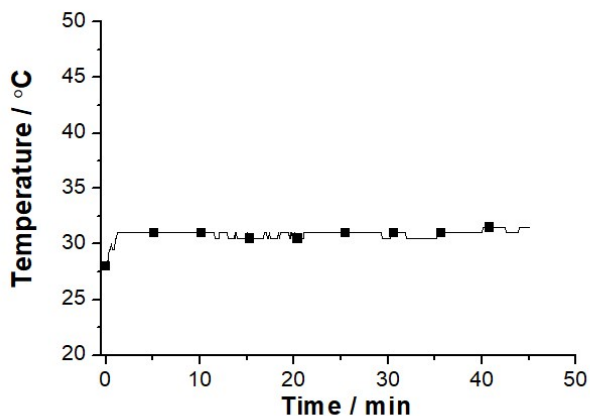
Figure S6: Plot tracking the temperature of the solution pure AuNPs as a function of time, recorded via a data logger.

V-   Sample Recyclability

To monitor the long-term stability of the micro-catalytic system, we recycled the Fe_3O_4-Au particles three times. At the end of each cycle, the particles were collected washed multiple time and re-introduced to a fresh solution of resazurin. The conversion was monitored as previously reported. The three cycles showed similar efficiency at different time intervals.
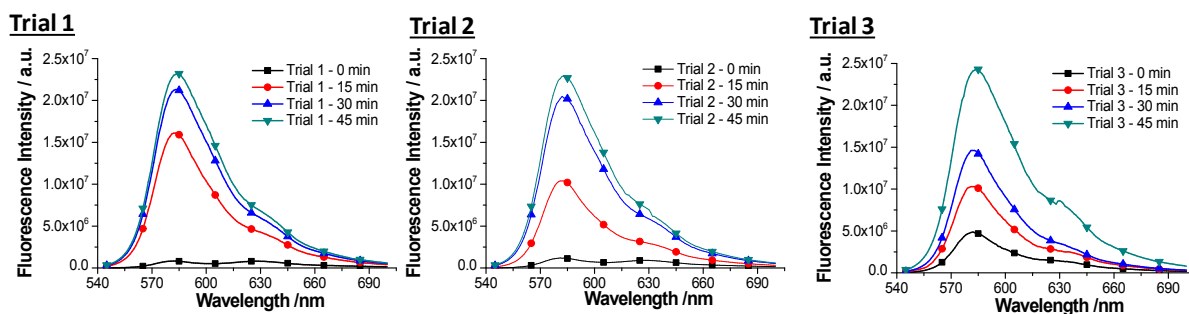

Figure S7: Recyclability of the MNPs/AuNPs complex tested over three cycles. Fluorescence intensities of resorufin acquired at 4 different time points 0, 15, 30, and 45 min for the same sample.

VI-   *Microscopy Imaging:*

A 5% agar gel sample was prepared and molded onto a microscopic slide and then left to solidify. Using a 0.3mm-thin insulin needle, few microliters of resazurin were injected into the gel. MNPs solution was poured on the gel's surface for few minutes to allow the magnetic nanoparticles to fill the cracks created by the needle. The solution was wiped away, and the slide is imaged with an upright fluorescence microscope Leica DM6 B. We then poured a solution of MNPs/AuNPs mixed with NH_2OH on the top of the gel again and left it in an alternating magnetic field. After two hours of heating in the MagneTherm, the gel surface was wiped and imaged for the second time under the same experimental conditions (5x objective and 1.5s exposure). Fluorescence intensities were quantified using the ImageJ software (Figure 7 and S8). For resazurin, a 541-551 nm excitation filter was used, and the emission was collected between 565 and 605 nm.
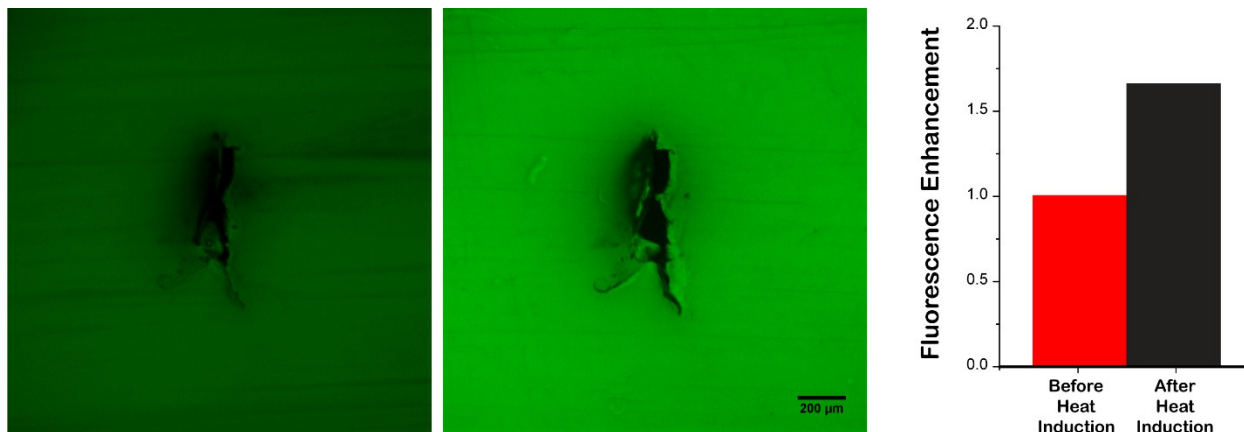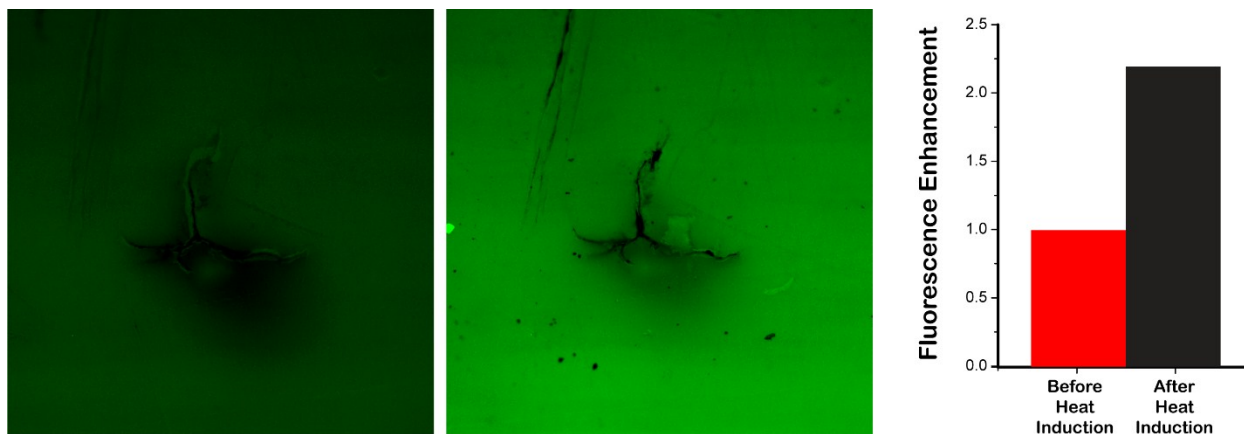
Figure S8: Fluorescent microscopy images of different agar gel samples before and after exposure to an alternating magnetic field in the presence of resazurin, NH_2OH, and MNPs/AuNPs complex. Images were acquired using a 5× objective with NA= 0.8 coupled with an excitation filter of 541-551 nm and the emission was collected between 565-605 nm.

References:

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