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Dual-Responsive Photocatalytic Polymer Nanogels

Calum T. J. Ferguson,^[a] Niklas Huber,^[a] Katharina Landfester*^[a] and Kai A. I. Zhang*^[a]

Abstract: Selective activation of photocatalysts under constant light conditions has recently been targeted to produce multi-responsive systems. However, controlled activation, with easy recovery of the photocatalysts, induced by external stimuli remains a major challenge. Mimicking the responsibilities of biological systems by multiple triggers can offer a promising solution. Herein, we report dualresponsive polymer photocatalysts in form of nanogels consisting of a cross-linked poly-N-isopropylacrylamide nanogel, copolymerised with a photocatalytically active monomer. Dual-responsive polymer nanogels undergo a stark reduction in diameter with the increase in temperature, above the lower critical solution temperature, shielding photocatalytic sites retarding activity. Temperature-dependent photocatalytic formation of the enzyme cofactor nicotinamide adenine dinucleotide (NAD+) in water demonstrates the ability to switch on/off photocatalysis. Moreover, photocatalysis of fine chemicals (benzaldehyde, benzyl-1-phenylmethanimine and 1,2dioctyldisulfane) has been conducted in the nanogels swollen state, demonstrating the utility of the designed material.

The employment of water-compatible heterogeneous polymer photocatalysts under visible light irradiation is of high research interest with applications in energy, environmental, and biological systems. Namely, water splitting,^[1] aqueous pollutant remediation,^[2] photodynamic therapy,^[3] and chemical redox reactions.^[4] The main challenges within these photocatalytic systems is maintaining efficient catalysis whilst producing a material that can be easily recovered. To achieve this, photocatalytic materials can be designed to transition between soluble and insoluble states, in response to external stimuli. Altering the materials solubility results in controlled activation or deactivation of the catalyst by controlling access of reagents to the catalytic sites.^[5]

In biological systems, functions or activities can be enabled or disabled by triggers, which lead to structural change in conformation and therefore activity control. For artificial materials, multiple stimuli have previously been reported that can be utilized to modify the physical properties of classical polymers most notably: change by light,^[6] pH value,^[7] and temperature.^[8] However, only a few examples of multi-responsive photoactive polymers have been reported. In particular, integration of pH-responsive moieties into the polymer structure was an efficient method to gain control of the water-compatibility of the polymer photocatalytic systems.^[9] Recently, our group has reported a CO_2 -triggered system, where enhanced wettability of a photocatalytic conjugated polymer can be triggered by the addition of CO_2 into the solvent.^[10]

Ideally, the photocatalytic species would be easily accessible, enabling efficient catalysis, but after the application of an external

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stimulus could undergo a conformational change, allowing easy extraction and recycling. A polymer nanogel system that can expand and contract, transitioning between gel and solid phases, could be utilised as a matrix for photocatalytic sites. This expansion and contraction may lead to the controlled activation or deactivation of the photocatalytic species. Moreover, the phase transitioning of such a material may aid in recovery after synthesis. To ensure control and efficient photocatalysis, it is important that the photocatalytic species are evenly distributed within the polymer matrix. If the photocatalytic species is concentrated at the surface of the nanogel, it still may be even catalytically active in the contracted state. Whereas, if the photocatalytic species are concentrated within the core of the nanogel, they may be even inaccessible in the swollen state.

Here, dual-responsive polymer photocatalysts have been synthesised in form of nanogels, where photocatalysis can be controlled by both light and temperature. These photoactive polymer nanogels undergo a stark transition in size upon elevation in temperature, as the polymer network is no longer effectively wetted by the aqueous media and phase separates. Phase separation of the polymer material at elevated temperature facilitates efficient recovery from the reaction solution, allowing efficient recyclability. Reversible transitions in size and solubility lead to a switchable deactivation/activation of the photocatalytic sites. This enables controllable photocatalysis, where reactions can only proceed within a certain temperature range. Furthermore, dual-responsive photocatalytic polymer nanogels can be utilised selectively stop/start catalysis, by simply controlling to temperature. At ambient temperature, polymer nanogels can be used for the regeneration of the enzyme co-factor NAD+, as well as dye degradation. Whereas, at elevated temperatures above the lower critical solution temperature (LCST) of the nanogel catalytic activity is retarded. Moreover, photocatalytic reactions can be undertaken under visible light at room temperature for the production of industrially relevant small molecules including synthesis of benzaldehyde from styrene, oxidation of phenylmethanamine to benzyl-1-phenylmethanimine and the formation of disulfide bridges between octanethiol molecules.



Scheme 1. Dual-responsive photocatalysts that can be selectively switched on or off as a function of temperature. Inclusion of photocatalytic units into a thermo-responsive nanogel matrix, which allows selective photocatalysis at low temperature in the swollen state but not at elevated temperatures in the contracted state.

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Dual-responsive thermoand light-sensitive polymer nanogels were designed so that upon application of temperature photocatalysis could be quenched. The contraction of the photocatalytic sites within the polymer gel network is demonstrated in Scheme 1, where upon elevation in temperature the gel network becomes insoluble and precipitates shielding the photocatalytic units and retarding reagent partioning into the network.^[5] Furthermore, the condensation of the nanogel network upon temperature elevation may limit light penetration into the gel network. Reduction in temperature to ambient conditions results in a rewetting of the gel network increasing the rate of transfer of reagents from the continuous phase to the active regions. This reversible 'switchable' behaviour of the photocatalytic nanogel enables photocatalysis to be turned on or off depending on temperature in a manor analogous to enzymatic functions within the body.



Figure 1. Dual-responsive photocatalytic nanogels. (a) Molecular structure of designed photocatalytic nanogels. (b) Nanogel diameter as a function of temperature measured by DLS. (c) Variation in transmission of nanogel solution, demonstrating reversibility. (d) Absorbance (black) and emission (red) spectra.

Dual-responsive photocatalytic polymer nanogels were synthesised using a similar surfactant free emulsion polymerisation route to literature.^[11] The nanogel was designed to encompass a hydrophilic gel network comprising of poly(N-isopropylacrylamide) (PNIPAM) crosslinked with PEGDMA that is copolymerised with a photocatalytic monomer N-(4-(7-phenylbenzo[c][1,2,5]thiadiazol-4-yl)phenyl)acrylamide

(PhBTPhAM) (Figure 1a). The photocatalytic monomer was specifically designed to encompass photocatalytic donor (phenyl) and acceptor (benzothiadiazole) units similar to species previously reported and with an acrylamide vinyl functional group, to enable polymerisation (Figure. S1 & 2). The acrylamide functional group was selected to ensure that the reactivity rate of the photocatalytic monomer was in the same order of magnitude as NIPAM. Equating the reactivity of both monomers results in a statistical distribution of photocatalytic sites throughout the nanogel network. The nanogel was synthesised in an aqueous environment and evaluated by ¹H-NMR spectroscopy (**Figure S3**). To confirm that the catalytic behaviour is due to the photocatalytic moieties and not residual Pd catalyst, inductively coupled plasma optical emission spectrometry (ICP-OES) was undertaken, with detected levels of Pd below 0.05 ppm (equivalent to nanogels without the photocatalytic monomer).

The diameter of the temperature dependent polymer nanogel was determined by light scattering (Figure 1b). Elevating the temperature above 30 °C lead to a sharp reduction in the diameter from around 190 to 70 nm, as expected. The data was fitted with a sigmoidal decay to yield a LCST of 31.6 °C, slightly lower than a pure PNIPAM system (LCST = 32 °C). Furthermore, the decay seems to be stretched compared to a non-doped system. These modifications to the nanogels behaviour may be due to the inclusion of the photocatalytic sites within the gel network, which do not contribute to the secondary bonding system. To demonstrate the reversible temperature dependent transition from a single phase to two phase system images were taken after heating and cooling the nanogels in a petri dish (Figure 1c). At ambient temperature the nanogel is translucent and upon elevation of the temperature the transmission significantly decreases producing an opaque suspension. Cooling of the system returns the translucent nature of the liquid as the nanogels rehydrate, which in turn can be cycled back to opaque by raising the temperature. The UV/Vis spectra of the dual-responsive nanogels have broad absorption peak in the visible light region up to 575 nm (Figure 1d).



Figure 2. Temperature dependent regeneration of enzyme cofactor NAD+ by dual-responsive photocatalytic nanogels, conversion determined by ¹H-NMR spectroscopy. (a) Regeneration of NAD+ at 25 °C but not at 40 °C. (b) Controllable on/off conversion of NADH by periodic fluctuations in temperature.

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The reversible activation/deactivation of photocatalytic sites as a function of temperature was investigated by monitoring dye degradation under visible light at constant ambient or elevated temperature (**Figure. S4**). In a typical experiment, the dualresponsive nanogel was dispersed in aqueous Rhodamine B solution, samples were irradiated under white light at 25 or 40 °C. At 25 °C, linear degradation of the dye molecule by the dualresponsive photocatalytic polymer nanogel is observed with over 90% of the dye degraded after 4 h. Conversely, at an elevated temperature of 40 °C, where the gel network is contracted, after 4 h irradiation less than 20% of the dye molecules have been degraded. Dye degradation at 40 °C can be attributed to the normal dye degradation caused by light irradiation.

The regeneration of the enzyme co-factor nicotinamide adenine dinucleotide (NAD) was utilised to further investigate the temperature dependent photocatalytic properties of the nanogel material produced. Within living cells NAD can be formed in either its oxidised (NAD+) or reduced state (NADH). Dehydrogenases within the cell remove electrons from their substrates and in turn reduce NAD+ to NADH.^[12] The reduced form of the cofactor can then be utilised in further enzymatic reactions by reductases, oxidising the NADH to NAD+. The temperature dependent oxidation of NADH was investigated at both 25 and 40 °C, where NADH (25 mM) was combined with the nanogel (1 mg/ml nanogel, 50 µg/ml photocatalyst) in an aqueous solution. This ratio of photocatalytic units to reagents is significantly lower than previously reported demonstrating the efficacy of the nanogel matrix for photocatalysis. Oxidation of NADH was monitored, in triplicate, by ¹H-NMR spectroscopy at both temperatures for 8 h (Figure S5). At ambient temperature, linear conversion of NADH as a function of time is observed, with over 70% of the NADH converted after 8 h (Figure 2a, red). Here, the NADH concentration converted was much higher than previously reported using a much lower concentration of photocatalyst.^[13] At elevated temperatures the oxidation reaction is severely limited with only around 5% of the enzyme cofactor oxidised (Figure 2a, blue). The stark differences in the conversion of NADH demonstrates the efficient deactivation of the photocatalytic sites at elevated temperatures, where the nanogels have phase separated and contracted.

Additionally, the reversibility of the activation and deactivation of the photocatalytic sites was investigated by monitoring conversion of NADH under a periodically cycling temperature regime (Figure 2b). Initially, under ambient conditions, the gel is swollen and the NADH is converted. No further conversion of NADH is observed in the subsequent period of elevated temperature. Upon reduction in the temperature, the conversion of NADH is resumed. This process of cycling activation and deactivation of the photocatalytic sites demonstrates fine control of photocatalysis using dual-responsive nanogels. Control scavenger experiments confirmed that ${}^{1}O_{2}$, $\cdot OH$, h+ and $\cdot O_{2}$ species are generated under light illumination at ambient temperature and are involved in NADH oxidation (Figure S6). From the control experiment, it can be observed that scavenging of singlet oxygen from the system has the biggest impact on NADH oxidation, resulting in less than 10% conversion over 20 h. The recyclability of the photocatalyst was investigated by monitoring NADH conversion over multiple additions, where no loss in activity was observed after 4 cycles (**Figure S7**).

The versatility of dual-responsive nanogels was further examined to catalyse a number of transformation reactions in an aqueous environment. Photo-oxidation of styrene, benzylamine and octanethiol was investigated. The photo-oxidation of styrene yields valuable carbonyl compounds, such as benzaldehyde, by carbon-carbon double bond cleavage. Typically, this reaction is undertaken with molecular and transition metal based photocatalysts, but recently metal-free photocatalysis has been conducted using conjugated mesoporous polymers.^[4a] However, this metal-free catalysis could not be conducted in a pure aqueous phase and required the addition of acetonitrile. Photocatalysis of styrene using dual-responsive photocatalytic nanogels at ambient temperature under visible light for 20 h led to conversion over 99%. Furthermore, an 84% selectivity for the production of benzaldehyde was achieved (Table 1, Figure S8 & S9). Conversely, when the experiment was repeated at 40 °C no conversion of styrene was observed (Figure S10). Using the dual responsive photocatalyst at ambient temperature yielded a higher conversion than previously reported for TiO₂ catalysed reactions whilst maintaining a similar level of selectivity.[14] Similar levels of conversion have been previously reported for heterogeneous organo-photocatalysts but the reactions must be conducted in acetonitrile.^[15] Moreover, the photocatalytic content used in both systems was significantly increased compared to the system presented. Indeed, this further demonstrates the enhanced efficiency of the photocatalytic units in the nanogel network.

Table 1. Photocatalytic conversion using dual-responsive polymer nanogelsat room temperature in aqueous media. All reactions undertaken under bluelight irradiation (λ = 460 nm).

25 °C 20 h

Conversion > 99 % , selectivity 84 $\%^{[a]}$





Reaction conditions: [a] Styrene (50 mM), nanogel (0.05 mg/ml nanogel, 2.5 μ g/ml photocatalytic units), 10 ml H₂O, RT, 20 h, conversion determined by GC-MS. [b] Benzylamine (50 mM), nanogel (0.5 mg/ml nanogel, 25 μ g/ml photocatalytic units), 20 ml H₂O, RT, 20 h. conversion determined by GC-MS. [c] 1-Octanethiol (100 mM), nanogel (5 mg/ml nanogel, 0.25 mg/ml photocatalytic units), 1 ml H₂O, RT, 40 h, conversion determined by GC-MS. Secondary product formed was dioctylsulfane.

The selective oxidation of amines to imines was undertaken using the dual responsive photocatalyst at room temperature in water. Previously, this reaction has been undertaken using both transition metal complexes and TiO_2 , with varying levels of

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conversion and selectivity. After 20 h using the dual responsive at ambient temperature photocatalyst over 87% of the benzyl amine was converted to the imine (**Table 1, Figure S11 & S12**). Whereas, less than 15 % of the imine was produced when the experiment was repeated at elevated temperature (**Figure S13**). Similar to the styrene oxidation reaction at ambient temperature, this reaction proceeded with a much higher concentration ratio of reagents to photocatalyst than previously reported.

To further demonstrate the flexibility of the dual responsive photocatalytic material produced a biologically relevant oxidative reaction was undertaken. The formation of disulfide bridges within cells is one of the most common post translational modifications of peptides that is undertaken. To mimic this the disulfide bridges were formed between a model compound, 1-octanethiol. Previously, a similar reaction has been photocatalysed using Mn(CO)₅Br; however, the disulfide bridge formation was undertaken in organic media (cyclohexane or benzene).^[16] Here, in a pure aqueous solution 1-octanethiol is converted to 1,2dioctyldisulfane and dioctylsulfane by the dual-responsive photocatalytic nanogels at room temperature. Furthermore, this is the first example of disulfide bridge formation utilising a pure organic photocatalytic system, with over 88% of the thiol groups converted after 20 h (Table 1, Figure S14 & S15). Conversely, at elevated temperature only 10 % of the thiol was converted (Figure S16).

The versatility and enhanced efficiency of the dual responsive photocatalytic material has been demonstrated compared to a range of different photocatalysts under differing reaction conditions. This improvement in performance may be due to several factors. First, the accessibility of the photocatalytic sites in the gel network in its swollen state is much higher than for other materials. In the swollen state, the gel network is fully expanded and can be described as a pseudo homogenous system as over 95% of the network is solvent, by volume. This allows for easy portioning of the reagents to the active sites throughout the network. Furthermore, as the photocatalytic monomer only constitutes a small portion of the network and is likely to be evenly distributed throughout the network, all units can be utilised for catalysis. Second, due to the highly translucent nature of the swollen gel, penetration of light is much greater compared to other solid photocatalytic systems, where only a fraction of the light directed at the sample is utilised, due to light scattering or absorption at the material surface. Finally, there may be a drive for reagents to partition into the gel network as it is more hydrophobic than the bulk continuous phase. This would drive the reagents into the gel, where they are converted into the targeted products.

In summary, a novel dual-responsive polymer photocatalytic system in the form of nanogels, consisting of a thermo-responsive matrix containing a small portion of photocatalytic moieties, have been produced. Temperature dependent shrinking/swelling enables tuneable photocatalysis in an aqueous environment. Controlled activation and deactivation of the photocatalytic unit by two external stimuli (light and temperature) has been demonstrated. The diffuse nature of the polymer network in its swollen active state enables enhanced catalysis at much lower photocatalytic concentrations than previously achieved. Furthermore, reactions can be rapidly quenched by changes in temperature and recovery of the photocatalyst can be undertaken. This new material and synthetic route produces highly effective polymeric photocatalytic nanogels in water with greater efficiency and tunability.

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Keywords: dual-responsive • polymer photocatalysts • heterogeneous photocatalysis • temperature dependent • NADH

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Stimuli-induced polymer for photocatalytic reactions: Inclusion of photocatalytic sites in a temperature responsive polymer nanogel network created a dual-responsive polymer photocatalyst that can be utilised to selectively catalyse numerous reactions at specific temperatures.



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