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Decontamination of nanoparticles from aqueous samples using supramolecular gels†

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The growing use of nanomaterials and their associated risks necessitate the emergence of efficient decontamination systems. The main objective of this study is to develop a new prototype based on artificial supramolecular hydrogel capable to remove nanoparticles (NPs) waste and nanomaterial by-products from aqueous suspensions. We demonstrate high trapping efficacy of the Low-Molecular-Weight Gelators (LMWG) for very small particles (quantum dots (QDs), gold nanoparticles (AuNPs), TiO₂ nanoparticles (TiO₂-NPs), below 50 nm in diameter) from aqueous suspensions. The performance levels in removing nanoparticles from contaminated effluents could lead to a competitive alternative to filtration and dialysis devices.

Nanomaterials exhibit novel properties that offer variety of new applications in different areas such as electronic,1 biomedical,2–4 pharmaceutical, cosmetic, energy,5 environmental,6 catalytic and materials. Owing to the potential benefits of nanotechnologies in various fields, there is a significant increase in the production and utilization of nanomaterials. The rapidly growing application of nano-products results in a potential increased exposure of human and environment to nanomaterials. The high reactivity of these nanomaterials may lead to adverse effects on biological systems, including human7 and ecological8 spheres. Consequently, the arrival on the market of nano-products raises crucial issues dealing with human/environment risk assessment and potential associated contaminations.9 Keeping in mind the risk associated with nanomaterials, it is essential to develop efficient decontamination methods to remove or subtract nano-particles (NPs) from contaminated wastes and environments including aqueous samples and surfaces. Surprisingly, despite the strong demand only few types of decontamination devices (i.e. coagulation and flocculation of NPs by organic polymers,10 polyaluminium chloride11) have been developed so far.12

In this context, we hypothesized that the use of the low-molecular-weight gelators (LMWGs) could serve as temporary scaffolds allowing a trapping of nanoparticles. These LMWGs offer several advantages to synthetic polymeric gels as they possess properties non-achievable by polymers.13–16 For example, water gelation by small molecules allows a rapid response of the gels to external stimuli, inherent gel-sol reversibility due to the non-covalent nature of the gel formation, and an easy elimination after use thanks to the gel-to-sol transition. Our interest is in using nucleoside-based amphiphiles capable of forming supramolecular systems. To this end, a large family of glycosylated-nucleoside-based amphiphiles featuring lipid (GNLs) have been synthesized and characterized.17–22 We discovered that these molecules form nanostructured hydrogels and organogels.17,18 In the present study, we have used a Glycosylated-Nucleoside Fluorinated amphiphile (GNF), as a trapping scaffold to address the nano-waste issue.18 We demonstrate the ability of nanostructured supramolecular hydrogels, offered by GNF, to entrap nanoparticles from aqueous samples (Fig. 1).

In order to evaluate the decontamination properties of GNF, the accumulation of various NPs in GNF’s hydrogel have been investigated. Initially, NPs derived from water soluble lipid-encapsulated QDs (previously synthesized in our lab), were suspended in water to prepare the contaminated samples.23 In a typical experiment, the GNF’s hydrogel was prepared and incubated in the presence of the QD’s suspension. After allowing this mixture to settle down for 48 h in the dark, a gel along with supernatant liquid phase was observed (Fig. 2A). The supernatant liquid was separated from the gel (Fig. 2B). As hypothesized, visualization under UV radiation (λmax=312 nm) revealed that all the encapsulated QDs were entirely entrapped in GNF’s hydrogel.
(red fluorescence) while no QDs left behind in the supernatant liquid (no red fluorescence) (Fig. 2C). The fluorescence spectra of the encapsulated-QDs solution and supernatant liquid (after hydrogel formation) were recorded. No emission peak corresponding to QDs was observed, indicating the absence of NPs in the supernatant (Fig. 2D). Interestingly, transmission emission microscopy (TEM) images of the gel phase revealed that the QDs were trapped in the nanostructured hydrogel matrix (Fig. 2E) (for better resolution see Fig. S4, SI).

To further investigate the trapping capability of GNF’s hydrogel, similar sets of experiments with borohydride-reduced lysine-capped gold nanoparticles (AuNPs) were realized. As mentioned earlier, GNF’s hydrogel was prepared and incubated in the presence of lysine-capped AuNPs solution (Fig. 3A). After 48 h of incubation at room temperature, a pink color gel appeared along with colourless supernatant liquid, indicating that all the lysine-capped AuNPs were trapped in the hydrogel (Fig. 3B). To confirm the absence of lysine-capped AuNPs in the supernatant liquid, the gel phase was removed (Fig. 3C) and UV-visible absorbance spectra of the supernatant were recorded. A strong absorption peak at 510 nm corresponding to the Lysine-capped AuNPs (green curve, Fig. 3D) and no such absorption peak was observed for supernatant liquid (dark blue curve, Fig. 3D). This indicates that a complete removal of lysine-capped AuNPs by the GNF hydrogel from the aqueous suspension was achieved. A TEM image of the gel phase shows that lysine-capped AuNPs were trapped as aggregates in the gel network (Fig. 3E) (for better resolution see Fig. S5, SI). Similar experiments were carried out with borohydride-reduced AuNPs (without lysine-capped). UV-visible absorption profile for borohydride-reduced AuNPs (without lysine-capped) and supernatant liquid after hydrogel formation were recorded (red and sky blue curve respectively, Fig. 3D).

Next, to explore the versatility of GNF’s hydrogel to trap NPs from aqueous suspension, the experiments were carried out with negatively charged titanium dioxide nanoparticles (TiO$_2$-NPs). TiO$_2$-NPs solution of required concentration (100 mg/L in 0.001 M NaCl) was prepared from commercially available solution (172.4 g/L in water). As usual, GNF was dissolved in TiO$_2$-NPs solution (Fig. 4A). To our surprise, TiO$_2$-NPs aggregate quickly after dissolution of GNF (< 5 min) and the solution changed it appearance from transparent to hazy (Fig. 4B). Along with time, more TiO$_2$-NPs started aggregating resulted in the increase in the particle size. After allowing it to stand for 2 h, all the TiO$_2$-NPs were trapped in hydrogel and settle down leaving behind the transparent supernatant liquid (Fig. 4C). UV-visible absorbance

**Fig. 2** QDs entrapped in GNF’s hydrogel (0.1 % (w/v)) (A) with supernatant liquid in normal and upside down position (B) under normal visualization (C) under UV visualization (λ_{max} = 312 nm) (D) fluorescence spectra (E) TEM image (scale: 100 nm)
spectra of supernatant liquid (red curve, Fig. 4D) were recorded to measure the concentration of TiO$_2$-NPs left behind and compared it with the UV-visible profile of TiO$_2$-NP solution (blue curve, Fig. 4D). No absorbance peak, corresponding to TiO$_2$-NPs, was observed in the case of supernatant liquid (red curve, Fig. 4D) indicating that all the TiO$_2$-NPs were aggregated in the GNF’s hydrogel. TiO$_2$-NPs samples (5.0 mg/L) was used to obtain standard UV-visible absorbance profile (blue curve, Fig. 4D).

Finally, the concentration of GNF left behind in the supernatant liquid (after hydrogel formation) was measured using UV-visible absorbance spectroscopy. These experiments revealed that only 0.8-1.1 % of total GNF left behind in the supernatant liquid (i.e. for 2 mg/mL GNF-hydrogel, the concentration of GNF in the supernatant liquid was 0.02 mg/mL). Regarding the toxicity of GNF left behind in the supernatant liquid, we have already reported biocompatibility of GNF-based hydrogels with cells and tissues which showed that similar amount of soluble GNF did not have any cytotoxic effects. 

One possible explanation of the unique trapping properties of the supramolecular gel would be a thermodynamically favorable evolution of the system. Indeed, the interactions of the nanoparticles with the 3D network of the gel would lead to a more stable state corresponding to nanoparticles attached to the supramolecular self-assemblies.

**Conclusions**

In summary, a facile and general method for the decontamination of aqueous samples containing nanoparticles is reported. By using the nanostructured gels based on a low molecular weight gelator, the GNF, the removal of nanoparticles from aqueous colloidal suspensions was successfully achieved at room temperature. To our surprise, the neutral GNF based hydrogel features high trapping efficacy for very small particles, including positive (QDs, AuNPs), and negative TiO$_2$-NPs nanoparticles, below 50 nm in diameter. The investigation described in this study seeks to move beyond past studies of decontamination.

![Fig. 3](image1)

**Fig. 3** Lysine-capped AuNPs with GNF (0.1 % (w/w)) (A) immediately after mixing (B) hydrogel formation after 48 h (C) supernatant liquid and hydrogel separated (D) UV-Vis absorption spectra (E) TEM image (scale: 100 nm)

![Fig. 4](image2)

**Fig. 4** TiO$_2$ with GNF’s hydrogel (0.1 % (w/v)) (A) immediately after mixing (B) aggregation after 5-10 min (C) aggregation and settling down after 2 h (D) UV-Vis absorption spectra.
systems involving membranes or flocculation systems. The novelty of this process is illustrated by the very limited literature concerning decontamination applications of NPs. Today, there is no filtration/flocculation system on the market capable of removing quantitatively NPs from waste. The performance levels observed with supramolecular gels in removing NPs from contaminated effluents could open many new industrial opportunities.

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