Temperature-triggered capture of dispersed particles using deposited Laponite with grafted poly(*N*-isopropylacrylamide) chains†

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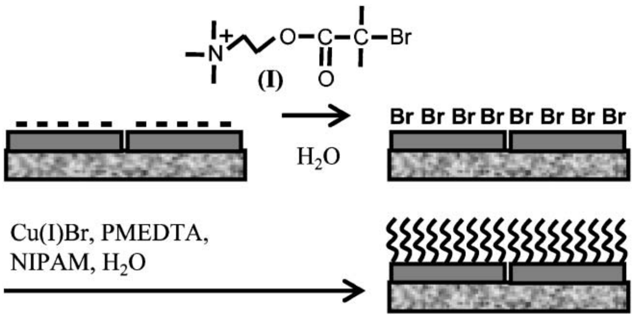
A method has been developed that enables a conductive surface to be modified so as to capture dispersed particles when the temperature is increased; poly(*N*-isopropylacrylamide) was grafted from electrodeposited Laponite particles using surface-initiated atom transfer radical polymerisation and used to capture dispersed polystyrene particles.

The ability of advanced medical diagnostic technologies to reach their full potential requires improvements in the sensitivity and versatility of immunoassay, genetic assay and cell sorting technologies. A key criterion that must be met by these technologies is the ability to perform assays using small (picolitre) sample quantities. This necessitates the use of microarrays.[1] Production of microarrays using photolithography[2] has speed and minimum spot size limitations. New technologies are required that will enable capture of dispersed material using nanometre spot sizes produced using non-photolithographic methods. One new general method for this could utilise nanometre-sized temperature-responsive surfaces prepared on nanometre-sized electrodes. These could be used to capture dispersed proteins using localised heating. This type of technology will require localised heating in the sub micrometer range. Important advances in localising heating in microarrays have been achieved in recent years using micro-heaters[3,4] and one of the most promising of these from the viewpoint of scaling down is the use of resistive heating.[5]

Laponite is a synthetic smectite clay which forms structured gels in concentrated dispersions.[6] It has an average diameter and thickness of 20.4 and 1.2 nm, respectively.[7] Previous work from our group showed that interfaces containing adsorbed temperature-responsive poly(*N*-isopropylacrylamide) (PNP) could be used to reversibly trigger adhesion of droplets.[8] PNP chains in solution exhibit a temperature-triggered coil-to-globule transition above the lower critical solution temperature (LCST). This transition leads to chain contraction for PNP chains grafted to interfaces and a loss of steric repulsion above the LCST. We reasoned that if Laponite particles could be deposited flat onto an electrode surface and PNP grafted onto the solution-facing particle face then temperature-triggered capture of dispersed colloid particles should be possible.

The general procedure employed to prepare electrodeposited Laponite–PNP particles is shown in Scheme 1. A 45 pore-per-inch carbon foam cylinder (170 ml) was used as the anode in a purpose built two-electrode, concentric electrochemical cell. A UV-visible technique based on formation of the Mg^{2+}–eriochrome black T complex[9] was adapted to measure the adsorption of Laponite onto the electrodes as a function of applied potential. The absorption at 550 nm was found to be the most sensitive for measuring Mg^{2+} concentration. The Laponite RD used contained 17.8 wt.% Mg. It was found that 100% of the Mg present within the Laponite was recovered when the clay was digested in nitric acid (pH = 2) at 65 °C for 29 h (See Fig. 1). These conditions allow determination of trace amounts of Laponite in dispersion.

The ATRP initiator (I) was synthesised using a modified version of a related synthesis reported by Bottcher *et al.*[10] Briefly, 2-bromoethanol was reacted with a slight excess of 2-bromoisobutyrate in THF at 0 °C. The product was subsequently reacted with a tenfold excess of trimethylamine in ethanol. ATRP was conducted under Ar at room temperature within the



Scheme 1 Laponite–PNP prepared from surface-initiated ATRP.

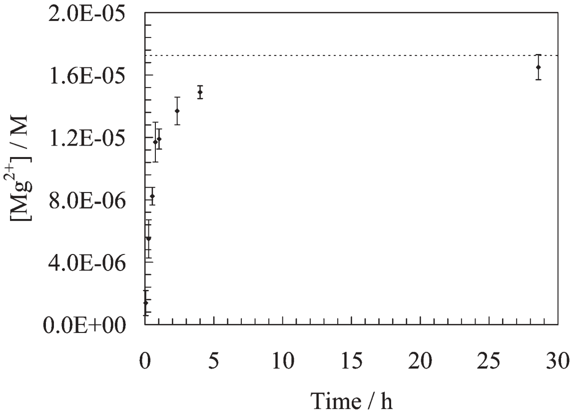


Fig. 1 Mg^{2+} concentration with time for dissolution of Laponite. The horizontal line corresponds to 100% Laponite RD dissolution.

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electrochemical cell. After electrodeposition of the Laponite, sufficient (I) was added to cover one face of the Laponite particles. A typical surface-initiated ATRP contained 4 wt.% NIPAM, 3 mM of PMEDTA and 1.5 mM of Cu(I)Br. After 18 h, the electrode was washed copiously with 10^{-3} M $NaNO_3$ until the blue colour of Cu(II)Br_2 and solution PNP could not be detected (*via* turbidity at elevated temperature). GPC analysis of solution PNP recovered during the washing step after polymerisation gave a number average molar mass (M_n) of 59,000 g mol^{-1} (PD = 6.5). The electrochemical cell was immersed in a temperature-controlled water bath during particle capture experiments. These were conducted using low polydispersity, anionic polystyrene latex (0.03 wt.%, 508 nm) prepared in-house using surfactant-free emulsion polymerisation. The dispersion was re-circulated through the electrode (bottom to top) using a flow rate of 100 ml/min. Polystyrene particle concentration was determined using turbidity *vs.* concentration measurements at 400 nm. The colloidal stability of the dispersed polystyrene particles was carefully monitored throughout the capture experiments using the wavelength-exponent method.[11] No particle–particle aggregation occurred during these experiments.

Fig. 2 shows the variation of fractional coverage of the carbon electrode by Laponite (θ_{Lap}) as a function of time during the course of potential ramping. The fractional coverage was calculated using the immersed surface area of the carbon foam (0.23 m^2), the average dimensions of Laponite (above) and its density (2.2 g cm^{-3}). Fig. 2 is the first data set that we know of that shows clearly the conditions required to obtain monolayer coverage of Laponite onto an electrode (*i.e.*, $\theta_{Lap} = 1$). The optimum coverage for this experiment was obtained using 1 V applied for 1 h. Laponite RD was used for this work because of its high proportion of exfoliated clay platelets. Therefore, a monolayer coverage of flat platelets is a reasonable approximation for the modified surface studied here.

The surface-initiated ATRP of *N*-isopropylacrylamide was conducted using a high concentration of monomer to minimise solution polymerisation. Nevertheless, sufficient solution polymer was collected from the washings to be analysed by GPC. The polydispersity (6.5) was high by ATRP standards and indicates the polymerisation was not controlled. One possible explanation for the high polydispersity was desorption of (I) from the Laponite particles during ATRP. This was investigated by measuring zeta potentials of *dispersed* Laponite particles containing adsorbed (I) using electrokinetic sonic amplitude measurements. The particles were washed and mixed in an equivalent manner to that which occurred before and during surface-confined ATRP using electrodeposited particles. These data show (See ESI†) that the zeta potential for dispersed Laponite containing (I) remained at about −10 mV in the presence of the same ionic strength as used during ATRP. It is therefore likely that no significant desorption of (I) occurred from electrodeposited Laponite during surface-confined ATRP. This conclusion is consistent with the known strong affinity of Laponite for quaternary amines.[12] It follows that the surface bound polymer contains a low proportion of polymer generated in solution and would be mostly brush-like.

The value for M_n can be used to estimate maximum layer thicknesses for surface-bound PNP brushes at room temperature if it is assumed that the solution and surface M_n values are comparable. (This assumption remains to be tested for these systems.) Extrapolation of published hydrodynamic thicknesses[13] of PNP brushes as a function of M_n gives a thickness of 85 nm.

The particle capture experiments were performed using temperature ramping. Fig. 3 shows the variation of the fractional coverage of adsorbed polystyrene particles as a function of time during temperature ramping. The fractional coverage (θ_{PS}) was calculated using polystyrene particle diameter (508 nm), surface area of the foam in contact with the dispersion during capture (0.216 m^2) and the density of polystyrene (1.05 g cm^{-3}). Particle capture experiments were conducted in the *absence* of an applied potential. The capture that occurred was temperature-induced. Fig. 3 shows a full curve that is a guide to the eye and is consistent with the error bars. There was a small adsorption of particles ($\theta_{PS} \simeq 0.005$) upon initial exposure of the modified electrode to particles. This remained constant for the first 24 h at 25 °C. The first temperature ramp resulted in a substantially increased proportion of captured particles (up to $\theta_{PS} \simeq 0.040$) which then remained constant upon cooling. A second temperature ramp resulted in an additional slight increase in capture. Temperature-triggered particle capture was not reversible for the modified electrodes used here.

The data from the first temperature ramp (25–50 °C) of Fig. 3 are replotted in terms of θ_{PS} as a function of temperature in Fig. 4. Turbidity *vs.* temperature data for linear PNP in solution are also shown for comparison. These data show clearly that temperature-induced capture of the polystyrene particles becomes pronounced

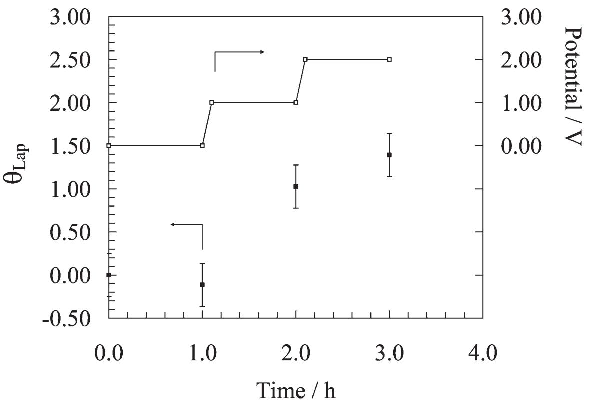

Fig. 2 Variation of θ_{Lap} in response to potential steps.

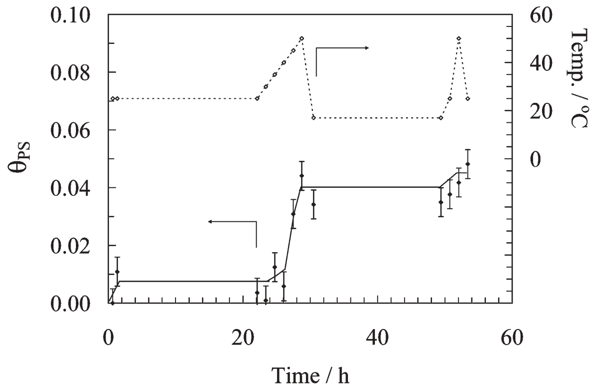

Fig. 3 Variation of θ_{PS} on the modified electrode in response to temperature ramping.

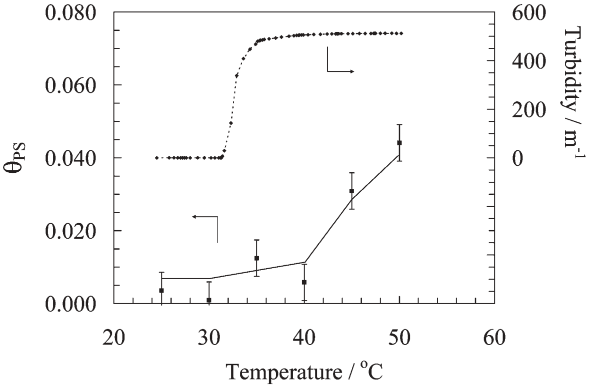

Fig. 4 Variation of θ_{PS} as a function of temperature for the first temperature ramp from Fig. 3. Turbidity data for solution PNP are also shown for comparison.

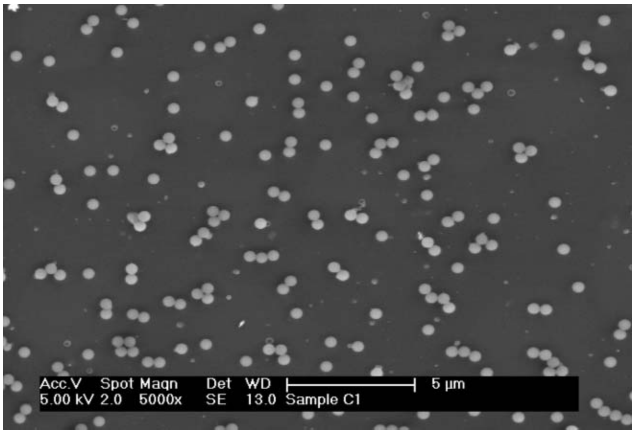

Fig. 5 Scanning electron micrograph of the modified electrode surface used to obtain the data shown in Fig. 3 after a further heating cycle.

above 40 °C. This is higher than the LCST of solution PNP (which is about 33.0 °C from the data shown here).

The modified electrode used to obtain the data shown in Figs. 3 and 4 was subjected to a further cooling and heating cycle, extensively rinsed with water at 50 °C and then immediately placed in an oven at 80 °C. Fig. 5 shows a representative SEM image from the modified electrode. It can be seen that the particles are randomly distributed as singlets and small clusters on the surface. The average value for θ_{PS} calculated from the SEM was 0.07. This value is consistent with the θ_{PS} values shown in Fig. 3.

There are a number of interesting points that come from the results shown in Figs. 3 and 4. The modified surface is able to (a) protect against significant adsorption until the temperature is increased, (b) give temperature-triggered capture to a fractional coverage that remains constant when the temperature is decreased and (c) cause capture at temperatures significantly above the LCST of the solution polymer. The most likely explanation for these observations is one which considers the modified Laponite–PNP surface to consist of a PNP layer that is electrosterically stabilised at 25 °C. The LCST for PNP layers at interfaces is well known to extend to higher temperatures compared to solution polymer and become continuous.[14] It has been shown that PNP grafted to gold surfaces[15] *via* surface-confined ATRP does not completely collapse until the temperature is 41 °C. As the temperature increases for the present systems, the PNP layer must increasingly contract and the steric contribution to the repulsive interaction between the Laponite–PNP surface and polystyrene particles must be increasingly diminished. This allows capture to occur due to the increased importance of the attractive van der Waals interactions between the underlying surface and the polystyrene particles. The data suggest that complete removal of steric stabilisation (above 40 °C) is a pre-requisite for significant particle capture. The low value for the maximum θ_{PS} observed in these experiments (*cf.* 1.0) is attributed to residual repulsive electrostatic interactions between the particles and surface.

By using Laponite–PNP composite particles prepared at an electrode surface we have established proof of principle of a new method to give conductive surfaces the ability to capture dispersed particles using temperature as the trigger. It should be possible to modify any conducting surface in this way. This new method could enable microarrays to be prepared in the future that contain nanometre sized electrodes that are able to be triggered to capture biocolloids.

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