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A thermosensitive hydrogel carrier for nickel nanoparticles

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ABSTRACT

Segments of a p(NIPA-co-AMPS) hydrogel synthesized from *N*-isopropyl acrylamide (NIPA) and 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) with *N*,*N*′-methylenebis(acrylamide) (BIS) acting as cross-linker stabilized nickel nanoparticles (Ni-NPs) of uniform size in an aqueous solution. The rate of catalysis of the borohydride reduction of 4-nitrophenol to 4-aminophenol by these nanoparticles shows a complex temperature variation consistent with the hydrogel changing from a contracted to an expanded state below a lower critical solution temperature, LCST, of ~310 K. These observations provide insights into nanoparticle stabilization and catalysis and indicate potential pathways toward stable sophisticated nanoparticle catalysts for use in aqueous solution.

Metal nanoparticles have attracted considerable interest as their chemical and physical properties differ substantially from those of bulk metals [1–5]. While these properties are of both fundamental and practical interest, their study has often been hindered by the tendency of metal nanoparticles to aggregate and precipitate from aqueous solutions which are of particular interest as water is environmentally benign. Consequently, a range of aqueous carrier systems exemplified by core–shell particles [6–10], dendrimers [11,12], hydrogels [13–17] polyelectrolyte brushes [18,19] and supramolecular structure such as cyclodextrins [20,21] has been developed. We are particularly interested in stable hydrogel carrier systems which are amenable to easy handling. Accordingly, we made the p(NIPA-co-AMPS) hydrogel from *N*-isopropyl acrylamide (NIPA) and 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) with *N*,*N*′-methylenebis(acrylamide) (BIS) acting as cross-linker. Solid segments of this copolymer hydrogel stabilize nickel nanoparticles of uniform size in aqueous solution. The catalysis of the borohydride reduction of 4-nitrophenol to 4-aminophenol by these nanoparticles exhibits a complex temperature dependence consistent with the p(NIPA-co-AMPS) hydrogel changing from a contracted to an expanded state below a lower critical solution temperature, LCST, of ~310 K. We view these observations as precursors to a major investigation into the effects of copolymer composition and metal nanoparticle identity on a range of nanoparticle catalyzed reactions.

The synthesis of the Ni-NP-p(NIPA-co-AMPS) hydrogel was achieved by the dissolution of NIPA (1.91 g) and AMPS (1.75 g) in 12 cm^3 in water followed by the addition of BIS (0. 013 g) to act as the cross-linker and AAPH (0.01 g) to act as the initiator with thorough mixing for 10 min. The solution was injected into a glass tube which was 15 mm in diameter and 15 cm long and the open end was sealed with parafilm after which it was irradiated for 2 h with a UV–vis lamp with a 200–600 nm range with a maximum intensity at 400 nm. The tube was then carefully broken open to release the solid cylinder of p(NIPA-co-AMPS) hydrogel which was cut into 4 mm thick cylindrical sections. Unreacted reagents were removed from these sections by immersing them in gently stirred deionized water for 24 h, during which time the water was changed at 4 h intervals. The hydrogel sections were then dried to constant weight in a vacuum oven at 323.2 K. A FTIR spectrum (KBr thin section) was run on a Nicolet-iS 10 FTIR spectrometer: 1040 (m), 1385 (m), 1550 (m), 1647 (m), 3134 (s), 3422 (s) cm^{-1} (Supporting information, Fig. S1).

Circular segments of the oven-dried p(NIPA-co-AMPS) (0.044 g each) were immersed in gently stirred aqueous 0.10 mol dm^{-3} $NiCl_2$ solution at room temperature for 48 h, during which time the decreasing Ni^{2+} concentration of the solution was monitored by inductively coupled plasma atomic emission spectroscopy, ICP-AES, using an IRIS 1000 instrument, until it stabilized after ~24 h, consistent with the hydrogel absorption of Ni^{2+} being complete (the maximum weight of

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$NiCl_2$ in the hydrogel was 9.5 mg). After washing with deionized water to remove extraneous $NiCl_2$, the green hydrogel was placed in a stirred 100 cm^3 0.5 mol dm^{-3} $NaBH_4$ aqueous solution under a nitrogen atmosphere for 12 h. The now black hydrogel segments were then removed and washed with deionized water three times to remove any extraneous Ni-NP on the surface. Prior to use in the kinetic studies discussed below, these hydrogel segments were dried to constant weight in a vacuum oven at 323.2 K. To determine the Ni-NP content a segment of the Ni-NP-p(NIPA-co-AMPS) hydrogel was dried to a constant weight of 48 mg several 3.5 mg segments of which were then dissolved in separate 5 cm^3 of 11 mol dm^{-3} hydrochloric acid solutions which were analyzed for Ni^{2+} by ICP-AES. This showed the dried Ni-NP-p(NIPA-co-AMPS) to be 9% Ni-NP by mass.

Prior to commencement of each catalytic kinetic run, a 48 mg segment of vacuum oven dried Ni-NP-p(NIPA-co-AMPS) was immersed in water at the temperatures corresponding to that of the kinetic run for 24 h under nitrogen. To initiate the kinetic run the Ni-NP-p(NIPA-co-AMPS) hydrogel segment was transferred into 100 cm^3 of a thermostated and stirred aqueous solution 0.00216 and 0.216 mol dm^{-3} in 4-NP and $NaBH_4$, respectively, under nitrogen in a stoppered flask. At appropriate time intervals, 0.10 cm^3 samples of this solution were extracted and delivered into 3.0 cm^3 volumes of deionized water at room temperature and the UV–vis spectra of the solutions were recorded.

The hydrogel structure and the morphology of the Ni-NP were determined by scanning electron microscopy, SEM, using a FEI-Nova450 instrument, and by high resolution transmission electron microscopy, HRTEM, using a JEM-2100F instrument respectively. In the kinetic experiments the UV–vis spectra were recorded in thermostated 1 cm pathlength quartz cells using a SHIMADZU UV-2550 spectrophotometer.

Scanning electron microscopy (SEM) shows the vacuum oven (323.2 K) dried copolymer to have the dominant macroscopic structure shown in Fig. 1. Small segments of the p(NIPA-co-AMPS) hydrogel in stirred aqueous 0.10 mol dm^{-3} $NiCl_2$ solution at room temperature for 48 h, during which time the decreasing Ni^{2+} concentration of the bulk solution was monitored by inductively coupled plasma atomic emission spectroscopy, ICP-AES. The bulk Ni^{2+} concentration stabilized after 24 h. This is consistent with the absorption of Ni^{2+} by the p(NIPA-co-AMPS) segments being complete and the copolymer absorbing water to form a hydrogel in which the sulfonic acid groups are dissociated. Subsequent stirring of these segments in 100 cm^3 of aqueous 0.50 mol dm^{-3} $NaBH_4$ solution under nitrogen for 12 h causes them to become black as Ni^{2+} is reduced to form nickel nanoparticles, Ni-NP, in a Ni-NP-p(NIPA-co-AMPS) hydrogel.

High resolution transmission electron microscopy (HRTEM) shows a uniform distribution of Ni-NP in the Ni-NP- p(NIPA-co-AMPS) hydrogel with a narrow distribution of Ni-NP diameters centered at 26.24 nm (Fig. 2). This is consistent with a regular pore size distribution within the hydrogel and probable interactions of either the amide or sulfonate groups, or both, controlling Ni-NP size and preventing aggregation. The Ni-NP content of the Ni-NP-p(NIPA-co-AMPS) hydrogel segments dried to constant weight was determined to be 9% Ni-NP by mass.

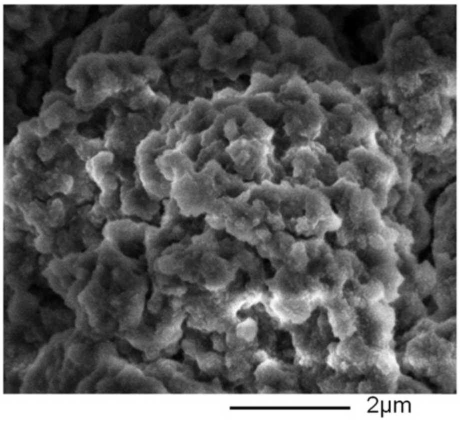

Fig. 1. SEM image of the vacuum oven dried p(NIPA-co-AMPS) copolymer.

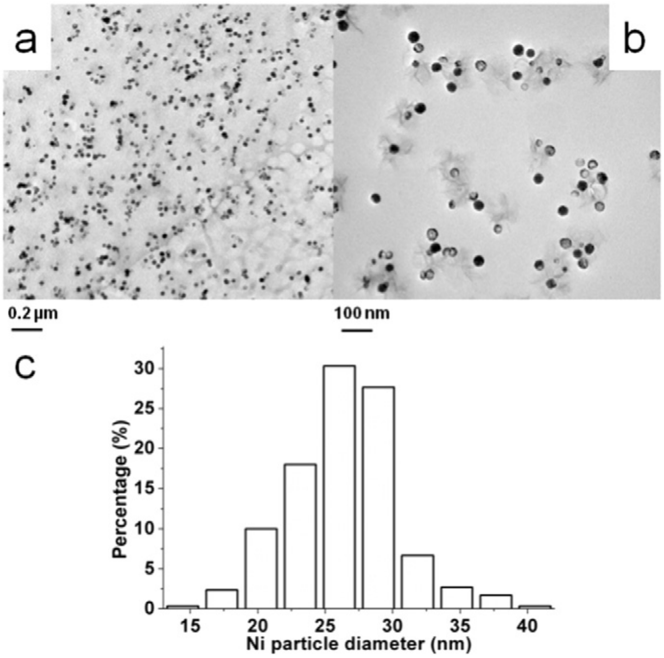

Fig. 2. HRTEM, images of Ni-NP-p(NIPA-co-AMPS) hydrogel at different magnifications in a) and b). Distribution of Ni-NP diameters are shown in c).

In the temperature range 293.8–317.1 K the Ni-NP-p(NIPA-co-AMPS) hydrogel showed a complex temperature dependence of the swelling ratio, *SR*, defined by Eq. (1):

$$SR = (W_T - W_\mathrm{d})/W_\mathrm{d} \tag{1}$$

were, W_T is the weight reached after suspension in water at temperature T and W_d is the dry weight determined over a range of temperatures by placing a weighed portion of the oven-dried hydrogel in thermostated deionized water from which it was removed and weighed at intervals until a constant weight was reached. The Ni-NP-p(NIPA-co-AMPS) hydrogel *SR* undergoes a gradual decrease as temperature increases from 293.8 K followed by a sudden decrease over the temperature range 308.9–312.0 K centered at ~310 K, the lower critical solution temperature, LCST. A constant *SR* is reached as temperature increases from 313.9 to 317.1 K (Fig. 3). Thus, the Ni-NP-p(NIPA-co-AMPS) hydrogel changes from an expanded state in the lower temperature range where it absorbs most water to a contracted state in the higher temperature range where it absorbs less water.

The borohydride reduction of 4-nitrophenol, 4-NP, to 4-aminophenol is catalyzed by metal nanoparticles [4–8] and was used here to test the catalytic capacity of the Ni-NP in the Ni-NP-p(NIPA-co-AMPS) hydrogel. In these studies the $NaBH_4$ concentration was in one hundred-fold excess over that of 4-NP such that the reduction occurred under pseudo-first order conditions. At each reaction temperature, a 48 mg segment of the Ni-NP-p(NIPA-co-AMPS) hydrogel (dried to constant weight in a vacuum oven at 323.2 K) was placed in 100 cm^3 of a thermostated and stirred aqueous solution 0.00216 and 0.216 mol dm^{-3} in 4-NP and $NaBH_4$, respectively, under nitrogen in a stoppered flask. At appropriate time intervals, 0.10 cm^3 samples of this solution were extracted and delivered into 3 cm^3 volumes of deionized water at room temperature and the UV–vis spectra of the resulting solutions were recorded (Fig. 4). The absorbance maximum at 400 nm arising from 4-nitrophenolate, 4-NP^-, decreased with time coincident with the increase in the maxima at 233 and 300 nm arising from the reduction product, 4-AP. Isosbestic points at 222, 247, 281, and 313 nm indicate that 4-NP^- and 4-AP were the