

Molecular Recognition by Core-Shell Nano-Particles

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The imprinting of synthetic polymers with organic compounds of interest in trace analysis is well known.¹⁻³ The methodology involves supramolecular organization of the target molecule with ligating agents that can also be polymerized. Following polymerization the template is removed leaving behind a shape specific site that can be used to selectively rebind the target. It is normally thought that polar solvents such as water disrupt the supramolecular complex that is formed prior to polymerization. However, metal imprinted nanoparticles can be used to selectively extract metal species from water. (e.g. refs 4 and 5) but these systems fail to extract non-amphiphilic organic compounds. The work presented here shows that adoption of core-shell morphology can overcome this limitation. In effect the imprinting process was forced to occur at the particle surface (on the shell).

Shell thickness was shown to be optimum at approximately 5-10nm. Below this value the particles behaved in a manner that was similar to the non-imprinted controls. Shells with thickness much beyond this value were also poor materials since it was not possible to extract the original template. Selectivity was found to be pH dependant. In most cases the best selectivity was obtained at pH = 7-8. One aspect of particular note from these data is that caffeine is extracted in preference to theophylline for nanoparticles imprinted against either caffeine or theophylline but the greatest selectivity for caffeine is seen on the nano-particle imprinted against caffeine.

In another set of experiments we examined core-shell particles templated with a series of tripeptides. Two Imprinted nanoparticles were imprinted with either YGG or MLF. Following extraction of these peptide templates the nanoparticles were exposed to ternary mixtures of the following peptides: GGH; TGG and MLF. The first observation to be made from these results is that GGH was extracted by each nano-particle, including the non-imprinted control. Similarly, the non-imprinted control also extracted MLF. The nanoparticles imprinted with MLF behaved in the same manner. Molecular recognition of peptide sequences was best illustrated with the nano-particle imprinted against YGG. In this case the non-specific extraction of MLF was completely suppressed whilst the imprint template, YGG, was extracted. GGH was also extracted. These results indicate that molecular recognition of peptide sequences by imprinted nanoparticles in water is possible but further molecular design of the polymer surface will be required so that non-specific extraction may be avoided.

- 1) G. Wulff, *Angew. Chem. Int. Ed Engl.*, **34**, 1812, (1995)
- 2) B. Sellergen, M. Lepisto, K. Mosssbach, *J. Am. Chem. Soc.* **110**, 5853 (1998)
- 3) S. Rimmer, *Chromatographia*, **46**, 470 (1998)
- 4) S. A. Piletsky, H. Matuschewski, U. Schedler, A. Wilpert, E. V. Piletska, T. A Thiele, M. Ulbricht, *Macromolecules* **33**, 3092 (2000)
- 5) K. Yu, K. Tsukagoshi, M. Maeda, M. Takagi, *Anal. Sci.* **8**, 701 (1992)
- 6) M. Yoshida, K. Uezu, M. Goto, F. Nakashio, *J. Chem. Eng.*, **29**, 174 (1996)