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PAPER

Magnetic nanocrystals coated by molecularly imprinted polymers for the recognition of bisphenol A^{\dagger}_{\dagger}

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Molecularly imprinted polymers were coated on the surface of magnetic nanoparticles using an original and simple chemical strategy combining aryl diazonium salt chemistry and the iniferter method. This approach provides dispersed, highly soluble and BPA imprinted poly(methacrylic acid-*co*-ethylene glycoldimethacrylate) coated magnetic nanoparticles.

Introduction

Magnetic nanoparticles (NPs) have been the subject of extensive research during the last decade because of their potential applications in many fields, such as magnetic ferrofluids,1 nucleic acid separation,^{2a,b} NPs/ligand targeting systems for drug delivery,^{2c-g} removal of environmental pollutants.3 For many of these applications, surface modification of the NPs is a key challenge. One promising approach consists of functionalizing the NPs by biomimetic polymers such as molecularly imprinted polymers (MIPs), in order to produce bifunctional materials with remarkable magnetic and recognition properties. Since the seminal work of Polyakov in the 1930s,4a using silica matrices, the reports of Wulff and co-workers4b on covalent imprinting protocols and those of Mosbach on the noncovalent imprinting approach4c a decade ago, several examples have been reported in the literature on the preparation of magnetic molecularly imprinted polymers (MMIPs).5 Usually, the MMIPs are composed of aggregates of superparamagnetic nanoparticles embedded within a molecularly imprinted polymer matrix. Although effective for extracting and sensing experiments, such beads containing multiple magnetic nanoparticles remain relatively large (with diameters larger than 60 nm), which severely undermines their targeting specificity in biomedical applications.⁶ The use of individual ultrasmall magnetic nanoparticles covered by a thin layer of molecularly imprinted polymer should be a promising alternative offering several advantages over larger conventional MMIPs: (i) control of the NPs size down to about 10–20 nm; (ii) higher surface-to-volume ratio; (iii) higher binding capacities and faster binding kinetics.

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We address this issue in the present paper by developing a facile methodology to grow molecularly imprinted polymers from individual metal oxide nanoparticles via an aryl diazonium salt-derived initiator. Aryl diazonium salts have been shown to be useful coupling agents for the grafting of polymer coatings on carbon-based,7 metallic8 (gold, platinum, palladium, ruthenium and titanium) planar or nanoparticle surfaces, affording strong carbon or metal-carbon linkages. Several substrates could be functionalized using this approach, by a range of grafting onto and grafting from methods, which were reviewed recently.9 For example, surface-initiated photopolymerization was conducted on gold surfaces modified by the electrochemical reduction of an aryl diazonium salt¹⁰ and gold-grafted ultrathin films of quercetin-imprinted polymers (Au-MIPs) were prepared by tandem diazonium salt chemistry and surface-confined ATRP.¹¹ As far as oxide surfaces are concerned, their functionalisation using diazonium salts has been reported for a long time¹² but its extension to the functionalization of iron oxide nanoparticles has only been reported very recently,13 by taking advantage of the transformation of diazonium species to diazoates in basic media.14,15 These species are unstable and dediazonize along a homolytic pathway to give aryl radicals which further react with the iron oxide NPs during their formation and stop their growth. Using this approach, our group could obtain monolayers of functional aryl groups¹³ grafted on the iron oxide NPs surface. However, the possibility to grow molecularly imprinted polymers from the aryl-modified NP surface has never been investigated so far. In this paper, we fill this gap by exploring the capacity of aryl diazonium coupling agents to initiate the growth of MIPs from individual iron oxide NPs.

Our strategy relies on a bifunctional initiator, 4-(((diethylcarbamothioyl)thio)methyl) benzenediazonium tetrafluoroborate (BF_4^- , $^+N_2$ -C₆H₄-CH₂-DEDTC) containing (i) a diazonium end group for surface anchoring and (ii) a *N*,*N*diethyldithiocarbamate¹⁶ (DEDTC) function able to activate surface-initiated photoiniferter-mediated polymerization (SI-PIMP), which is a versatile and robust method widely used in

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"graft-from" strategies.¹⁷ We demonstrate this approach, schematized in Fig. 1, by grafting cross-linked molecularly imprinted co-polymers of methacrylic acid and ethylene glycoldimethacrylate on magnetic iron oxide nanoparticles, in the presence of bisphenol A (BPA) as the template molecule.

BPA is a xenoestrogen that can disrupt endocrine function and adversely affect the reproductive systems of wildlife and humans.¹⁸ The MIP-coated magnetic nanoparticles developed in this work should therefore open up new opportunities for rapid extraction of trace amounts of BPA.

Results and discussion

Iron oxide cores functionalized with benzyl DEDTC groups on the surface (NP-DEDTC) were synthesized by one-step coprecipitation of Fe²⁺/Fe³⁺ under alkaline conditions, in the presence of the diazonium salt BF4-, +N2-C6H4-CH2-DEDTC (see details of the procedure in the ESI[†]). The synthesis was performed within a few minutes at room temperature in slightly basic aqueous medium (pH 9). Then, the polymerisation could proceed, mixing the NP-DEDTC particles with methacrylic acid (MAA) as the monomer, ethylene glycoldimethacrylate (EGDMA) as the crosslinking agent and bisphenol A (BPA) as the template molecule. The deoxygenated mixture was irradiated under UV light for 4 h. The final product consisting of nanoparticles coated by a molecularly imprinted polymer (NP@MIP) was washed several times and separated by magnetic separation. The morphology, adsorption, and recognition properties of these magnetic molecularly imprinted nanomaterials were investigated by IR, DRX, TGA and TEM. A reference non-imprinted polymer sample (NP@NIP) was prepared using the same procedure, but without addition of the template.

The X-ray diffraction (XRD) patterns of the powders are characteristic of the spinel phase with broadened peaks (see Fig. S2†). The cell parameter and the size of coherent diffraction domain ($\langle L_{\rm XRD} \rangle$) were determined with the MAUD software¹⁹ which is based on the Rietveld method combined with Fourier analysis. The Rietveld refinement analysis agrees well with the formation of nanocrystalline spinel iron oxide while Raman spectroscopy evidenced a maghemite Fe₂O₃ phase.²⁰ As previously observed for the *in situ* functionalization of iron oxide NPs by diazonium salts,²¹ the crystal size appears to be dependent on the presence of the diazonium salt, with lower diameters measured after functionalization (\sim 30% diameter decrease), compared to bare NPs. This result indicates that the coating limits the crystalline growth, in agreement with previously reported works.²²

As shown in Fig. 2, transmission electron microscopy (TEM) revealed the production of quite isotropic particles with sizes around 8 and 16 nm for NP-DEDTC and NP@MIP, respectively. Although the particles seem to be aggregated after DEDTC grafting, they appear well separated after polymerization, suggesting a steric stabilization provided by the polymer overlayer. HRTEM images of NP@MIP nanoparticles (displayed in the ESI†) show a crystalline core corresponding to the iron oxide, covered by an amorphous layer corresponding to the polymer coating. Note that in the case of NP-DEDTC, the proximity between the crystal size inferred from XRD and the inorganic core diameter deduced from TEM (see Table 1) suggests that the produced particles are single crystals and that their coating is very thin, close to a single molecular shell.

Fig. 3 shows the IR spectra of the Fe₂O₃ NPs recorded after each treatment step. Bare NPs display one intense band at ~590 cm⁻¹, characteristic of the Fe–O stretching vibration. The IR spectrum of NP-DEDTC shows the appearance of new bands at ~1630 ($\delta_{C=C}$), 1450 (ν_{C-N}), 950 (ν_{C-S}) and 890 (ν_{SCS}) cm⁻¹ due to the phenyl and thiocarbamate group vibrations.²³ It is noteworthy that the N \equiv N stretching mode near 2280 cm⁻¹ appearing in the IR spectrum of the free diazonium salt (see Fig. S3†) is not visible in the spectra of the functionalized NPs, indicating the release of the N₂ group as a consequence of the cleavage of the diazonium moieties during the grafting process. Strong modifications appear in the spectrum of NP@MIP: a very intense band is seen at *ca*. 1730 cm⁻¹ due to the C==O stretching mode together with two medium bands at ~3400 cm⁻¹ (ν_{O-H}) and 2950 cm⁻¹



Fig. 1 Scheme depicting the synthesis of iron oxide nanoparticles functionalized by bisphenol A-imprinted polymer films.



Fig. 2 Transmission electron micrographs and histograms of the particle size distributions for (a) NP-DEDTC and (b) NP@MIP after 4 h polymerization.

Table 1 Characteristics of the NPs

Sample	$\langle L_{\rm XRD} \rangle / \rm nm$	$\langle D_{\rm TEM} \rangle / {\rm nm}$	Org. ^{<i>a</i>} (wt%)
Bare NPs	11	11 ± 1	4
NP-C ₆ H ₄ -CH ₂ -DEDTC	8	8 ± 1	18
NP@NIP			43
NP@MIPwith BPA		16 ± 1	60
NP@MIP without BPA ^b			47

^a Organic weight percents determined from TGA.



Fig. 3 FT-IR spectra of (a) bare iron oxide NPs, (b) NP-DEDTC and (c) NP@MIP.

 (ν_{C-H}) . These features, characteristic of poly(methacrylic acid), indicate that the polymerization step has been effective.

To quantify the organic coating of the produced hybrids, thermal gravimetric analyses were performed, in the temperature range of 20-800 °C with a heating rate of 10 °C min⁻¹ under a flow of air at 80 mL min⁻¹. The observed total weight losses (reported in Table 1) were assumed to be due to desorption and/ or decomposition of the organic coating shell leading to a direct measurement of the organic weight in the studied hybrids. A total weight loss of 18% was observed on heating NP-DEDTC to 800 °C while the uncoated NPs showed a weight loss of only 4% (probably due to some contamination species). This result suggests a high grafting density of initiators on the nanoparticle surface. Taking into account the average inorganic core diameter $D_{\text{TEM}} \approx 8 \text{ nm of single functionalized particles obtained from}$ TEM, and the density of ferric oxide of \sim 4.9 g cm⁻³, a specific surface area²⁴ of 153 m² g⁻¹ is obtained which yields a surface coverage Γ of $\sim 3.6 \times 10^{18}$ aryl molecules m⁻². It is noteworthy that this value is in the same order of magnitude as the surface concentration of a close-packed monolayer Γ_{CPML} of phenyl (or 4-substituted phenyl) groups estimated from molecular models,²⁵ $\Gamma_{\rm CPML} = 8.1 \times 10^{18}$ aryl molecules m⁻². In comparison, the weight losses measured for NP@NIP and NP@MIP are sharply higher, reaching 43 and 60%, respectively (see the TGA profiles in Fig. S4[†]). This strong increase in organic weight percent after polymerization indicates a high polymer surface coverage. It is worth noting that the 60% organic weight loss measured on NP@MIP falls to 47% after BPA extraction. From the difference between these two values, one could deduce approximately the

amount of BPA molecules bound to the NP@MIP which is around ${\sim}13\%.$

The produced NP@MIPs were dispersed in water at different pH values (Fig. 4). After sonication, the suspension in basic medium (pH 8) appears more stable than that in deionized water (pH 5.5). This result indicates a self-aggregation process caused by the pH-induced charge property change of the particle surface. This self-assembled behavior can be readily reversed by adjusting the pH. Furthermore, the NP-MIP particles are magnetically responsive in both tested media. They can be attracted under magnetic field under more or less aggregated state, Fig. 4c.

The binding properties of NP@MIP nanoparticles towards bisphenol A were determined by measuring the uptake of bisphenol A in ethanol over a range of concentrations from 50 to 400 μ mol L⁻¹ (see Fig. 5). The results show that the NP@MIP nanoparticles have much higher binding capacity than the control NP@NIP, suggesting that the molecular recognition sites were generated on the surface of the MIP particles by the BPA template involved in the polymerization process.

To gain further insight into the phenomenon of bisphenol A binding by the NP@MIP nanoparticles, the binding data were fitted into a Langmuir isotherm model. In the Langmuir model, the equilibrium dissociation constant (K_d) and saturation capacity ($B_{max} = B + B_{unbound}$) can be estimated graphically from a linearized version of the model by plotting the adsorption isotherm in a Scatchard format:²⁶

$$B/[BPA] = (B_{max} - B)/K_d$$

The Scatchard plot (inset of Fig. 5) was not linear indicating that the binding sites in NP@MIP are heterogeneous with respect to the affinity for BPA. Because there are two distinct sections within the plot which can be regarded as straight lines, it reveals that two classes of binding sites were produced in NP@MIP. In contrast, the plot was almost linear for NP@NIP, in agreement with the presence of nonspecific binding sites only. From the slopes and intercepts of the straight area in the range of 0-12 μ mol g⁻¹ of binding amounts (corresponding to the higher binding amount region for the NP@MIP), the values of affinity constants K_{A1} ($K_A = 1/K_D$) and B_{max} for the NP@MIP were found to be \sim 3 times higher than the values calculated for the NP@NIP (see Table 2). From results shown in Table 2, it is clear that although the chemical compositions of both NP@MIP and NP@NIP are similar, their spatial structures are different with the presence of specific rebinding sites for BPA in the polymer



Fig. 4 Numerical photographs of aqueous dispersions of NP@MIP particles (a) in deionized water, (b) in basic medium (pH = 8), and (c) in the presence of a magnet.



Fig. 5 Binding isotherms of NP@MIP (squares) and NP@NIP (circles) for BPA. The inset shows the Scatchard plot for the binding of BPA.

Table 2 Affinity constant (K_a) and maximum number of binding sites (B_{max}) for NP@MIP and NP@NIP

Sample	$K_{\rm a}/10^4$ L mol ⁻¹	$B_{\rm max}/\mu{ m mol}~{ m g}^{-1}$
NP@MIP	1.5 ± 0.2^a .	17.3
	0.47 ± 0.01^{b}	26.0
NP@NIP	0.43 ± 0.06	5.3

^{*a*} Value of K_{A1} corresponding to the high affinity binding sites. ^{*b*} Value of K_{A2} corresponding to the low affinity binding sites.

overlayer of the MIP particles. These specific rebinding sites offer a steric and an electronic microenvironment complementary to that of the compounds of interest to be bound.

To determine the binding selectivity of NP@MIP for BPA, BPF was selected as an interfering molecule since its molecular structure is quite similar to BPA. The results, displayed in the ESI (Fig. S6†), show that NP@MIP exhibit good adsorption selectivity for the template BPA with a higher binding capacity for BPA ($B_{\text{max}} = 17.3 \ \mu\text{mol g}^{-1}$) than for BPF ($B_{\text{max}} = 6.5 \ \mu\text{mol g}^{-1}$).

Binding experiments from variable-temperature runs were used to evaluate thermodynamic properties according to the Van't Hoff equation.²⁷ This approach can offer an insight into the nature of the interaction between the template and polymer and help to elucidate the chemical forces underlying the interactions. From the slope of a Van't Hoff plot $(\ln(Q_c/C_e))$ vs. 1/T, a value for ΔH^0 of -8.8 kJ mol⁻¹ could be determined. The negative value of ΔH^0 indicates an exothermic adsorption mechanism of BPA onto MIP, probably due to interactions. The adsorption of BPA on MIP is therefore more favourable at low temperature.

Fig. 6 presents the adsorption kinetics of 0.1 mmol L^{-1} BPA solution onto MIP. The time profile indicates an initial rapid increase in the adsorption capacity (during the first 30 min) and then a slower approach to a limiting value.

For the imprinted materials of non-thin films, it takes generally 12–24 h to reach adsorption equilibrium.²⁸ Therefore, in our case, BPA molecules reach the surface imprinting cavities of MIP easily and take less time to reach adsorption saturation, implying



Fig. 6 Curve of adsorption kinetics for BPA to NP@MIP ($C_{BPA} = 0.1 \text{ mmol } L^{-1}, m_{MIP} = 3 \text{ mg}, T = 20 ^{\circ}\text{C}$).

good mass transport and thus overcoming some drawbacks of traditional packing imprinted materials. Such fast kinetics is consistent with the thin shell imprinted layers generated over the iron oxide nanocores.

Conclusion

In summary, we have successfully synthesized ultra-small dispersed magnetic nanocrystals coated by a thin layer of a molecularly imprinted polymer, using a combination of aryl diazonium salt chemistry and the iniferter method. Our approach offers several advantages over conventional methods: (i) ease and rapidity of NPs surface functionalization using diazonium salts; (ii) stability of the covalent link between the inorganic core and the organic coating; (iii) formation of small and dispersed NP@MIP. We do believe this synthetic approach will not only pave an additional way for the preparation of BPA imprinted nanoparticles but also provide a new general nanomaterial strategy design for the detection of toxic molecules.

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