CSIRO PUBLISHING

Aust. J. Chem. **2012**, *65*, 680–685
http://dx.doi.org/10.1071/CH12168

Full Paper

Novel Phosphopeptides as Surface-Active Agents in Iron Nanoparticle Synthesis

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We report the dramatic effect of rationally-designed phosphopeptides on the size and shape of iron-iron oxide core-shell nanoparticles prepared in a one-pot synthesis by sodium borohydride reduction of an iron salt. These phosphopeptides are effective at small ratios of peptide to metal, in contrast to the behaviour of conventional capping agents, which must be added at high concentration to control the particle growth.

Manuscript received: 23 March 2012.
Manuscript accepted: 17 April 2012.
Published online: 29 May 2012.

Introduction

Controlling and modifying the size and shape of metallic nanoparticles is an area of great practical interest. This is particularly true for magnetic nanoparticles where these features strongly affect magnetisation behaviour.[1–5] Iron-iron oxide nanoparticles are of particular interest because they exhibit strong ferromagnetic properties due to their iron core but are resistant to oxidation due to the protective layer of iron oxide.[6–8] Core-shell iron-iron oxide nanoparticles usually form when iron nanoparticles are left exposed to air and the thickness of the protective oxide layer usually stabilises around 2–5 nm.[9–11] Amongst the many methods available for the synthesis of iron nanoparticles, wet chemical techniques involving the reduction of aqueous iron salts are popular.[12,13] The method usually requires the use of additives in order to template the growth of the nanoparticles and prevent their aggregation. Common additives includes surfactants, in which case particle size is limited by the size of the micelles, or capping agents that can adsorb on the growing face of nanoparticles and affect the growth mechanism of these nanoparticles.[14–18] Other templating methods such as dendrimer cages[19] or even viruses[20] have also been reported. The problem with these techniques is that a high ratio of additive to iron is required for the synthesis. Afterwards, these compounds usually remain attached to the particle surface and ligand exchange is needed in order to improve the biocompatibility and reduce the toxicity of the material for medical applications.

A rational approach to this problem would be to design capping agents with functional groups that specifically interact with the iron surface, these functional groups being positioned at the correct spacing to bring about selectivity on the crystal facets where the capping agent adsorbs. Peptides are of particular interest as potential growth habit modifiers for several reasons: they are easily synthesised; functional groups can be placed along a backbone in any desired sequence with a well defined geometrical relationship to one another; and almost any functional group can be added onto the backbone by the use of a suitably functionalised amino acid. There are advantages to this approach, particularly biocompatibility and ease of subsequent functionalisation of the peptide-capped particles.[21] The idea of using particular peptide sequences for growth modification of a wide range of materials is not new.[22–29] Currently, peptides have been successfully used to control and mediate the growth of nanoparticles of palladium,[30,31] platinum,[32–38] gold,[33,39–43] silver,[42,44,45] and other noble metals.[45,46] However, to our knowledge, no examples of iron nanoparticle preparation using peptides as capping agents have been reported to date.

Discussion and Conclusions

Here, we describe a one pot synthesis of core-shell iron-iron oxide nanoparticles in aqueous solution using various phosphopeptides as additives. Phosphopeptides have been chosen because of the well known affinity between phosphate groups

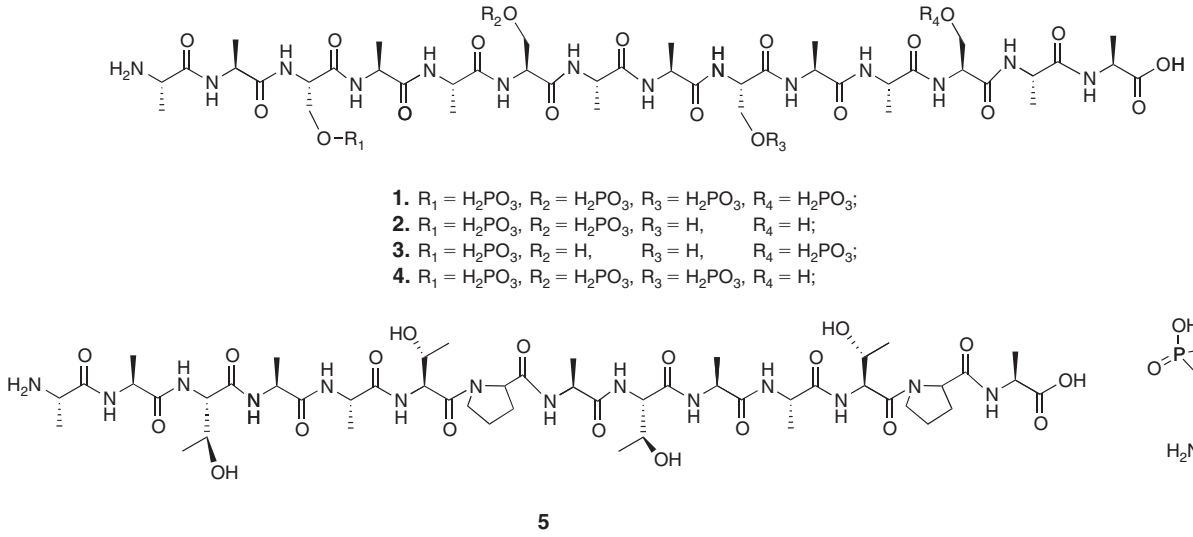

Fig. 1. Phosphopeptide analogues used in this study.

Table 1. Particles size and iron oxide shell thickness

Experiment	Additive	Particle size [nm]	Shell thickness [nm]
a.	No additive	58 ± 13	3.2 ± 1
b.	Sodium citrate	67 ± 22	3.6 ± 0.9
c.	**1**	20 ± 5	3.9 ± 0.8
d.	**2**	19 ± 4	3.3 ± 0.5
e.	**3**	19 ± 4	5.0 ± 1.6
f.	**4**	18 ± 5	3.5 ± 0.9
g.	**5**[A]	49 ± 7	4.0 ± 1.0
h.	**6**[A]	29 ± 8	4.4 ± 1.4

[A]Control experiments.

and iron. We have aimed for a peptide that might fold such as to allow multiple binding interactions of the pendant phosphates with the iron surface on the one hand and present a stabilising interface with water on the other. So, proceeding by analogy, the peptide backbone designed to carry the phosphate groups has been chosen to mimic the action of some glycopeptides found in Antarctic fish which have the ability to modify the normal growth of ice crystals.[47–50] These 'antifreeze' glycopeptides, which have a two-face configuration in water,[51–55] are made of a repetition of the same unit (alanine-alanine-threonine) with a disaccharide (Gal-GalNAc) attached to the hydroxyl of the threonine.[56–58] We have simply replaced the disaccharide with a phosphate and changed the threonine to a serine. Adopting this mimetic approach, a range of simple peptides containing different numbers of phosphate-serine residues, organised in different patterns, were prepared (analogues **1**–**4**, Fig. 1). The effects of a very small mole ratio of these analogues (20 : 1 iron : phosphopeptide) on the size, shape and composition of the resulting iron nanoparticles were investigated using transmission electron microscopy (TEM) and selected area electron diffraction (SAED) techniques. The effects of these phosphopeptides were compared with the effects of sodium citrate, a capping agent commonly used for the preparation of metal nanoparticles.[12,59] Control experiments where only a bare peptide sequence (**5**) or the phosphoserine building block itself (**6**) was added instead of phosphopeptide were also carried out.

Reduction of iron (II) salts in water using $NaBH_4$ under stirring (experiment *a*) gave rise to core-shell nanoparticles with an overall size of 58 ± 13 nm (Table 1) and a shell of 3.2 ± 1 nm (Fig. 2a). These particles were attached to each other to form chain-like structures that extended beyond a few hundred nanometers. Due to their large size, these structures did not form a stable dispersion in solution. They aggregated and precipitated out of suspension after a few seconds. The same experiment repeated in the presence of sodium citrate (10 : 1 metal : salt) produced particles with size and morphology that were very similar to those produced in experiment *a*. These structures showed a weaker tendency to agglomerate compared to those of experiment *a* (Fig. 2b). Hence, they remained stable in suspension for a longer period of time. Such stabilisation was attributed to the fact that sodium citrate adsorbs on the surface of metal nanoparticles and stabilises them by electrostatic repulsion.[59]

The introduction of a very small molar ratio of phosphopeptides **1**–**4** (20 : 1 iron : phosphopeptide) (experiments *c–f*) in the synthesis reduced the observed average diameter of the iron nanoparticles from ~60 nm to around 20 nm (Table 1). The results in terms of size and shape of the particles prepared in the presence of peptides **1**–**4** were similar within the variance calculated. As shown by the TEM results (Fig. 2c, d, e, f) these iron nanoparticles also joined together to form chain-like structures. In contrast with experiments *a* and *b*, these structures formed stable suspensions when dispersed in ethanol.

Experiments carried out using just the bare peptide sequence (analogue **5**, experiment *g*) gave rise to large iron nanoparticles with a diameter of 49 ± 7 nm, showing that the peptide sequence alone was not affecting the growth of iron. The use of phosphoserine **6** in experiment *h* led to the formation of irregularly shaped iron nanoparticles with an average diameter of 29 ± 8 nm. The structure of these particles combined chain-like spheres as observed for experiments *a*, *b* in some areas and aggregated randomly shaped particles as observed for experiments *c–f* in other areas.

The presence of iron in the samples was confirmed by both energy-dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (Figs S1–S8 in the Supplementary Material). The presence of iron oxide in the sample was confirmed by

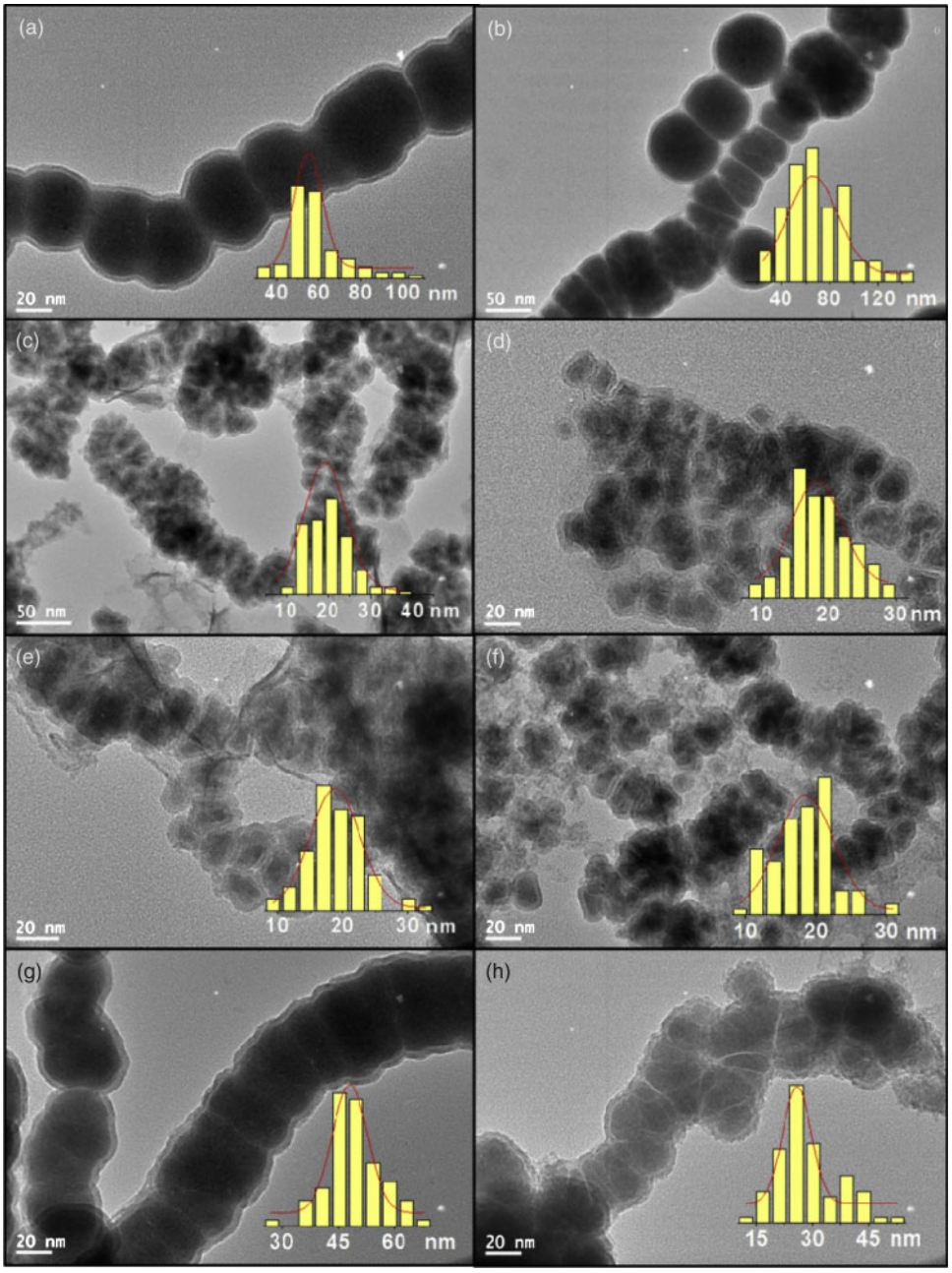

Fig. 2. TEM images and histograms of particle size distribution of the iron nanoparticles synthesised in the presence of (a) no additive; (b) sodium citrate; (c) analogue 1; (d) analogue 2; (e) analogue 3; (f) analogue 4; (g) analogue 5; and (h) analogue 6 as an additive.

selected area electron diffraction for experiments *c*–*h*. It was impossible to differentiate magnetite from maghemite due to a similarity between the diffraction patterns.[60,61] However, the formation of iron oxide on the surface of iron nanoparticles exposed to air has already been studied and the literature describes this layer as mainly magnetite (Fe_3O_4) with a small ratio of maghemite (γ-Fe_2O_3) present.[13,62–64] Diffuse electron diffraction rings implied that all of the samples had low crystallinity. This was further confirmed by high-resolution transmission electron microscopy (HRTEM) of the samples (Figs S1–S8 in the Supplementary Material), where no lattice fringes were observed for any sample, showing the absence of long range ordering of the iron atoms within each nanoparticle. Magnetic measurement done on the iron nanoparticles grown in the presence of analogue **1** and grown in the presence of sodium citrate both showed a clear ferromagnetic behaviour (see Supplementary Material).

Two factors may influence the growth mechanism of the iron nanoparticles and explain the size diminution induced by the addition of phosphopeptides in solution. First, phosphopeptides **1**–**4** may bind onto the growing surface of iron nanoparticles and affect the rate of incorporation of the iron atoms onto the growing particles. Such binding would slow the growth of the particles, resulting in more nucleation and therefore smaller nanoparticles. Whilst direct examples of iron(0) – phosphate interactions could not be found in the literature, surface complexation interaction between phosphates and iron oxides such as goethite,[65] maghemite,[66–68] and magnetite[69] has been reported.[70–73] The second

factor that needs to be considered is the interaction between the phosphopeptides and the iron salt in solution. Phosphates[52–54] and in particular phosphate-bearing amino acids[70,74,75] are well known to strongly complex with iron (III), but have not been reported to form complexes with iron (II). Alternatively, iron (II) in solution could interact with the phosphopeptide to form ferrous phosphate salts ($Fe_3(PO_4)_2{\cdot}8H_2O$; $K_s = 1 \times 10^{-26}$). Formation of these various complexes would reduce the quantity of the free iron salt available and, assuming that the rate of nucleation remains unaffected, result in the formation of smaller nanoparticles. However, the fact that there is 20 times less phosphopeptide than iron precursor in solution at the beginning of the reaction argues against a major role for the consumption of the iron precursor, which may only involve a small fraction of the initial salt. This argument is further supported by the fact that the particles produced in the presence of peptides **1**–**4**, which have different numbers of phosphate moieties, are similar in shape and size. The stabilisation of the particles in suspension induced by the addition of the phosphopeptides, and the fact that they can be easily redispersed, also argues for the adsorption of the phosphopeptide onto the surface of the nanoparticles.

The difference in the chain structure of the particles observed between experiment *a* and *b* on one hand, and experiments *c*–*f* on the other hand, can be described as a direct consequence of the competition between the undisturbed nanoparticle growth and a magnetic self-assembly process. Lu et al. proposed a mechanism in which iron nuclei start to form when $NaBH_4$ is introduced and tend to grow as spherical nanoparticles, protected from oxidation by the H_2 formed in situ.[13] Further growth of these nuclei would then compete with the magnetic attraction between freshly nucleated particles, the resulting shape of the particles being highly dependent upon the rate of reduction of the iron salt. In the present study, such competitive growth would account for the observation of 'flattened sphere' nanoparticles observed in the nanochains of experiment *a* and *b*, which are typical for ferromagnetic particles above 50 nm.[13,76] Similarly, addition of the phosphopeptide, which induces the formation of an increased number of iron nuclei due to slower growth, results in important magnetic interactions that overwhelm the normal process of nanoparticle growth, thereby explaining the irregular shapes observed in the case of experiments *c*–*f*.

The effect of phosphoserine **6** on the growth of iron nanoparticles shows that one phosphate moiety is sufficient to interact with the growth of the iron surface. However, the weak effect of **6** on the synthesis of iron nanoparticles in comparison with the effect obtained with peptides **1**–**4** demonstrates that the interactions between the phosphate groups and the iron are dramatically enhanced by the presence of multiple phosphates on the peptide backbone. Considering the similar results obtained in the presence of peptides **1**–**4**, it can be argued that two phosphate groups are enough to enhance the interaction between phosphate and iron and that having more phosphates on the peptide did not further affect the growth behaviour.

In conclusion, we have demonstrated the first example of iron nanoparticle growth modification using rationally designed peptides as capping agents. The one-pot aqueous reaction in the presence of a very small mole ratio of phosphopeptide gave rise to iron-iron oxide core-shell nanoparticles with a diameter of around 19 nm including a 3–5 nm layer of iron oxide. We suggested that the phosphopeptides act by slowing the rate of growth of the particles, probably by adsorbing onto the growing surface of the particles, resulting in smaller nanoparticles with irregular shape due to increased magnetic constraints. Although at this stage we have not achieved control of shape or crystallinity of the nanoparticles, nevertheless this work demonstrates proof of concept for the development of novel peptide-based capping agents for the preparation of metal nanoparticles. In the future, we hope to use phosphopeptides to create smaller nanoparticles that exhibit superparamagnetic properties or create phosphopeptides that preferentially adsorb onto specific faces of the iron crystal in order to produce iron nanoparticles of various shapes.

Experimental

Solid phase peptide synthesis of the (phospho)peptides **1**–**5** was carried out using a fluorenylmethyloxycarbonyl (Fmoc)/*tert*-butyl (tBu) strategy on a TributeTM Peptide Synthesizer using commercially available Fmoc-Ser(HPO_3Bzl)-OH. Final purification and characterisation was performed using reverse-phase HPLC and LC-MS. For more details about the synthesis and characterisation of synthetic analogues **1**–**6**, see the Supplementary Material.

Core-shell iron-iron oxide nanoparticles were prepared under nitrogen atmosphere by adding a freshly prepared solution of sodium borohydride (1.3×10^{-5} mol in 1 mL DI-H_2O) to a solution of iron (II) sulfate heptahydrate (7×10^{-6} mol in 2 mL DI-H_2O). Prior to the addition of reducing agent, trisodium citrate (7×10^{-7} mol) was added for experiment *b* (Table 1), peptides **1**, **2**, **3**, **4**, and **5** (3.5×10^{-7} mol) were added for experiments *c*, *d*, *e*, *f*, and *g* respectively and phosphoserine **6** (1.4×10^{-6} mol) was added for experiment *h*. A black precipitate quickly appeared and the mixture was further stirred for 10 min under nitrogen atmosphere. The particles were then magnetically decanted and washed three times with ethanol, dried, and stored under nitrogen atmosphere.

The samples for TEM studies were prepared by resuspending the dry particles in ethanol using sonication and then depositing a few drops of ethanol suspension on a carbon coated copper TEM grid and allowing evaporation in ambient conditions. Transmission electron microscopy (TEM) images, electron diffraction patterns, and EDS data were acquired digitally with a JEOL 2010 operated at an accelerating voltage of 200 keV and equipped with an Oxford Inca EDS detector. Magnetisation measurements were made using a superconducting quantum interference device (SQUID) magnetometer.

Supplementary Material

Detailed synthesis and characterisation of the compounds, characterisation of the nanoparticles and magnetic measurements are available on the Journal's website.

Acknowledgements

We thank the MacDiarmid Institute for Advanced Materials and Nanotechnology and the Maurice Wilkins Centre for Biodiscovery for financial support.

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