THE AUTHOR
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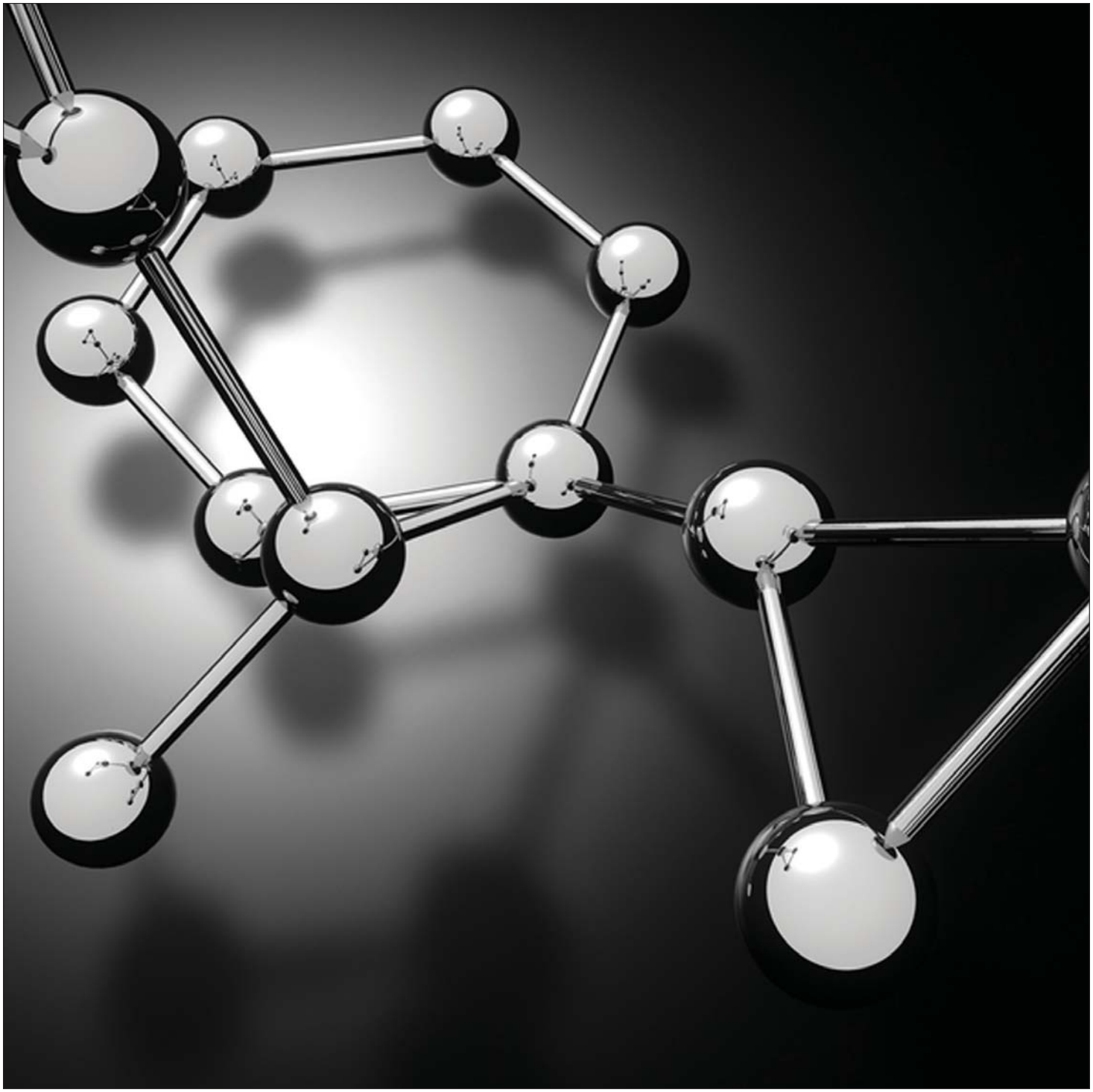
Nature shows its metal



By borrowing a few tricks from nature scientists have discovered a new way of creating advanced aluminium materials

WORK at Nottingham Trent University has demonstrated the predominantly electrostatic nature of protein-aluminium interactions. This advance brings science a step closer towards being able to build novel aluminium-composite materials using naturally occurring biological processes. A Zetasizer Nano ZS particle characterisation system from Malvern Instruments is now being used by the research team for both zeta potential and sub-nanometer particle size measurements.

This use of biological processes to engineer nano-composite material structure is referred to as biomimetic-nanotectonic manipulation. By combining aluminium nanoparticles with proteins, the research team took advantage of spontaneous biological assembly to fabricate highly organised structures called Keggin ions. These are the building blocks for advanced aluminium materials with highly specific properties used

Feature: Nanotechnology

in applications such as antiperspirants, biosensors, environmental control systems and biomedical devices.

Manipulation of materials combining biological molecules with nanoparticles relies heavily on understanding interparticle interactions. Many of these are dominated by the effects of surface charge on the participating particles and surrounding media.

In mildly acidic conditions at concentrations above the solubility limit of aluminium hydroxide, monomeric Al species can undergo condensation reactions. This can lead to the formation of small oligomeric Al species, and further transformation into large Keggin ions and the recently characterised Al_{30}-mer. These have been used in a number of applications, including antiperspirant actives, the preparation of Al_2O_3 nanoparticles and composite materials.

Previous studies of protein-aluminium interactions have largely concentrated on elucidating the bioavailability of the element, and absorption/elimination pathways in living organisms. A better understanding of the interactions of aluminium species with biomolecules is a necessary pre-requisite for the successful application of a combined biomimetic-nanotectonic approach to advanced aluminium-containing materials. This study reports on the effects of a model protein, bovine serum albumin (BSA), on the generation and properties of hybrid Al-protein composite materials formed from various high-purity, Al-containing, aqueous nanosized precursors.

When used as an adjuvant, aluminium hydroxide has a considerable effect on the structure and function of bovine serum albumin (BSA)[1]. One potential influence may be the effect of the aluminium hydroxide's surface charge on what are predicted to be predominantly electrostatic interactions with the protein. Recent work carried out at Nottingham Trent University's School of Science and Technology, provides evidence supporting this hypothesis[2].

An investigation of the interactions between sub-nanometer Al_{13}-mer and Al_{30}-mer polyoxocations and larger BSA protein involved characterising and comparing zeta potential measurements made on Al-BSA complexes using a Zetasizer Nano ZS. The same system was used first to measure particle sizes using DLS at a temperature of 25°C. As seen in Figure 2, a typical correlation function obtained for the Al_{13} and Al30-mers exhibits two visible decay rates. The more rapid decay rates (A) most probably arise from the diffusion of Al nanocluster particles while the slower decay rates (B) are interpreted as heavier, slower aggregates. Further analysis of the correlation functions (using a non-negative least squares fit) provided the intensity size distributions (Figure 2) which were then converted (using Mie theory) to volume size distributions (Figure 3).

A series of sample complexes containing 0.2M Al-BSA, with BSA concentrations varying from 0 to 25mg/mL in 2.5mg/mL, were measured. Solutions containing only BSA at similar concentrations gave negative zeta potentials of -8.6 ± 0.4nm and the mean diameter of BSA was measured as around 8 to 9nm. All Al-BSA complexes produced positive zeta potentials at all concentrations with only small differences between samples containing the alternative Al cation types.

Although the solutions containing only Al_{13} and Al_{30} polyoxocations produced no discernable results in terms of zeta potential because of the small size of the particles, once BSA was added to the Al nanoparticles, the average particle size increased to ~10.7 ± 0.5nm, enabling the reproducible measurement of zeta potential. As summarised in Figure 4, while the average size of particles within samples containing Al_{13}-mer remained stable for increased concentrations of BSA, those samples containing Al_{30}-mer saw increasing particle size with increasing BSA concentrations above 17.5mg/ml.

These unexpectedly large particle sizes may be a result of the adsorption of Al_{13}-mer clusters on the negatively charged surface of BSA in the mildly acidic (pH < 5.0) conditions. This theory is supported by the positive zeta potential measurements which decrease with increasing concentration of BSA. As shown in Figure 5, the ratio of Al polyoxocations to protein falls. Their neutralising effect on the negative surface charge of the BSA particles is reduced suggesting that this aluminium-protein interaction is indeed predominantly electrostatic.

The interaction between aluminium sub-nanometer polyoxocations and the model protein, BSA, can be characterised using dynamic light scattering techniques utilising non-invasive backscatter optics. Advances in sensitivity of dynamic light scattering equipment now make it possible to both quantify sub-nanometer particle dimensions and qualify their bimolecular interactions as being strongly determined by their surface charge. LN

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2. Deschaume, O., Sahfran, K.L. & Perry, C.C (2006) Langmuir 22, 10078-10088

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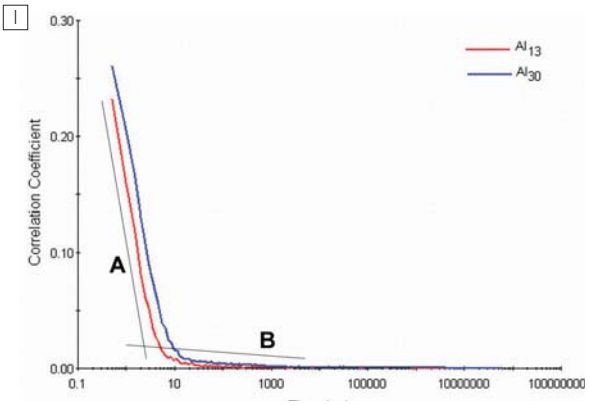

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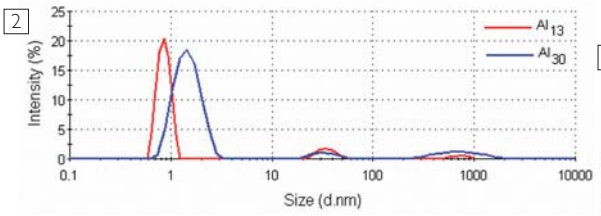

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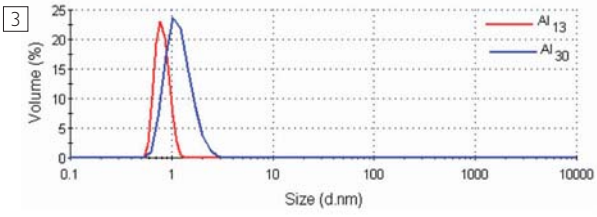

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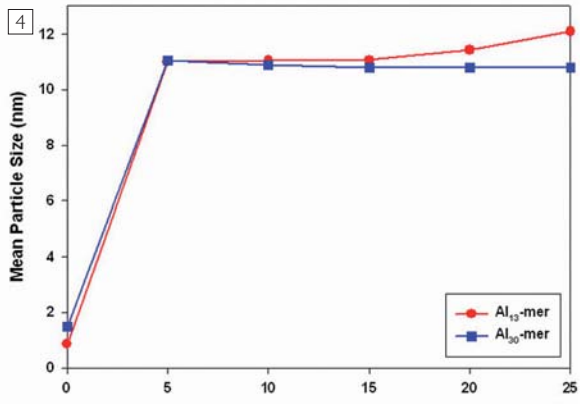

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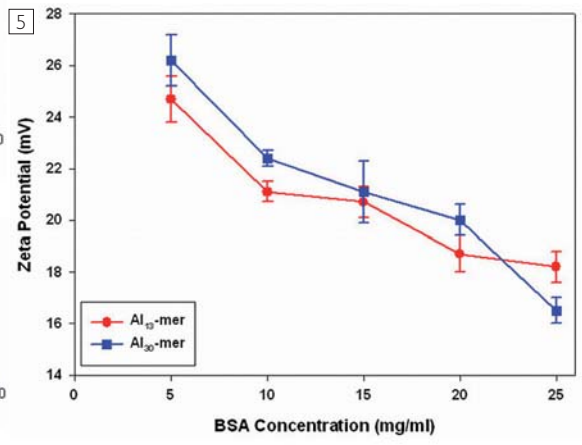

Figure 1: Typical correlation functions obtained for the Al_{13} and Al_{30}-mers showing visible decay rates for Al nanocluster particles (A) and aggregates (B)

Figure 2: Intensity particle size distributions obtained for the Al_{13} and Al_{30}-mers

Figure 3: Volume particle size distributions obtained for the Al_{13} and Al_{30}-mers

Figure 4: Increase in the mean particle size of Al-BSA complexes as a function of BSA concentration

Figure 5: Zeta potential values for Al-BSA complexes as a function of BSA concentration