



Figure 1. A model for structural organization of Mn in photosynthetic reaction centre II of higher plants⁸. D1, D2: heterodimeric proteins of reaction centre II; P680: Special pair Chlorophyll a absorbing at 680 nm; Chl: Chlorophyll a; Pheo: Pheophytin a; Q,Q: Quinones A and B.

possible to discover the nature of this cluster (two dimers or a tetramer) as well as the hide out (amino acid residues ligating to Mn cluster) in the heterodimer proteins D1/D2, even after an untiring endeavour of almost two decades by scientists with elegant techniques like electron spin resonance (ESR)³ and extended X-ray absorption fine structure spectroscopy (EXAFS)⁴. X-ray crystal-

lographic structure determination of purple bacterial photosynthetic reaction centre and its similarity with oxygen evolving reaction centre II, inspired building of a number of models for the catalytic site of reaction centre II.

Recently, site-directed mutagenesis has shown promise to locate the manganese hide out. Debus and colleagues have reported some amino acid residues as

probable ligands to Mn through mutant study in cyanobacteria^{5,6}. The probable Mn binding ligands are H332, E333 and H337 of D1 protein. Earlier in 1990 Vermaas *et al.*⁷ had reported probability of E69 of D2 protein in cyanobacteria (E70 of D2 in higher plants)⁷. These results coincide with theoretical propositions made earlier. We had reported in 1990 in a theoretical model of reaction centre II, H332, H337 of D1 and E70 of D2 as ligands to Mn (Figure 1)⁸. The theoretical model of Coleman and Govindjee also proposes E70 of D2 and E333 of D1 to be possible Mn ligands⁹.

Though cumbersome the site-directed mutagenesis appears to be the only effective technique next to X-ray crystallography to discover the Mn hide out.

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Giant magnetoresistance: New concepts

Magnetic coupling has played a key role in the discovery of the Giant Magnetoresistance (GMR) effect in thin films. In certain multilayers consisting of alternating ferro- and non-ferromagnetic films

(e.g. Co/Cu), adjacent ferromagnetic films couple to each other through the nonferromagnetic film separating them. When an external magnetic field is applied to overcome this coupling, the ferromagnetic moments align and as a result, a change in the electrical resistance of an unprecedented magnitude is observed. This is referred to as Giant Magnetoresistance or GMR effect.

The large drop in electrical resistance of a solid in a magnetic field is an important phenomenon that has a potential application in magnetic storage media like magneto-optical recording and magnetic sensing devices. Lanthanide manganites doped with alkaline earth metals like calcium or strontium having the formula $\text{La}_{1-x}\text{A}_x\text{MnO}_3$, (A = Ca, Sr) exhibit a

perovskite structure. Such oxides also exhibit a spectacular magnetoresistance effect and suppress the resistance in magnetic field of ~6 Tesla to ~100% at room temperature. While its utility is yet to be exploited commercially, at the fundamental level, the underlying cause of GMR effect has to be understood.

Among the hypotheses put forth so far by experts in this field, one hypothesis believes that the crucial cause of GMR is the so-called double-exchange (DE) phenomenon which involves the hopping of electrons between heterovalent Mn^{3+}/Mn^{4+} pairs in the lanthanide oxide. Additionally, a strong Jahn–Teller distortion associated with the octahedrally coordinated $Mn^{3+} : 3d^4$ experienced in these materials also contributes to GMR.

An interesting development is the discovery of the GMR effect in another manganese oxide ($Tl_2Mn_2O_7$) which exhibits an entirely different type structure (the 'pyrochlore structure'). A recent paper in *Science* by Subramanian *et al.* (1996, 273, 81) has established that the GMR effect caused by this oxide is due to neither of the two earlier effects noticed among the earlier oxides. This new oxide is actually a stoichiometric compound having no mixed valency that is characteristic of the Mn^{3+}/Mn^{4+} group. It has been postulated that magnetic ordering driven by superexchange and a strong spin-fluctuation scattering above the Curie temperature are the causes of GMR in this oxide. In addition, thallium(III) has also been implicated to have a role in GMR, as it tends to complicate the electronic structure by its own mixed valency (Tl^I/Tl^{III}). This role has already been well-established in thallium cuprate superconductors.

J. Gopalakrishnan

Once upon a (Jurassic) time . . .

Was the Archaeopteryx really the 'early bird'? For that matter, during the course of evolution, did crocodiles ever go vegetarian? Recently, old skeletons that have tumbled out from the lands of the Far east have provided several interesting answers to these queries. Avian fossils from

the Liaoning province in Northern China have thrown light on the existence of a new fossil bird, about the size of a pigeon, that is reverently referred to as *Confuciusornis sanctus* (Lian-Hai Hou *et al.*, *Nature*, 1995, 377, 616). Its external features bear the resemblance of both the modern birds (in the Cretaceous times) as well as the bird that existed during the earlier period (viz. the Archaeopteryx). These discoveries are considered to be very exciting in as much as they have questioned the existing views of Archaeopteryx ancestry to modern birds. Evidence now points out to a possibility of the existence of other side branches to the Avian tree. While the Archaeopteryx may also be one such branch, it had somehow met with a dead end. These findings lead to the obvious conclusion that if birds were already diverse in the Jurassic period, the still more primitive of the species must have taken to wings as early as the late Triassic—some 60 million years before Archaeopteryx even flapped its own, in the Jurassic skies.

Three decades ago, Chinese geologists surveying for petroleum in the Hui province of Central China stumbled upon a fossil of a strange animal that probably existed 120 million years ago. The fossil that found a home in Toronto museum was recently re-examined and has been identified as belonging to the crocodile family (Xiao-Chun Wu *et al.*, *Nature*, 1995, 376, 678). The reptile, called *Chimeraesuchus paradoxus*, showed a variation in its skeletal features to other crocodiles. The most striking difference was that unlike the sharp conical teeth characteristic of carnivorous crocodiles, this reptile had multicuspid molar teeth which strongly indicated that the latter was actually herbivorous. This was obviously the period of the 'green (r)evolution'!

A. V. Sankaran

Small is beautiful

One of the objectives in the study of materials today is the synthesis and design of matter at a nanometer scale. Patterning material at this scale is helpful in the manufacture of miniature electronic components. In 1856, Michael Faraday had observed that material properties are

strongly size-dependent and thus can actually be tuned to sensitivity.

Earlier approaches towards the preparation of coupled quantum dots included the co-colloids of cadmium selenide–zinc oxide and cadmium sulphide–silver iodide. Aggregates of gold could also be synthesized using small molecule cross-linking agents. While the properties of nanocrystals have been studied earlier using organic monolayers and crystallization, it was not known whether self-assembly methods could be employed to generate complex nanocrystals.

Molecules in biological systems are held together several types of bonds including the strong covalent force as well as the weaker hydrogen bonds. Due to the complex nature of recognition systems that exist in biological organisms, it becomes necessary for such bonds to be specific and precise. Can biological molecules be exploited in the design of nanostructures?

Paul A. Alivisatos and his colleagues at the University of California at Berkeley, USA have addressed this question in an elegant manner (as reported in *Nature*, 1996, 382, 609–611). Small stretches of DNA (oligonucleotides) were modified at their ends with sulphhydryl groups. These were then coupled with an excess of mono-maleimido-gold particles. Following this coupling, the oligo-gold conjugates were then combined with set amounts of complementary single-stranded oligos. The resulting double-stranded complexes were then purified and analysed both with biochemical methods as well as through direct observation using transmission electron microscopy.

Results demonstrate that the use of oligonucleotides in the synthesis of nanoparticles has great potential. For one thing, by altering the base composition of the oligonucleotide, it is possible to generate flexibility in the oligo structure. Due to the nature of bonds that exist in DNA, it is possible to reverse reaction using heat, unlike the situation that exists when organic synthetic methods are used. With the further improvement in the methodology like the use of shorter and more rigid linkers and the use of other ligands apart from gold, a wider range of physical phenomena can be investigated in nanostructure architecture. For the present, one can but admire the 'gold zari' made out of Nature's own exquisitely beautiful threads of DNA.