Template-Constrained Synthesis and Characterization of Nanomagnetic Materials

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The broad objective of this effort is to establish an interdisciplinary research and training team focussed on the directed synthesis of nanophase magnetic particulate materials whose magnetic properties are tailored by the size and composition of the particles, and by their assembly into mono- and multi-component two-dimensional ordered arrays. The broad goals of this program are to create new magnetic materials whose component constituents are magnetic clusters that can be tightly tailored in size and magnetic composition, and whose mesoscopic magnetic properties (individual cluster moment, anisotropy, etc.) can be independently varied over a broad range. Furthermore, through the use of an appropriate interstitial material, the assembly of these magnetic building blocks into ordered two-dimensional arrays would allow for tunable and externally controllable inter-particle interactions that modify the macroscopic material properties for future application as superior performance magnetic memory, sensors, and ultra-high speed device architectures. This synthesis and characterization program will elucidate correlations between physical and magnetic properties of the materials, and thus, lay a foundation for chemical design of magnetism in nano-materials.

We have utilized the well-defined protein cage architectures from viruses and ferritin iron storage proteins for the controlled synthesis of nanoscale inorganic materials. The protein cages act to constrain the size of inorganic materials and encapsulate them in the organic template. Our aims include the utilization of protein cages in highly monodisperse sizes ranging from 5 to 24 nm ID (8.5 to 28 nm O.D.) as mineralization templates for the preparation of highly uniform metal oxide particle cores; 2) the reduction of these oxides to yield the corresponding monodisperse metal particles. Mineralization has been demonstrated for the Fe and Co systems and reduction of the Fe systems has been achieved and should be extendable to other transition metal materials. The present work aims to build upon this foundation with two key objectives. First, we aim to expand the library of core compositions by introducing dopants and, ultimately forming alloys at the mineralization step. Second, we aim to create two-dimensional arrays of these particles and binary mixtures of different particles. Strategies for assembly will begin with self-assembly of the wild-type protein cages and be extended, through site-directed mutagenesis of the cages, to program the assembly and to fortify it with chemical crosslinks. As an additional means to tailor the inter-particle magnetic interactions, the use of chemical crosslinks with magnetic functionalities will be explored. The mesoscopic and macroscopic structural and magnetic properties will be extensively characterized through a battery of the electron microscopy, light-scattering, X-ray scattering, magnetic resonance, and magnetometry techniques.

The specific aims of the proposed research are:

1) **Control and variability of mesoscopic (particle) magnetic properties.** To synthesize and characterize mono-disperse magnetic nanoparticles in a library of sizes ranging from 5 to 24 nm by biomineralization within various protein cages. Mineral cores to be synthesized will include neat, doped, and alloyed metal oxides, which, upon reduction, will yield particles of the corresponding metals.
2) **Synthesis of single component 2D arrays.** To assemble these magnetic particles in two-dimensional arrays of micron size and characterize the physical structure and magnetic properties of these assemblies.

3) **Synthesis of multi-component 2D ordered arrays.** To assemble and characterize random and ordered two-dimensional arrays formed from binary mixtures of magnetically distinct nanoparticles.
4) **Control and variability of macroscopic magnetic properties.** Fine-tuning of magnetic properties of these assemblies by incorporation of chemical crosslinks and spin-coupling modulators that mediate and may allow for external control of the inter-particle magnetic interactions.

This research brings together a team of five scientists at Montana State University in three academic departments. Their areas of expertise spans virology, molecular biology, bioorganic and synthetic chemistry, physical and materials chemistry, spectroscopy, solid-state physics, and magnetism. It builds on some established interactions. In particular the collaborations of: Mark Young and Trevor Douglas in the core area of template-constrained synthesis of metal-oxide and metal particles: and Mary Cloninger and David Singel in spin-clustering on dendrimeric macromolecular templates. With the addition of MSU physics faculty member, Yves Idzerda, who has expertise in magnetism and experience in the characterization of magnetic systems, as PI of the team, we have the nucleus of our magnetic NIRT.

We have shown that the use of protein cage architectures can result in a high degree of control over the size, morphology, and composition in the synthesis of nanomaterials. We have used three protein cages as synthetic templates; the plant virus CCMV (Cowpea chlorotic mottle virus), mammalian ferritin, and the ferritin-like protein from *Listeria innocua*. Using these proteins, and genetic mutants therof, we have shown that we can synthesize nanomaterials such as Co_3O_4, Fe_3O_4 [2] in discrete sizes from 3 nm diameter to 20 nm in diameter depending on the specific protein cage template (Figure 1).

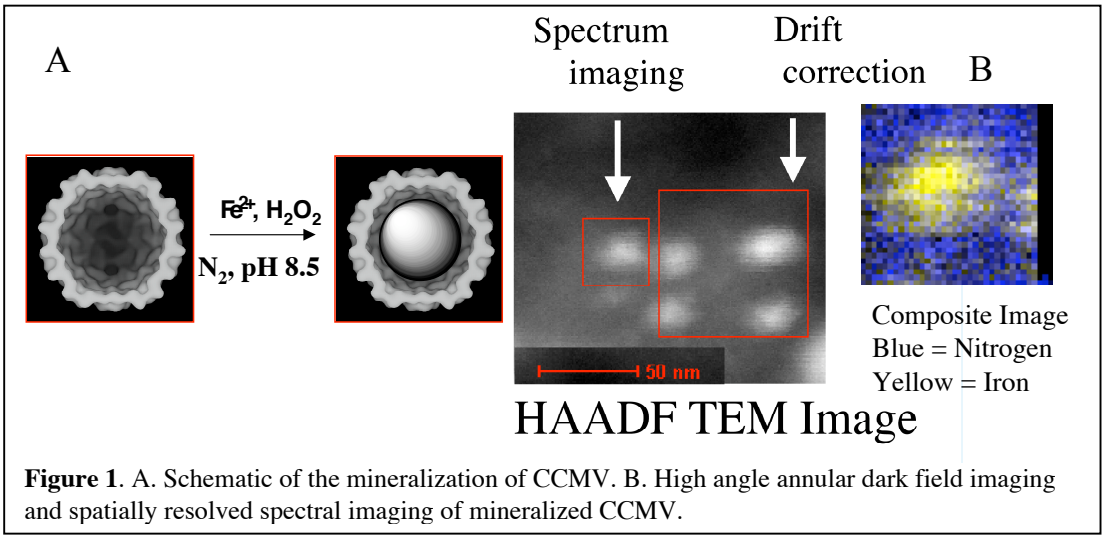

Figure 1. A. Schematic of the mineralization of CCMV. B. High angle annular dark field imaging and spatially resolved spectral imaging of mineralized CCMV.

In addition, we have shown that we can assemble these mineralized protein cages into 2-D arrays on solid substrates through introduction of reactive functional groups on the exterior surface of the cages. To this end we have chemically broken the symmetry of these high symmetry particles [3] to achieve uni-directional attachment to Au surfaces (Figure 2 and 3). Other protein cages are being explored, as templates for synthesis and patterning,for their unusual thermal and chemical stability [4].

We have initiated a team-taught graduate course on nanomaterials, in which all members of the

research team participate. This course has drawn on the expertise of faculty from across the campus, from 4 different departments. Graduate students (12) from 4 departments participated in the first teaching of this class.

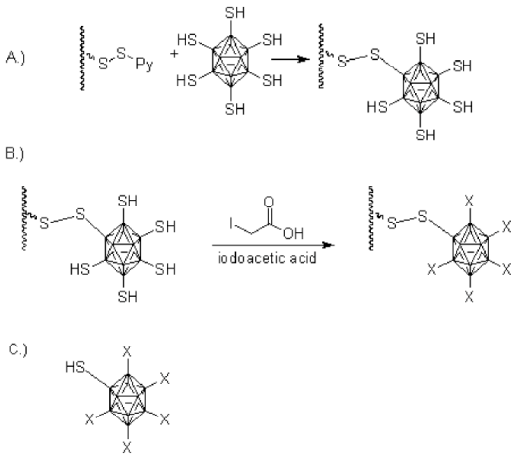

Figure 2. Symmetry breaking of the A163C viral cage: (A) reaction scheme for the thiol binding of the viral cage to an activated resin; (B) passivation of unbound cysteine residues with IAA; (C) removal of the symmetry-broken A163C by reduction.

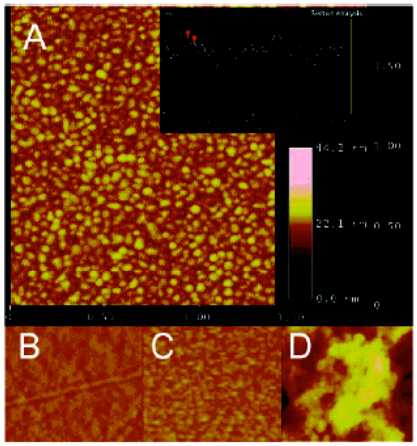

Figure 3. Tapping mode AFM imaging on CCMV Au substrate: (A) symmetry-broken A163C with distance and height profile (inset); (B) wild-type CCMV with no exposed thiols; (C) A163C treated with IAA to passivate all exposed thiols; (D) untreated A163C with surface-exposed thiols. All scans shown are 2 μm in length.

The research and educational effort for this NIRT program has developed as a focal point for interest in interdisciplinary research and teaching across campus.

References

[1] For further information about this project link to **http//:www.chemistry.montana.edu/nano** or email **tdouglas@chemistry.montana.edu myoung@montana.edu idzerda@physics.montana.edu**

[2] M.A.Allen, D. Willits, M. Young, T. Douglas "Constrained Synthesis of Cobalt Oxide Nano-Materials In the 12-subunit Protein Cage From *Listeria innocua*" *Inorganic Chemistry* (2003) 42, 6300-6305.

[3] M. T. Klem, D. A. Willits, M. J. Young, and T. Douglas "2-D Array Formation of Genetically Engineered Viral Cages on Au Surfaces and Imaging by Atomic Force Microscopy " *JACS* (2003) 125, 1056-1057

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