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1) Solution Phase Routes to Transition Metal Doped TiO2
2) Scott Chambers' microscopy shows ferromagnetic Co-enriched TiO2 islands on his thin film samples. The challenge is to use solution phase routes is to make the islands a separate entity.
3) With solution phase routes, wet chemical control can help predetermine oxidation states, use precursors to do novel things, make different structures for long term goals, etc.
4) Different length scales of interest
5) Above around 200 nm, colloidal particles will sediment out.   There are 2 pathways to synthesis. We choose the pathway to internal doped with surface bound, and then use chemical tricks to get only internally bound Co, resulting in a true DMS.
6) For solution phase routes, lyothermal route eliminates Ti_OH groups, providing better fluorescence. The catalyzed sol-gel route is popular, and uses excess water. For inverse micellular sol-gel, a small, limited amount of water is used.
7) For the lyothermal route, the ligands are switched on the Ti precursors. This is not used for doping since Co is mobile in TiO2, and this could cause segregation.
8) The partial charge model is used to rationalize why metals behave in certain ways. For hydrolysis, water is a nucleophile. Then M-OH groups combine with other M-OH groups in condensation step. But how do we incorporate Co? Literature shows Si(Oet)4 and Ti(Oet)4 does not result in a mixture, but they segregate since there are different hydrolysis and condensation rates. We control the water content to control the rate of the reaction.
9) In an inverted micelle, water is on the inside. AOT provides a well characterized micelle. With low mole water/moles surfactant ratio, there is no free, loosely bound water to do chemistry. Co is solvated, then Ti is intercolated into the micelle. The slow reaction forces a reaction with Co.
10) Preparation begins with an air-free transfer of the Ti precursor to the Co micelle, and the color changes. If this is exposed to air, color changes to blue. This is due to change in Co coordination. The autoclave then provides heat and pressure treatment. The initial polymeric species after transfer of Ti is amorphous, but the phase transition to anatase (10 atm) is forced at a lower temperature with pressure in the autoclave.
11) The octahedral Co transition of the Co precursor is weaker than tetrahedral Co since tetrahedral transition is more allowed. Can use this to help determine geometry. The spectrum of Scott Chambers' thin film of Co:TiO2 (dashed line) matches that of solution route synthesis (blue line).
12) The Co surface species can be removed with TOPO. TOPO is intercolated, and since TOPO is a stronger ligand than AOT, TOPO scrubs off surface Co. We are unsure whether this pulls Co out of the nanocrystal.
13) A piece of printed paper is behind the cuvettes. The Co:TiO2 color is orangish. The band edge is visible, with possibly a charge transfer, and weak d-d transition in the absorption spectrum of Co:TiO2.
14) Sherrer widths of powder diffraction fit TEM data. Possibly 2 nanocrystals fused together in TEM, so maybe a broad size distribution resulted, typical of micelles, but of the right size.
15) (Summary of Part I)

16) The ligand field bands of Co:TiO2 are in the inset. The bottom spectra shows MCD for 0-6 Tesla in 0.5 T increments. 2 regions on right include d-d transitions and charge transfer transitions. There is saturation with increasing field as seen from MCD intensity at 2 different energies (shown on right). This fits roughly to a S=3/2, not ½, based on orbital calculations. Signal at higher energy (>18,000 cm^{-1}) fits 6 coordinate hexagonal. Lower E feature shows sharp bands (d-d) which indicates crystallinity. This is probably 4-5 coordinate, possibly interstitial, so indicating there are 2 different species. Don't see same ratio in every synthesis. The higher E transition is assigned as 6 coord, and this E doesn't change much with coordination. There are about 50-100 Co per 5 nm particle.

17) Past experiments with Cu^{+}, Cu^{2+} have shown interstitial sites are 4 coordinate in TiO2.

18) There are long axial bonds in one interstitial site. Co^{2+}, Cu^{2+} have similar radii, so may behave similar.

19) 2nd interstitial site in TiO2.

20) This shows the change from octahedral geometry to D_{2d} under rhombic distortion.

21) The Co-O bond is shown to be longer than Ti-O. C.N is 5.1 +/- 0.3. This indicates there is an oxygen vacancy next to Co. The film from Scott Chambers is similar to the nanoparticle film, and different from Co metal. The Co edge data and Ti edge data are well behaved. A question was asked on whether equatorial vs axial or substitutional vs interstitial can be distinguished. EXAFS may not be able to observe the longer axial bond, and the equatorial bond doesn't change much. EPR shows high spin behavior.

22) Different length scales for magnetism studies.

23) In the bottom right, magnetism of capped colloidal powder is shown. The isolated Co:TiO2 nanocrystals are paramagnetic. The oxygen that we kick out isn't giving charge carriers, and the Co can't communicate through the itinerant electrons. Magnetic data fits S=3/2. Next step, ligands are stripped off to try a different length scale.

24) For the meso scale, the nanopaticles are precipitated without ligands. Powder diffraction shows the sizes.

25) Without annealing (after the autoclave), there is a small amount of ferromagnetism present (0.001 Bohr magnetons). Heating makes larger particles, increases the electronic coupling between particles, resulting in saturation magnetization of 0.02 Bohr magnetons. The particles can be sintered together. Both graphs are of same films, different scale.

26) The colloids were spin-coated to produce a transparent film for the microscale. A larger degree of ferro (top graph- 0.3 Bohr magnetons) results, similar to other thin film results. A substrate dependence was found- this works best on polycrystalline sapphire. There is no evidence for Co metal. A comment suggested that sapphire changes the interface, (in unpredictable ways). Annealing at 320 C removes 80-90% of the ligands. The thin film has insulative conductivity.

27) Summary