Nanoparticle Strain by QED induced electron loss?

Stiffening observed in iron nanoparticles caused by oxygen diffusion is superseded by the triaxial stress state produced by Coulomb repulsion of charged iron atoms in the oxide film upon the loss of electrons by the QED induced photoelectric effect

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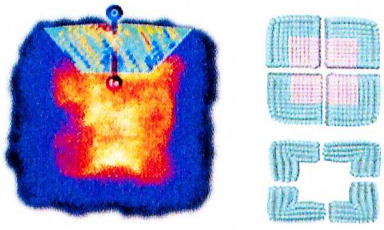
Introduction

NPs may contain unusual forms of structural disorder that significantly modify material properties [1] and cannot be considered as small pieces of macroscopic bulk material, e.g., zinc-sulfide NPs have higher Einstein vibration frequencies than in bulk zinc sulfide, implying structural stiffening that cannot be explained by the observed 1% radial compression. NP stands for nanoparticle. It is generally thought NPs are placed under internal strain by the irregularity of the surface, but the mechanism by which the strain is induced is not fully understood.

Similarly, research [2] reported in *Nature Materials* showed oxidation of iron is accompanied by large strains proceeding many orders of magnitude faster in iron NPs than in micron sized iron particles. Strain induced in the oxidation of cubical iron NPs was measured at the atomic level with unprecedented resolution using scanning transmission electron microscopy, the image of the reconstructed strain shown in the thumbnail - the oxide film blue and the iron in red and yellow. Oxygen is shown diffusing through the oxide film to slowly oxidize the iron and induce the strain. Initially cubical, the NPs became spherical after 2 years. The large strain in the NPs was thought caused by competing relaxations from the cubical surface, but the source of the strain itself was not identified. See https://www.york.ac.uk/news-and-events/news/2013/research...



2D Cubical iron NP strained by oxide film - Experiment and MD simulations

Problem

The rapid oxidation of iron NPs is not consistent with the slow diffusion of oxygen required for complete oxidation. Another mechanism explains the rapid oxidation of iron NPs.

Proposal

Oxidation of iron NPs need not require diffusion of oxygen through the oxide layer. Oxidation may be extended to any chemical reaction in which electrons are removed from a reactant. In this regard, the photoelectric effect by QED induced EM radiation is proposed as the mechanism for the prompt oxidation of the iron NPs by the removal of electrons. QED stands quantum electrodynamics and EM for electromagnetic. EM radiation induced by QED is a consequence of QM that precludes atoms in NPs from having the heat capacity to conserve the exothermic heat of oxide film formation produced in oxidation by an increase in temperature. QM stands for quantum mechanics.

Instead, the cubical iron NPs conserve the heat of oxidation by QED inducing the creation of EM radiation standing between cubical surfaces having half-wavelength $\lambda/2 = nd$, where n and d are the respective NP refractive index and characteristic dimension, the latter taken as the distance between cubical surfaces. By the Planck law, the EM confinement to produce short wavelength EM confinement necessary for a vanishing heat capacity is a natural consequence of the high surface-to-volume ratios of nanostructures, i.e., almost all of the heat of oxidation in forming surface films in NPs is confined to their surface.

The QED induced EM radiation in NPs at nanoscale wavelengths is more than sufficient to charge the atoms, e.g., 10 nm cubical iron NPs having a refractive index in the UV of about 1.5 convert the heat of formation of iron-oxide to 40 eV EM radiation having a wavelength of 30 nm. Since the source of the EM radiation is the heat of formation absorbed in the NP surface, and since the EM radiation once formed requires the EM confinement to vanish, the EM radiation may escape the NP unless absorbed by atoms

inside the NP. See diverse QED applications at http://www.nanoqed.org, 2010-2016.

MD Simulations

Classical MD that assumes the atom always has heat capacity was modified to simulate the observed high strain found in iron NP oxidation. The MD model is a quarter of a 2D slice taken through a 5 nm cubical iron NP including the oxide film comprising 169 atoms as shown in the thumbnail. MD simulations of Coulomb repulsion between charged iron atoms in the oxide film produce severe compressive distortion of the iron NP as exaggerated by the deformation of the oxide film in the absence of the iron NP. Only the oxide film is assumed to produce Coulomb repulsion between iron atoms, i.e., the oxide film with a low dielectric constant acts as an electret that maintains the iron charge over long periods of time while the atoms in the iron NP do not maintain charge because of their infinite dielectric constant. The Lennard-Jones repulsion for iron atoms in the oxide film was found insignificant to balance Coulomb repulsion, the MD deformations solutions of which illustrated above never reached equilibrium.

Summary and Conclusions

1. The structural stiffening observed in the oxidation of iron NPs is a consequence of the QED induced triaxial stress state produced by the Coulomb repulsion between atoms in the oxide film having a low dielectric constant. NP stiffening by compressive strain is relatively insignificant. Iron atoms not in the oxide film do not undergo Coulomb repulsion as the electrostatic force vanishes in the very high dielectric constants of metals.

2. Similar to the oxidation of iron NPs, QED induces stiffening of zinc NPs because of the Coulomb repulsion between atoms in the surrounding sulfide electret even with strong surface chemical passivation. Zinc atoms not in the sulfide film do not undergo Coulomb repulsion.

3. NPs in general, and iron and zinc NPs in particular, conserve heats of formation of iron-oxide and zinc-sulfide films by creating charge instead of increasing in temperature. The films as electrets maintain the QED induced charge over extended periods of time.

References

[1] B. Gilbert, et al., "Nanoparticles: Strained and Stiff," Science, 305, 651-4, 2004.
[2] A. Pratt, et al.,"Enhanced Oxidation of Nanoparticles through Strain-Mediated Ionic Transport," Nature Materials, November, 2013.

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