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# Electron microscopy of organic–inorganic interfaces: Advantages of low voltage

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ABSTRACT

Low voltage electron microscopy has been applied to many types of materials in the last several decades with great success. The extremely strong interaction of the low voltage electrons with the sample gives high scattering contrast, however it can also result in significant damage of the specimen. Irreparable damage to several types of organic materials results from their large cross section for ionization, or radiolysis, at low voltage. Knock-on damage, which is significant at high voltages for many ceramics, semiconductors, minerals and ordered carbonaceous material such as graphene, is often reduced at low voltages. For organics which damage by radiolysis, measured beam stability increases at higher voltages, but the mass–thickness contrast is also reduced. An increased defocus can be used to generate phase contrast at higher voltages, although it comes at the expense of resolution, as the first zero in the contrast transfer function moves toward larger length scales with increasing defocus. Several examples of low and high voltage (5 kV up to 300 kV) experimental TEM images of organic–inorganic interfaces are used to demonstrate these phenomena.

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## 1. Introduction and motivation

Interfaces in materials are of significant interest because new properties arise there which do not occur in the respective bulk counterparts. Interfacial properties strongly influence material behavior in thin films, self-assembled monolayers, brushes, core-shell particles, nanocomposites, and suspensions. Organic–inorganic hybrid nanoparticles are of significant interest due to their widespread application in the fields of medicine, chemical sensing, catalysis, and energy, among others. However, due to their small size, low chemical contrast, heterogeneity, and often complex shapes, organic–inorganic materials and their interfaces can be difficult to characterize. As such, advanced characterization techniques are required to probe interfaces with enhanced resolution, fidelity and information content. Methods such as X-ray [1] and neutron reflectivity [2], NMR [3], XPS [4], TOF-SIMS [5], and Brioulln scattering [6] can characterize interfaces with varying degrees of chemical and spatial resolution, however none offer the direct ability to image structures at sub-nm or even sub-Å resolution, as is the case in transmission electron microscopy (TEM). When coupled with analytical techniques such as Electron Energy Loss Spectroscopy (EELS), Energy Filtered TEM (EF-TEM) and X-ray Energy Dispersive Sprectroscopy (XEDS), TEM becomes an extremely powerful imaging and spectroscopic tool. The main challenges for organic–inorganic interfaces are twofold: (1) limiting beam damage, and (2) generating sufficient and interpretable contrast between materials.

Mechanisms for beam damage in materials have recently been reviewed [7] and it has been demonstrated that if the primary damage mechanism is knock-on damage, then reducing the electron energy below a certain threshold level can have a significant reduction in beam damage. It is often assumed by the inorganic materials community that this relationship holds for all materials which undergo beam damage processes, however it has been shown that for organic materials in which radiolysis is the primary damage mechanism, the reverse is true. As the electron beam energy is reduced, the apparent damage increases. This is due to the significant increase in inelastic cross section at low kV, as demonstrated in quantitative calculations and experimental measurements of the cross section for carbon K-shell ionization [8,9].

In TEM, mass–thickness contrast increases with decreasing electron accelerating voltage, and therefore LVEM is useful for characterization of low atomic number materials such as biological and polymeric materials which typically have small local differences in density. Low voltage electron microscopy has shown increased contrast in inorganics [10,11], organics [9], and several ordered forms of carbon such as nanotubes and graphene [12]. Low dose high resolution electron microscopy has been applied to several technologically relevant functional organic materials for applications such as energy harvesting [13,14], field effect

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transistors [15–17], optoelectronics [18], and field emitters [19]. For the techniques to be applied to organic–inorganic materials, which will be critical for development and insertion of these materials into applications, further research is necessary to build a deep understanding of the effects of voltage and dose on the ability to form images and gather information from organic–inorganic interfaces. Herein, the increase in contrast with decreasing accelerating voltage is quantified for organic–inorganic interfaces. Increased phase contrast can be generated at high accelerating voltage by defocusing the objective lens, however significant resolution is lost in doing so. The analysis presented herein experimentally quantifies how much contrast is generated, and in turn how much resolution is lost, as defocus is increased. Beam damage and how it relates to the dependence of contrast on electron energy is also examined.

## 2. Experimental

### 2.1. Instrumentation

Two different electron microscopes were used to generate the data shown. The first is a Delong LVEM5 TEM/SEM/STEM operating in transmission electron microscopy mode at a 5 kV. The LVEM5 uses a Schottky filed emission gun and permanent magnets to form the image on a YAG screen, which is then further magnified by a conventional optical microscope. The design allows for considerable miniaturization and the instrument sits on a table top. The spherical aberration coefficient ($C_s$) of the LVEM5 is 0.64 mm. The second instrument is a $C_s$-corrected FEI Titan (image corrector) operating at accelerating voltages of 80 kV and 300 kV with $C_s = 5\ \mu m$ in both cases. Images were collected on Gatan SC1000 2k by 2k CCD.

### 2.2. Materials

M13 bacteriophage-Montmorillonite (M13-MMT) was produced as previously described [20], and deposited on 10 nm amorphous carbon support films on 1000 mesh Cu grids. Polyacrylic acid (PAA)-Au–Ag nanostructures were synthesized as previously described [21], and deposited over holes on a holey carbon films so that freestanding regions could be imaged. Polystyrene (PS)-functionalized $TiO_2$ nanoparticles were synthesized using a grafting-to approach as previously described, [22] self assembled into a free standing film imaged near an edge of the film. PS-functionalized $SiO_2$ particles were synthesized using a grafting-from approach as previously described [23], and deposited on 10 nm amorphous carbon films.

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## 3. Results and discussion

### 3.1. Imaging of organic–inorganic interfaces

Direct imaging of organic–inorganic interfaces is becoming ever more critical as new hybrid materials, architectures and devices rely on assemblies of disparate and traditionally incompatible materials. Imaging these interfaces is difficult in many cases, due primarily to challenges in forming sufficient image contrast as well as beam damage of one or more of the components. Other challenges, such as the 2D–3D projection problem, point to the need of additional models for data interpretation. For example, because the projection of the spherical core goes to zero thickness at the edge, the interface between the core and the shell is often just a just an indiscriminate feature on a sloped background, often

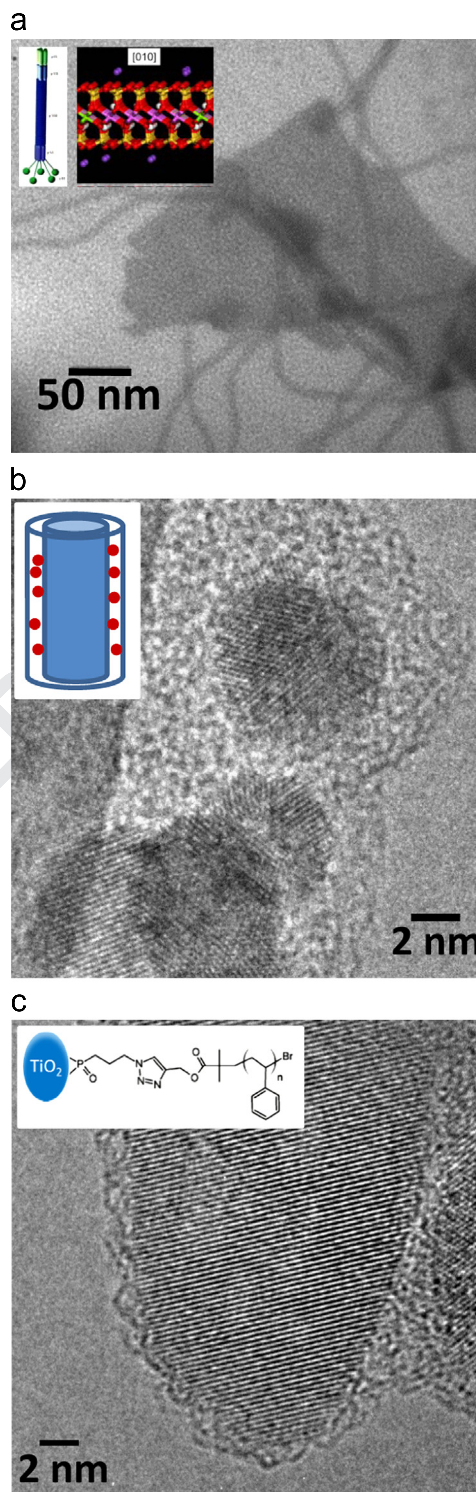


**Fig. 1.** (a) LVEM image taken at 5 kV of genetically engineered bacteriophage binding to a single 1 nm thick $Na^{+}$ montmorillonite layer. (b) Au nanoparticle in a polyacrylic acid shell on a Ag nanowire. 300 kV accelerating voltage. (c) Polystyrene functionalized $TiO_2$ nanoparticle taken at 300 kV. All images have schematics of the material inset.

buried in the noise. Fig. 1 depicts some of the successes and points to some challenges in imaging these materials and interfaces.

For direct imaging of organic–inorganic interfaces between crystalline nanoparticles and amorphous polymers, the interfacial region can often be visualized using phase contrast High Resolution Electron Microscopy (HREM). Fig. 1b is a 300 kV HREM image

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