Supporting Online Material for

Graphitic Tribological Layers in Metal-on-Metal Hip Replacements

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Materials and Methods

Materials

A total of seven high-carbon CoCrMo retrieved hip resurfacings were investigated and the TEM results are from three of them. The first sample (ASR, 42 mm in diameter, as-cast alloy made by DePuy Orthopaedics) was removed after 604 day's service in a patient (BMI=25.1); the second (ASR, 48 mm in diameter, wrought alloy made by Depuy Orthopaedic) was removed after 350 day's service (BMI=28.7); the patient's clinical data of the third retrieval (Recap, 46 mm in diameter, as-cast alloy made by Biomet Orthopaedics) were not disclosed to us. They were removed due to loosening of the acebabular component and did not show excessive wear. The replacements were rinsed to remove blood and placed in 10% formalin for sterilization and storage. Note that the rinsing and formalin will remove weakly-bound proteins and other materials at the surface (verified by control experiments), not the strongly-bound tribological layer. The specimens were then sectioned using a precision cut-off-machine (Accutom-5, Struers) cooled by distilled water. During all handling, care was taken in order not to touch the bearing surface. Specimen sections were cleaned using ultrasound in methanol before inspection or TEM specimen preparation.

The other four retrievals were made by DePuy Orthopaedics and were examined using non-destructive Raman spectroscopy only. The information for the retrievals is: the fourth sample was made of cast alloy, the patient was 48 years old at implantation and the in-situ time was 41 months; the fifth sample was made of wrought alloy, the patient was 49 years old at implantation and the in-situ time was 12 months; the sixth sample was made of cast alloy, the patient was 65 years old at implantation and the in-situ time was 46 months; the seventh sample was made of wrought alloy, the patient was 53 years old at implantation and the in-situ time was 79 months. The replacements were rinsed to remove blood and placed in 10% formalin for sterilization and storage.

TEM specimen preparation

The tribological layer was scrapped off using a tungsten probe in a FIB from both head and cup components. The use of electron beam and ion beam was kept minimal. The thin film was subsequently transferred to an Ominiprobe TEM grid. For the control experiments, bovine calf serum (GIBCO) was dried on a CoCrMo substrate and TEM specimens were produced using the same procedure in the FIB. In addition, serum was dried directly on copper TEM grids (#300 mesh) or silicon membranes.

EELS

Samples were analyzed using a Gatan Imaging Filter (Gatan Tridiem) in a JEOL 2100F at 200kV. All the data shown is for low dose conditions. The dose rate was calibrated using information from the vendor by using the drift tube of the camera. The drift tube is electrically isolated when the prism is shut off and can be used as a Faraday cage. The element molar fractions were determined by comparing the peak intensity (*I*) and inelastic scattering cross section (σ) by

$$\frac{N_A}{N_B} = \frac{I_A}{I_B} \cdot \frac{\sigma_B}{\sigma_A}$$

where the cross section was calculated using a Hartree-Slater model *(25)* implemented in the DigitalMicrograph software. The EELS spectra were calibrated using HOPG and amorphous carbon (Ted Pella, lacey carbon). The sp^2 fraction (x) in the tribological layer was determined by comparing the ratio of the π^* and σ^* peak intensity with that of HOPG using the following equation:

$$\frac{I_\pi / I_\sigma}{(I_\pi / I_\sigma)_{graphite}} = \frac{3x}{4-x}$$

HREM

Imaging was performed in a JEOL 2100F at 200 kV. The total dose was high, but from the EELS data we know that the effects of the electron beam on the graphitic material was minor.

Raman

Raman spectra from the pole and side areas of both the head and cup components from the first retrieval used for the TEM studies as well as from other retrievals and simulator tests were obtained using an Acton TriVista CRS Confocal Raman system with excitation radiation of an Ar-Kr 514.5 nm gas laser at ~10 mW. Spectra were recorded in the range of 1100-1900 cm^{-1}. The typical collection time was 30s and the results reported were the accumulation of 10-30 measurements. The graphitic domain size *(29)*, L_a, was calculated using the formula *(30)*:

$$\frac{I_D}{I_G} = \frac{C}{L_a}$$

where the constant C=4.4 nm for a 514.5 nm laser beam. The ratio of D and G line intensity, obtained by fitting the curves shown in the body of the text, was 0.98. A Nanophoton RAMAN-11 with a 532 nm laser beam was used for the Raman imaging.

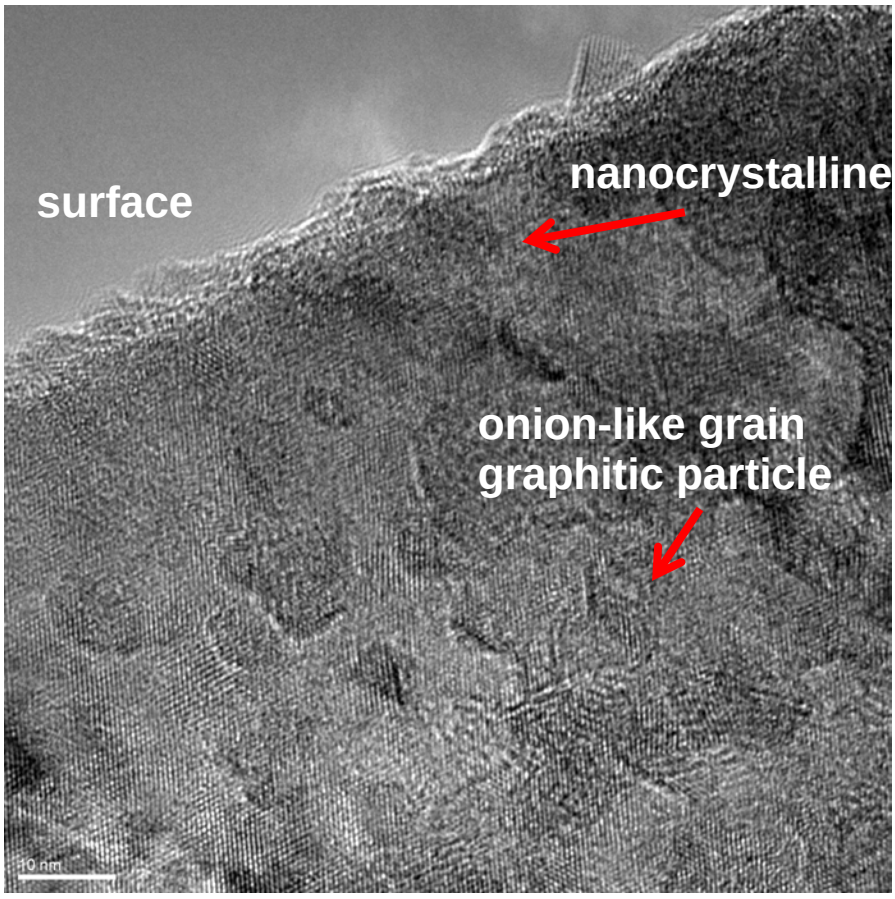

Fig. S1
HREM image of surface of a retrieval prepared using conventional methods showing nanograins and a graphitic particle. The graphitic material is suggestive, but not definitive because of the possibility of artifacts from the sample preparation.

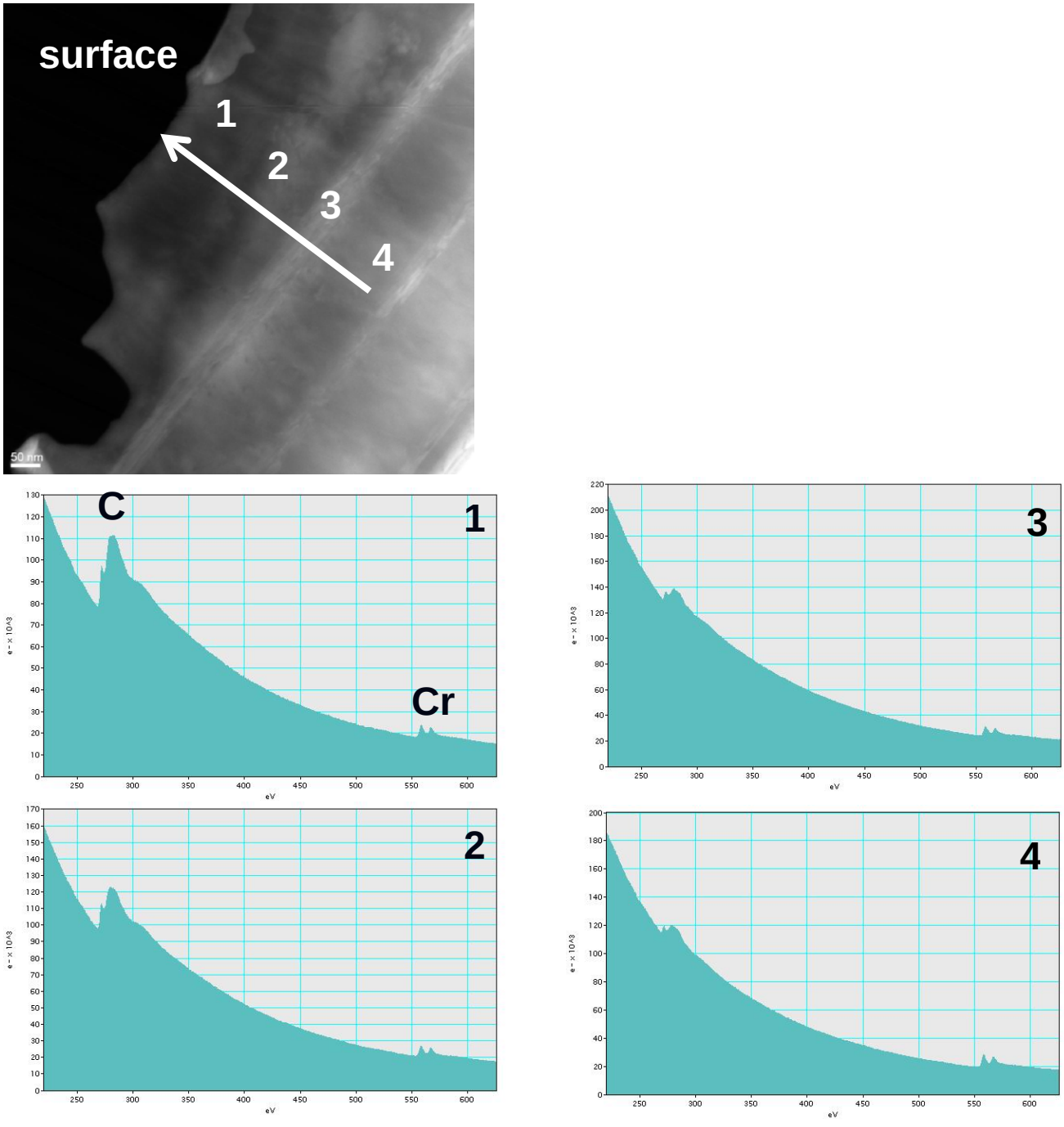

Fig. S2
EELS spectra taken from a conventional TEM sample made from retrieval, for the four regions 1-4 as marked on the image. The implant has a higher carbon concentration at the surface. The EELS edge at 285 eV corresponds to a π* pre-edge peak suggesting that graphitic material is present. Similar to the HREM data of fig. S1, this result is suggestive but not definitive.

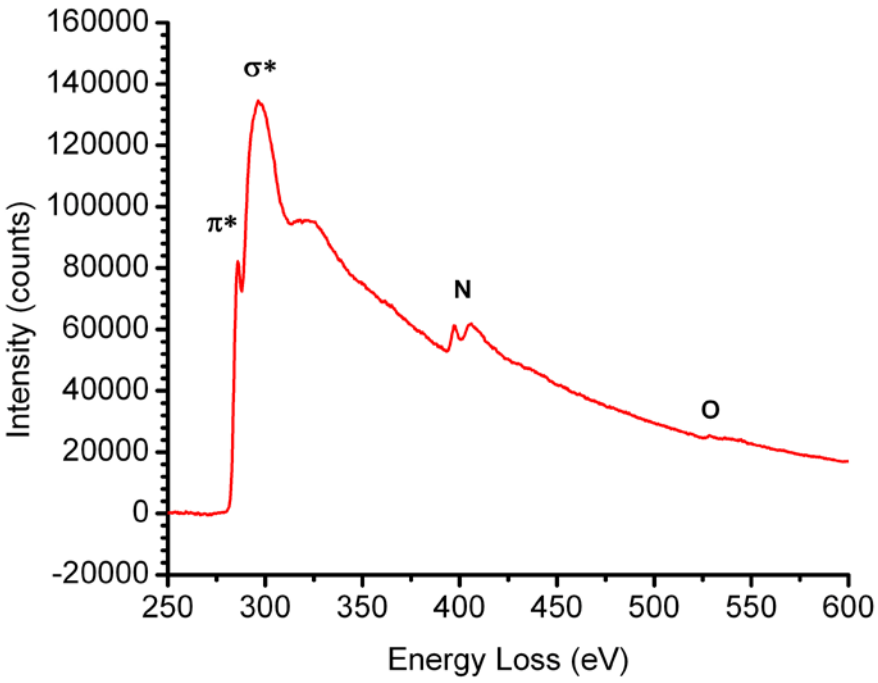

Fig. S3
EELS spectrum of dried bovine serum showing a π* peak with a dose of 5 x 10^8 electrons/ $Å^2$. Note the presence of strong nitrogen and oxygen peaks, different from what is found for the tribological layer.

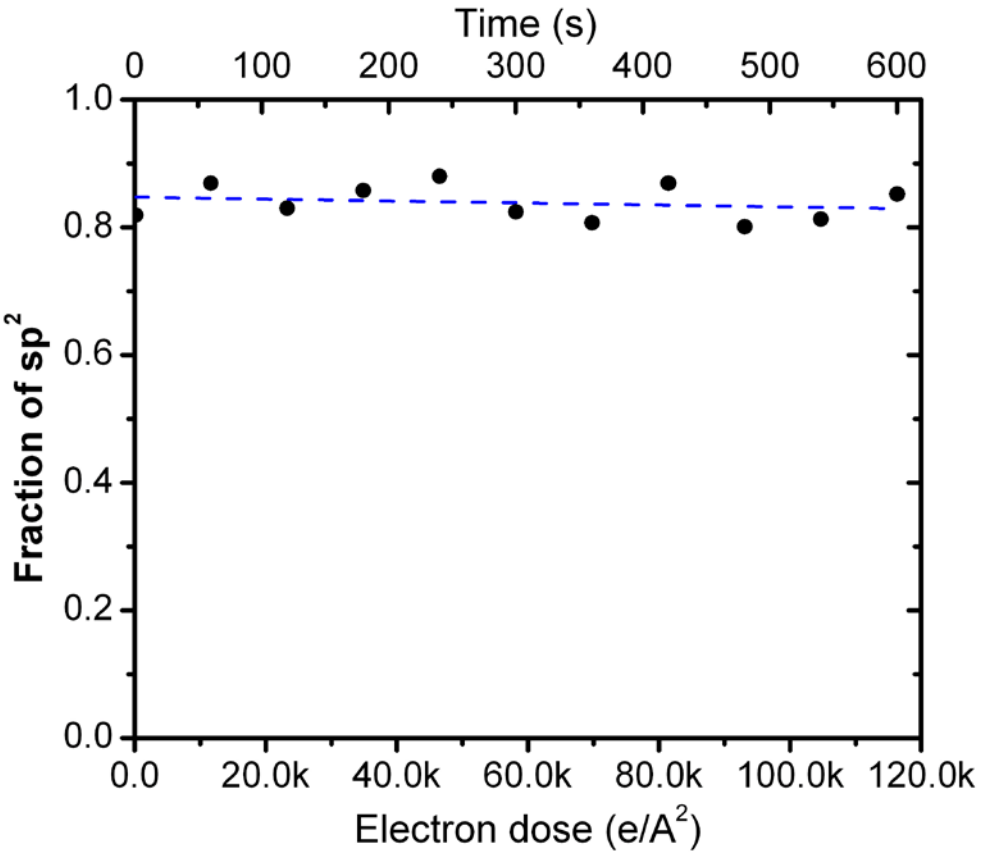

Fig. S4
Sp^2 fraction of the tribological film as a function of electron dose. No discernible change was observed.

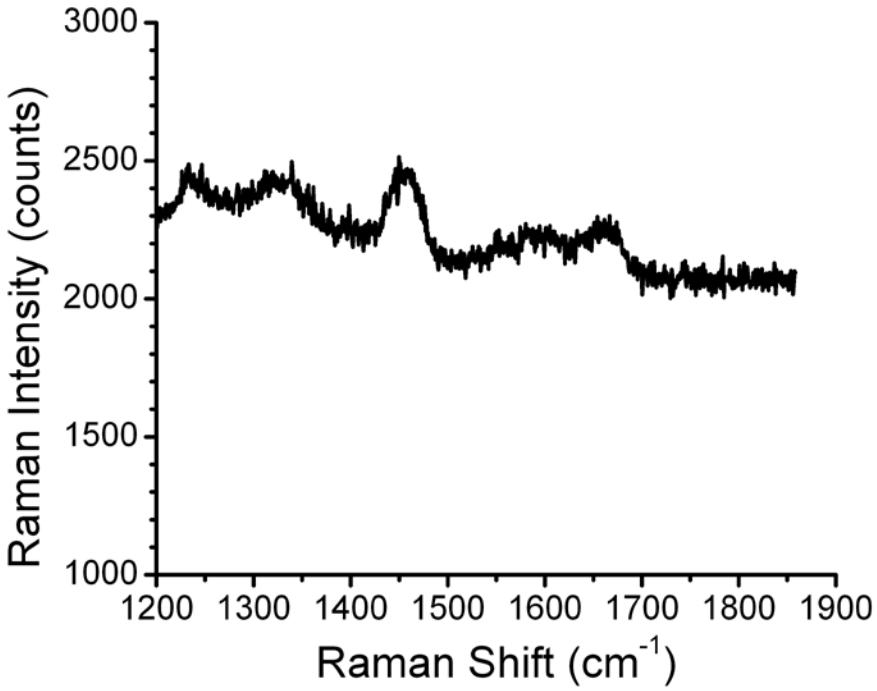

Fig. S5
Raman spectrum of dried bovine calf serum on a CoCrMo substrate. The G and D lines are absent.

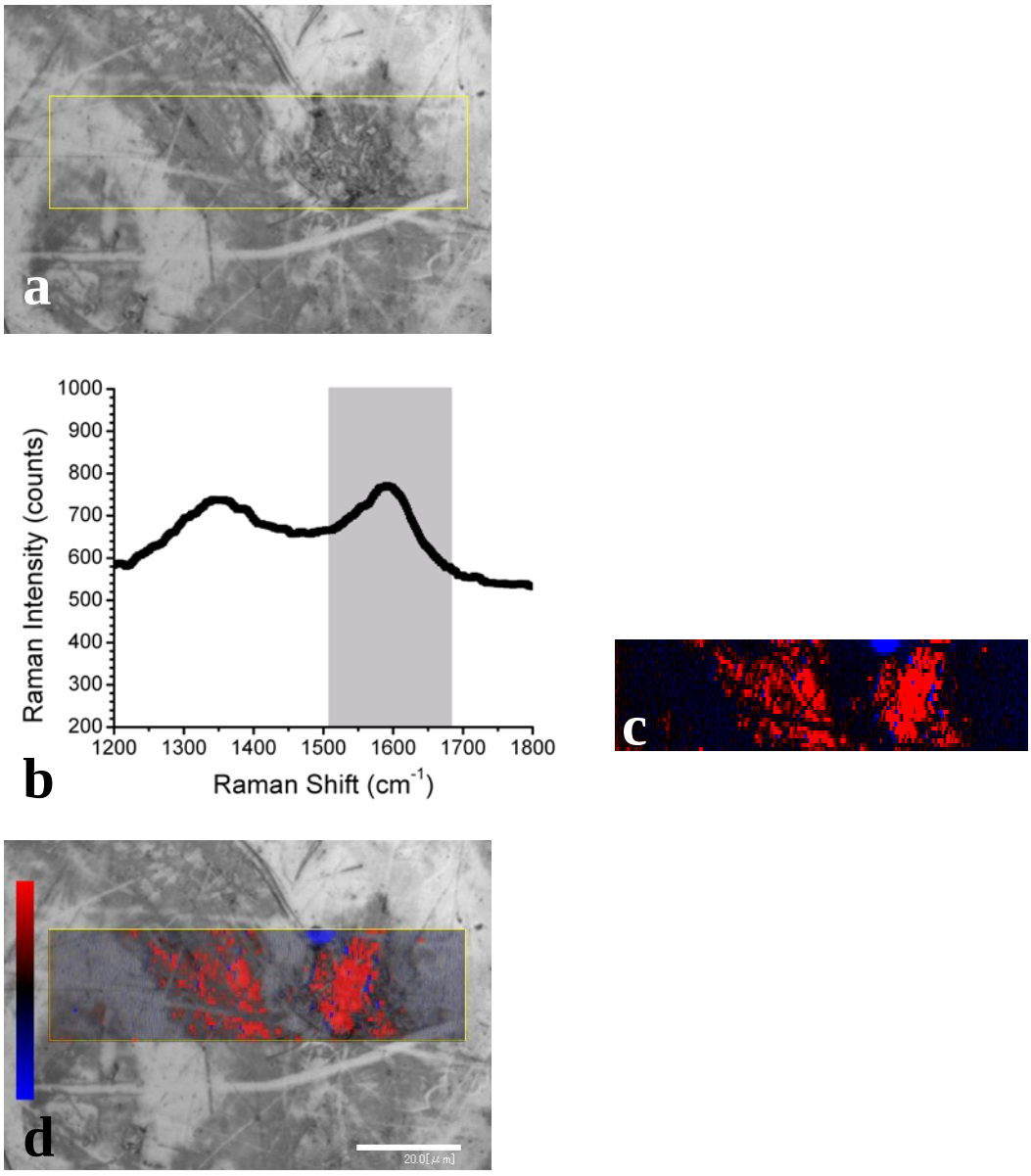

Fig. S6
Raman imaging of the first retrieved MoM hip implant using a Nanophoton RAMAN-11. (a) The optical image of the surface. (b) Raman spectra were collected from each pixel. (c) Filtered image using the carbon G band. (d) Superimposed image showing the distribution of graphitic carbon, which matches the optical image.