

Supplementary information

Preparation of Ti, Ti/TiC or Ti/TiN based hollow fibres with extremely low electrical resistivity

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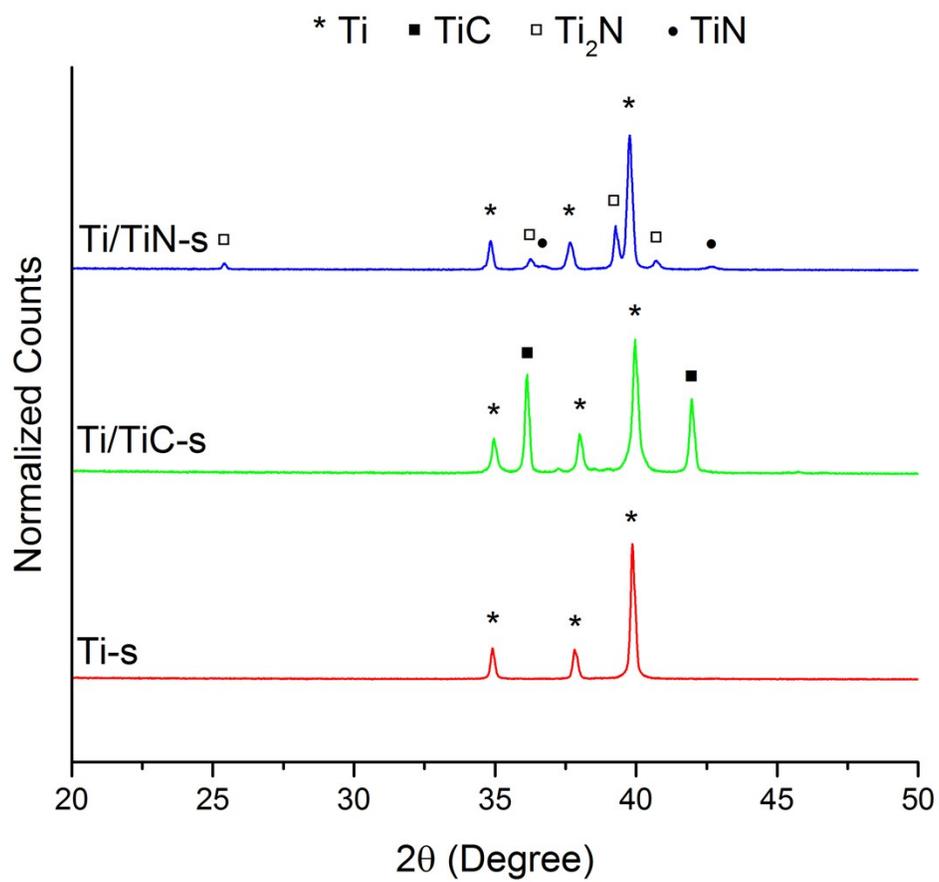


Figure S1. XRD of Ti-s, Ti/TiC-s and Ti/TiN-s

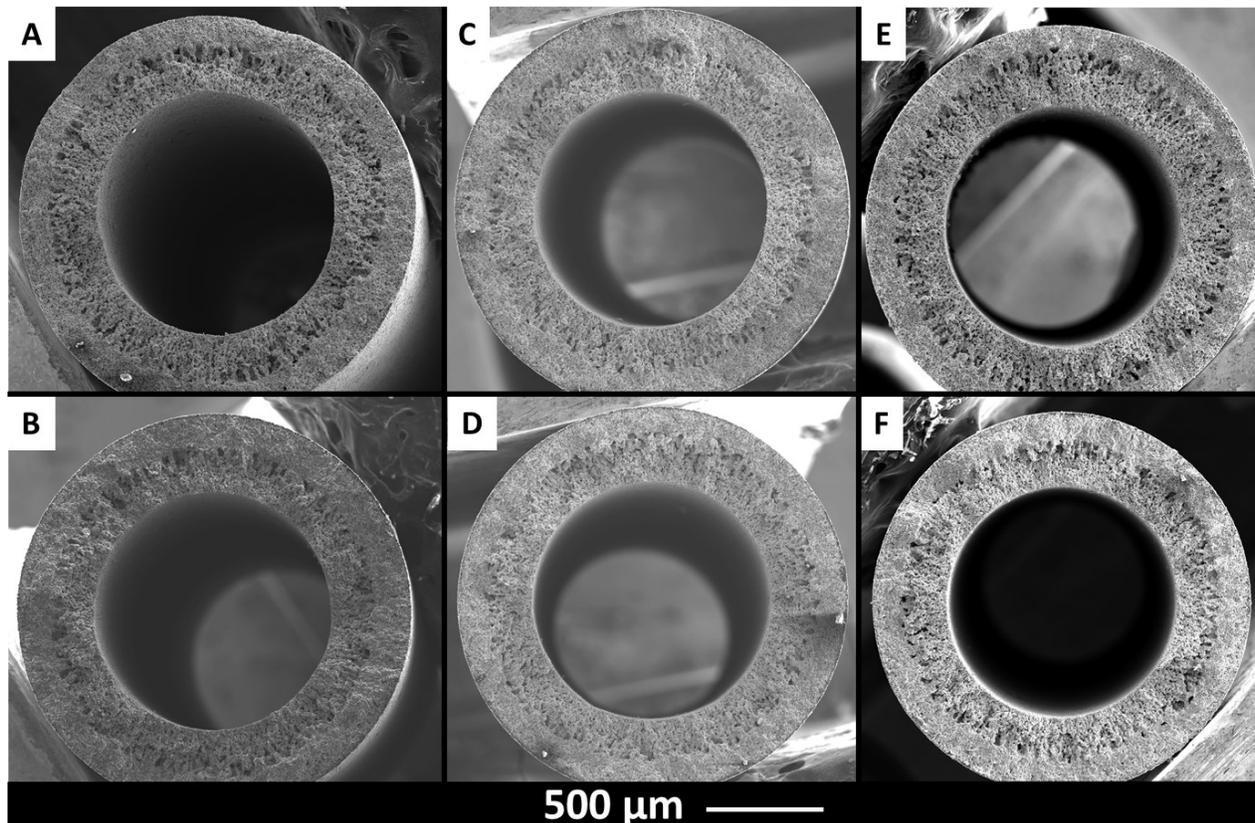


Figure S2. Cross-sectional SEM images of (A) Ti, (B) Ti-s, (C) Ti/TiC, (D) Ti/TiC-s, (E) Ti/TiN, (F)Ti/TiN-s.

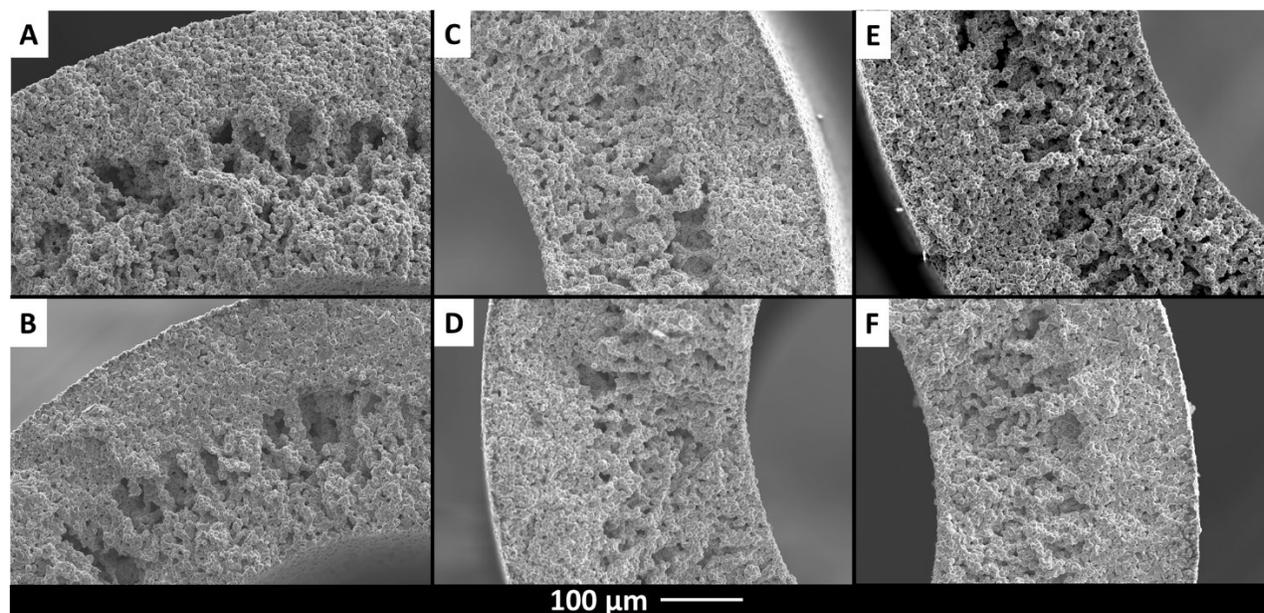


Figure S3. Cross-sectional SEM images of (A) Ti, (B) Ti-s, (C) Ti/TiC, (D) Ti/TiC-s, (E) Ti/TiN, (F)Ti/TiN-s at higher magnification.

XPS Analysis

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Quantera SXM (scanning XPS microprobe) spectrometer from Physical Electronics, in which X-rays were generated from an Al K α source, emitting at 1486.6 eV. The oxygen content and the carbon content are quite high in the spectra of the samples *as is*. After these scans, the acquisition areas for the core spectra were sputtered for 2 minutes with a 3kV 3x3mm² Ar ion source. On flat titanium this would remove approximately 10 nm of material. Since the hollow fibres are composed of sphere like particles, sputtering is likely less effective, and does not remove surface contaminations entirely. General references that have been used for interpretation of the spectra include:

- Handbook of X-ray Photoelectron Spectroscopy, J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, Eden Prairie (1992)
- NIST X-ray Photoelectron Spectroscopy Database 20, Version 4.1 (Web Version), Data compiled and evaluated by Alexander V. Naumkin, Anna Kraut-Vass, Stephen W. Gaarenstroom, and Cedric J. Powell Standard Reference Data Group National Institute of Standards and Technology, Gaithersburg, (2003); <http://srdata.nist.gov/xps>

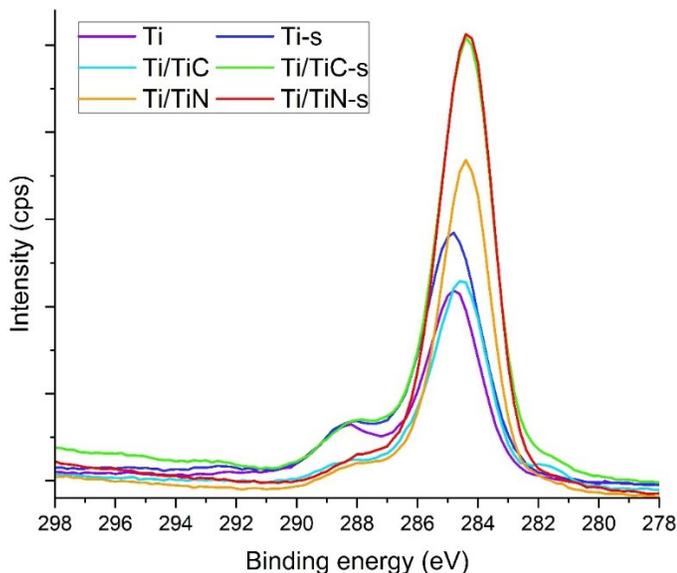


Figure S4. C 1s spectra of the Ti, Ti/TiC, and Ti/TiN samples before and after sintering (indicated by the 's'). The peak at 284.5 eV till 285.5 eV is typically assigned to adventitious carbon. TiC can be identified by the peak at ~282 eV. Please see:

- J. Luthin, Ch. Linsmeier, Characterization of Electron Beam Evaporated Carbon Films and Compound Formation on Titanium and Silicon, *Physica Scripta*, **T91** (2001) 134-137

The peak at 288 eV is due to the presence of some surface carbonate.

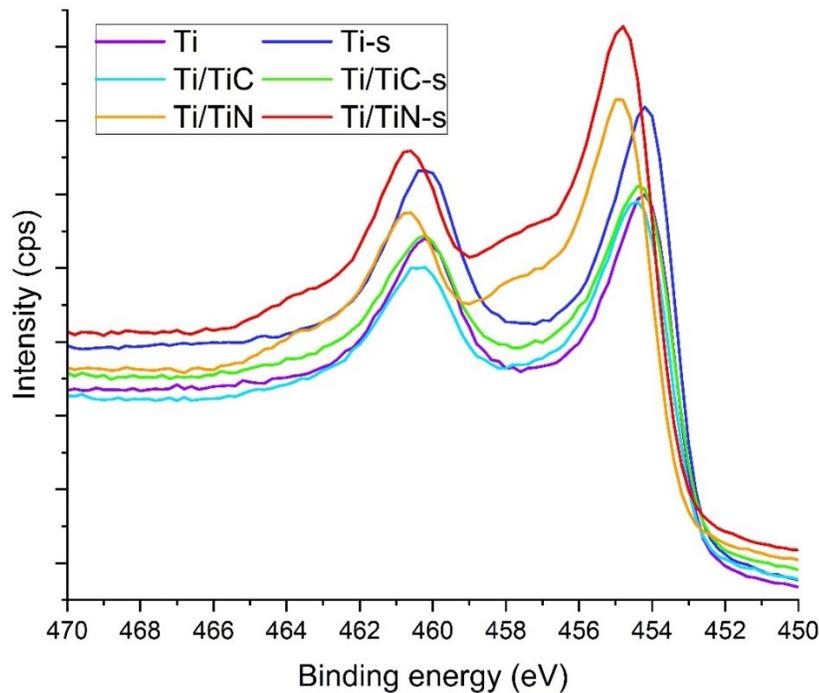


Figure S5. Ti 2p spectra of sputtered Ti, Ti/TiC and Ti/TiN, and their sintered analogues. Sputtering has reduced the amount of oxide present on top of the layer although as mentioned before this, due to the sample structure, this only has a limited effect. Ar ion sputtering removes the metal-oxide layer which would should allow for better interpretation of the metallic state, however due to the oxygen scavenging nature of Ti this still remains in a lower valence oxide state (likely the majority is Ti^{3+}). However the Ar ion sputtering of a metallic compound in the vicinity of a carbon source, results in conversion to a metal carbide. Hence TiC is dominant in the spectra of Ti and Ti/TiC, and unfortunately the thickness of the TiC layer cannot be estimated from these experiments. For further information please see:

- M.C. Biesinger, L.W.M. Lau, A. Gerson and R.St.C. Smart, Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Sc, Ti, V, Cu and Zn, *Applied Surface Science*, **257** (2010) 887-898
- J. Luthin, Ch. Linsmeier, Characterization of Electron Beam Evaporated Carbon Films and Compound Formation on Titanium and Silicon, *Physica Scripta*, **T91** (2001) 134-137

The spectra of the Ti/TiN composites are significantly shifted towards higher binding energy, indicating TiN is still a dominant species at the surface after sputtering. This indicates the TiN shell is likely at least 10 nm in thickness, although contributions of TiN in smaller layer thickness might still be present due to ineffective sputtering of spherical particles.

- D. Jaeger, J. Patscheider, A complete and self-consistent evaluation of XPS spectra of TiN, *J. Electron Spectrosc. Relat. Phenom.* **185** (2012) 523-534

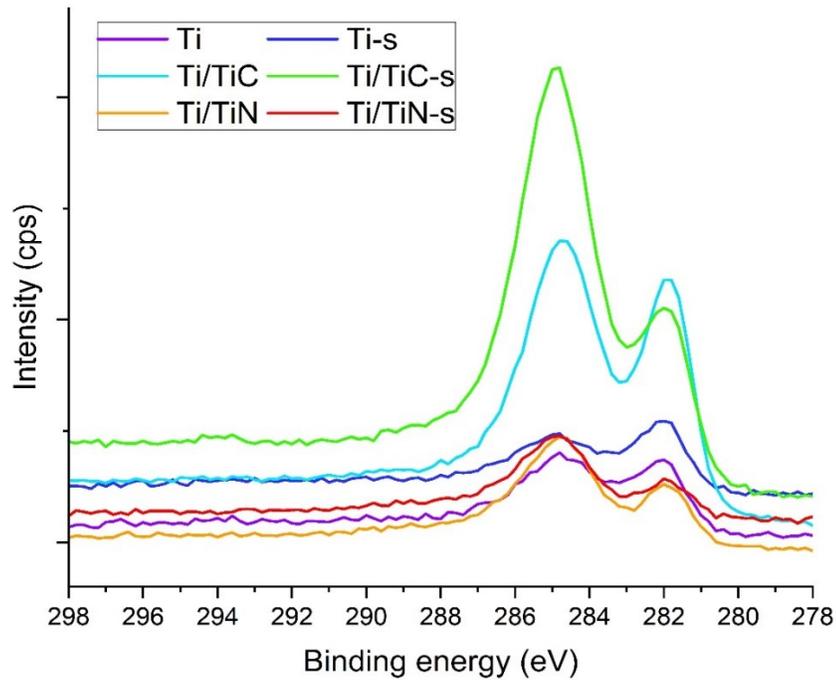


Figure S6. C 1s spectra of sputtered Ti, Ti/TiC, and Ti/TiN samples before and after sintering (indicated by the 's'). The peak at 284.5 eV till 285.5 eV is typically assigned to adventitious carbon. TiC can be identified by the peak at ~282 eV. The TiN samples are less prone to carbide formation. For further interpretation, please see:

- J. Luthin, Ch. Linsmeier, Characterization of Electron Beam Evaporated Carbon Films and Compound Formation on Titanium and Silicon, *Physica Scripta*, **T91** (2001) 134-137

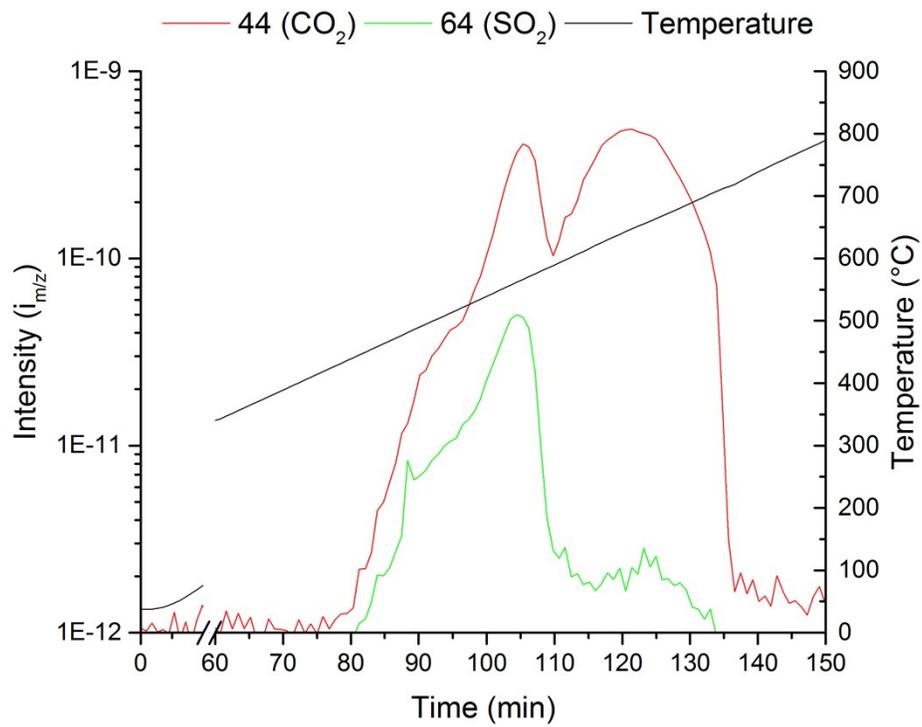


Figure S7. TGA-MS of PES in Air.

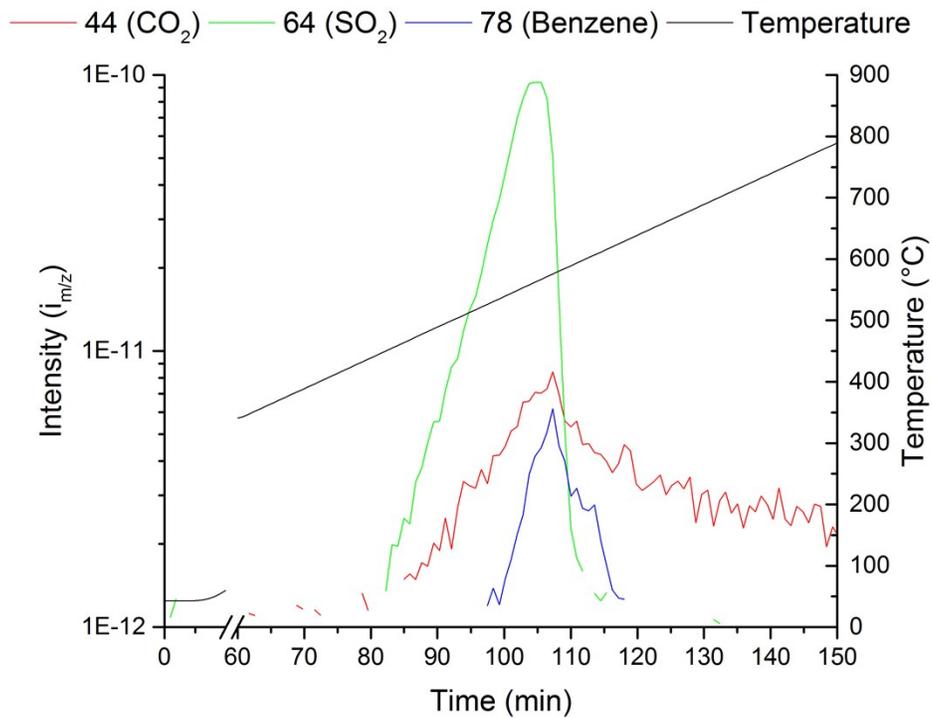


Figure S8. TGA-MS of PES in Ar.

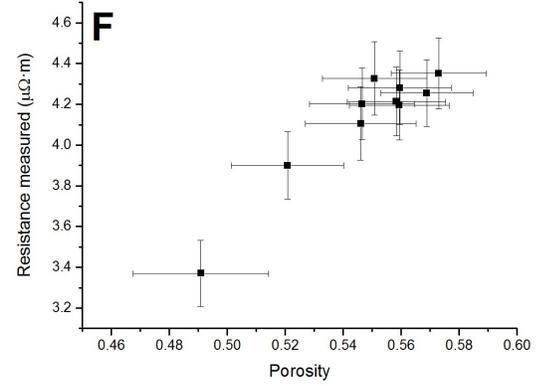
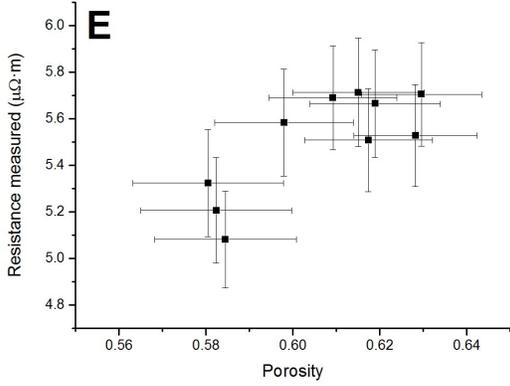
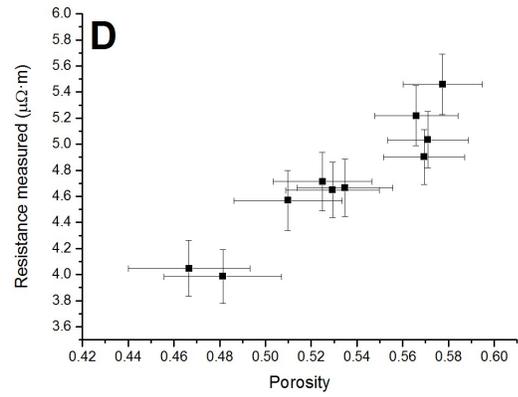
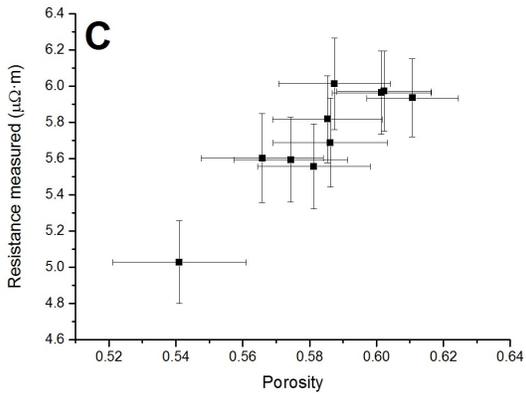
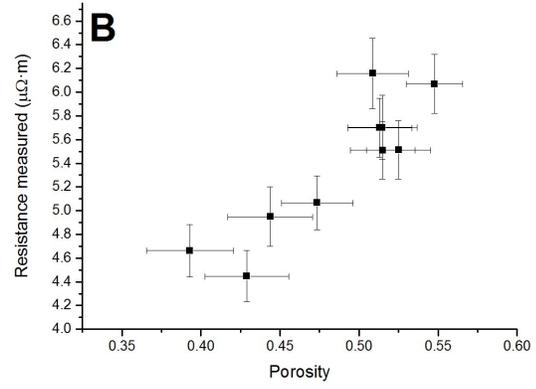
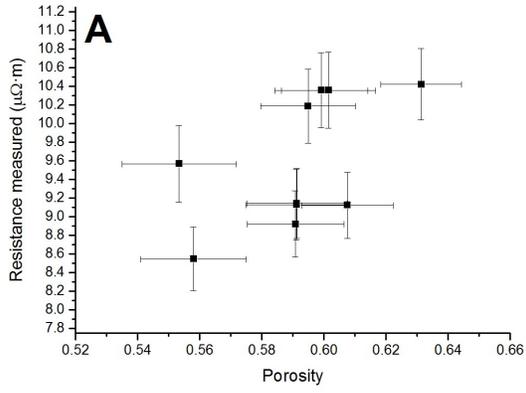


Figure S9. Resistance of (A) Ti, (B) Ti-s, (C) Ti/TiC, (D) Ti/TiC-s, (E) Ti/TiN, (F)Ti/TiN-s versus porosity.

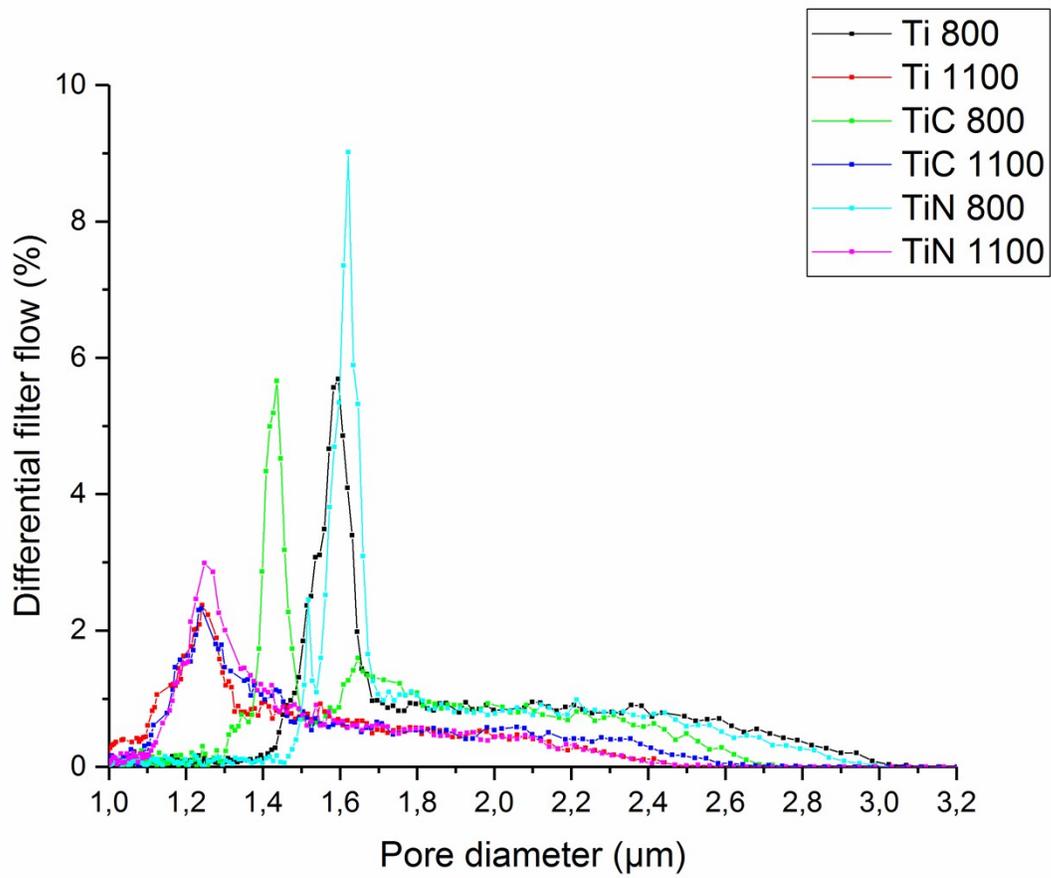


Figure S10. Pore size distribution obtained by capillary flow porometry.

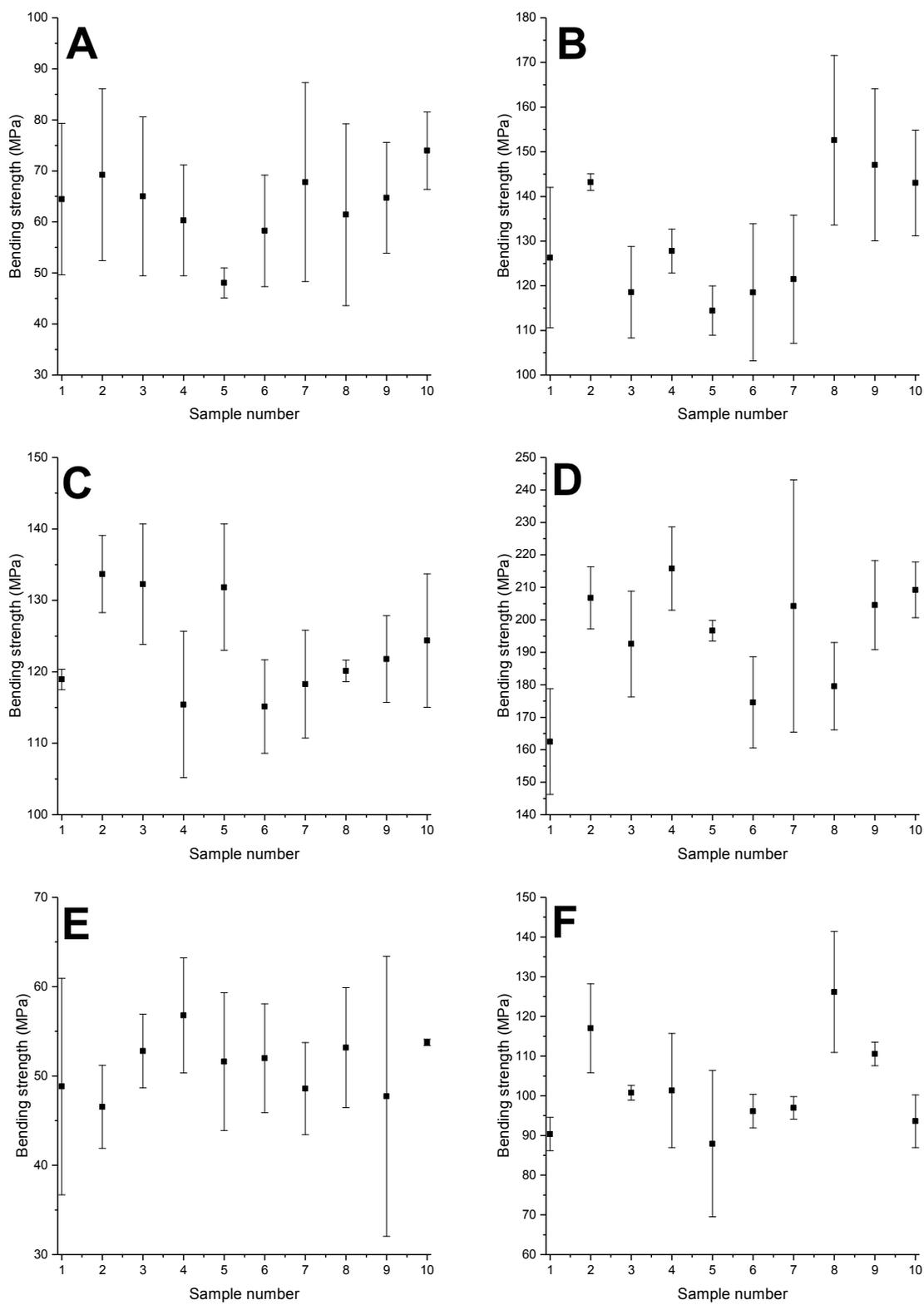


Figure S11. Bending strength of (A) Ti, (B) Ti-s, (C) Ti/TiC, (D) Ti/TiC-s, (E) Ti/TiN, (F)Ti/TiN-s measured on 10 different samples. Error bar indicate spread over 3 repetitions.