

## Electronic supplementary information

### Supplementary experimental

#### Preparation of the MAPTMS/TMOS/TEP hybrid sol and deposition on Ti6Al4V alloy

Mixtures of MAPTMS (98%) and TMOS (98%) from Aldrich were used as organopolysiloxane matrix precursors. Anhydrous ethanol (EtOH; absolute grade, Carlo Erba) and deionised water (Elga, Maxima Ultra-Pure Water model, 18.2 MOhm•cm) were used for alkoxysilane hydrolysis at a molar ratio of 1:4 TMOS/MAPTMS. The molar ratio of silane/water/EtOH was 1:3:3. The phosphorous precursor dopant TEP (Fluka, 98%) was added to the prepared MAPTMS/TMOS mixture at a volumetric ratio of 0.3, 0.6 and 0.9 mL TEP per 20 mL MAPTMS/TMOS. The mixture was stirred at 700 rpm for 12 h at RT.

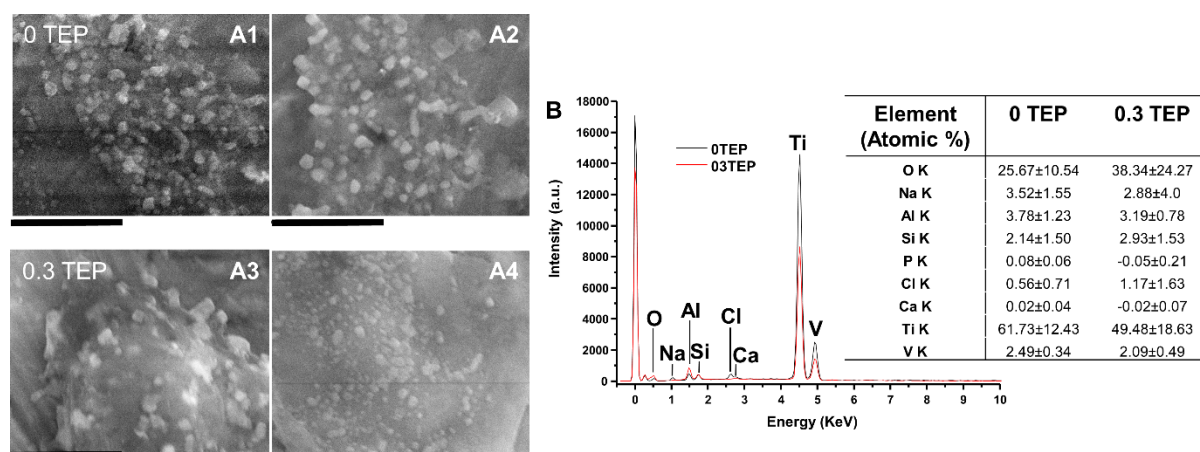
Ti6Al4V disks (2 cm diameter x 0.4 cm thickness and 0.9 cm diameter x 0.4 cm thickness) were ground using grit sand papers starting from 320 to 2000 grit size to achieve a uniform surface. Specimens were rinsed with ddH<sub>2</sub>O and ultrasonically cleaned in EtOH for 10 min then dried in air. Hybrid coatings were deposited at ambient temperature by immersion of Ti6Al4V alloys in a freshly prepared sol, holding for 1 min, followed by withdrawal at 9 cm/min using a dip-coater. Coated surfaces were cured for 2 h at of 120°C to remove loosely associated water and avoid decomposition of the organic component in the hybrid.

#### Mineralisation of MAPTMS/TMOS/TEP hybrid films

*In vitro* bioactivity was assessed for the TEP coatings in simulated body fluid (SBF) solution as described by Kokubo *et al.*<sup>[1]</sup> The solution was buffered at pH 7.4 using tris(hydroxymethyl) aminomethane/HCl and filtered (0.22 mm Millipore filters) to avoid bacterial contamination. SBF treatment was carried out at 37°C, using a sealed polyethylene container under continuous orbital stirring (600 rpm) in an Ecotron HT incubator. After 15 days immersion specimens were removed from solution, rinsed with ddH<sub>2</sub>O and dried at room temperature before analysis by XRD, SEM and EDXa.

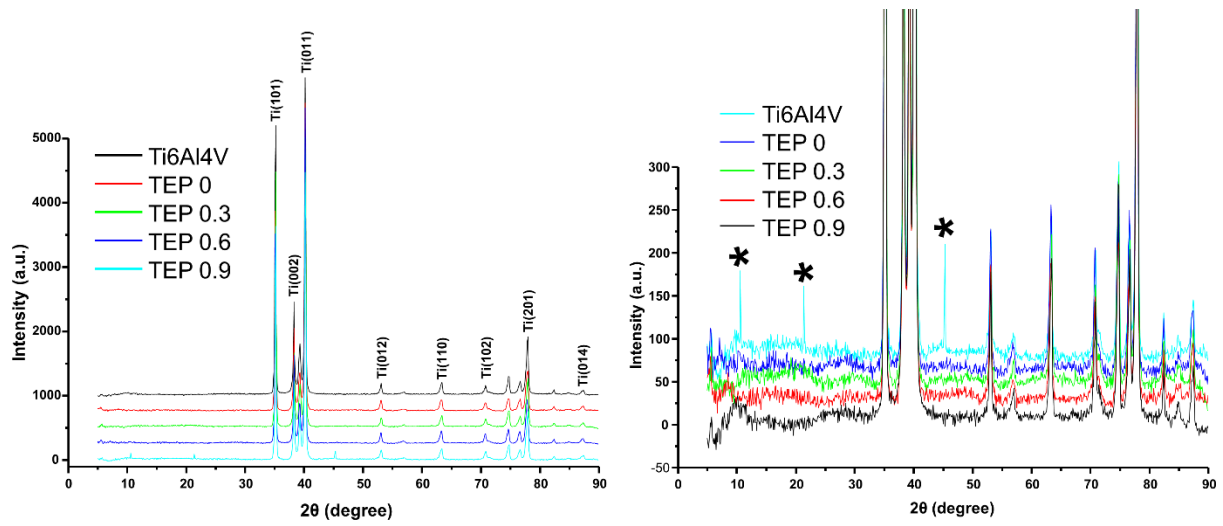
### Results and discussion

With respect to the immersion studies, precipitates were observed for some the coatings post immersion but the nature of these was not possible to determine conclusively. Scanning electron microscopy of these precipitates (after washing of the samples) is presented in figure S1 for 0 (A1-2) and 0.3 (A3-4) TEP coatings where precipitates were visible. EDXa detected trace amounts of Ca and P (more predominately for the 0 TEP coating) but also the presence of Na and Cl suggested a simple salt.



**Figure S1:** SEM micrographs (A) collected after exposure to SBF for days for 0 TEP (1, 2) and 0.3 TEP (3, 4) showing precipitates. Corresponding EDX (B) spectra, with elemental quantification are also provided representing mean and standard deviation.

XRD was used to attempt to demonstrate phase change over time, the predominant peaks detected were readily identified as the Ti6Al4V substrate (see fig. S2). The only discernible change noted with time was for 0.9 TEP at the end of the 15 day period (see \* on fig. S2). Though no match could be found with hydroxyapatite (25.879, 32.054, 39.673, 46.789, 49.498), apatite (23.391, 25.803, 28.681, 31.704, 46.789), hydroxylapatite (32.054, 32.902, 34.062) or calcium phosphate (25.354, 28.494, 23.901), octacalcium phosphate (25.956, 31.475, 31.589, 38.610), dibasic calcium phosphate dihydrate (15.927, 14.251, 24.572, 27.186, 28.681, 31.937).



**Figure S2:** XRD diffractograms showing the final state of the coatings after exposure to SBF for 15 days.

- 1 T. Kokubo, H. Kushitani, S. Sakka, T. Kitsugi and T. Yamamuro, *J. Biomed. Mater. Res.*, 1990, **24**, 721.