A mixed modification of the surface microstructure and chemical state of PEEK to improve its antimicrobial activity, hydrophilicity, cell adhesion and bone integration

Rui Ding[a], *Taijun Chen*[a], *Qizhen Xu*[a], *Ran Wei*[a], *Bo Feng*[a], *Jie Weng*[a], *Ke Duan*[a], *Jianxin Wang*[a,*], *Kai Zhang*[b], *Xingdong Zhang* [a, b]

[a]Key Laboratory of Advanced Technologies of Materials, Ministry of Education, School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, P.R. China

[b]National Engineering Research Center for Biomaterials, Engineering Research Center in Biomaterials, Sichuan University, Chengdu 610064, China

As shown in Figure 1, when the volume ratio of HNO_3 to H_2SO_4 was 1:2, shallow island-like structures with irregular and different sizes were formed on the surface of PEEK. In addition, some cracks appeared along the edge of the island-like structure, however, no nano-pore structure was observed. When the ratio of HNO_3 to H_2SO_4 was 1:3, micron-sized island-like structures with cracks resulted from the treatment were observed. Micro-nanostructure could be observed in the region between adjacent island-like structures. However, there was no regularity in the shape and arrangement of island-like structure at this ratio. In addition, the density of pores was obviously less than that at 1:1 ratio.

As shown in Figure 2, when the volume ratio of HNO_3 to H_2SO_4 was 1:4, the modified PEEK surface presented arc-shaped and short linear cracks with a width of 1-5μm. When the ratio of HNO_3 to H_2SO_4 was 1:5, island-like structures and nanopore structures resulted from the

[*]**Correspondence to:** J. Wang; E-mail: jwang@swjtu.edu.cn

treatment became irregular, and the sizes of the nanopores ranged from several tens of nanometers to 300 nm. In addition, compared with the results obtained from when the ratio was 1:1, the minimum size of the nanopores was smaller, and the sizes of most nanopores were below 100 nm. When the volume ratio of HNO_3 to H_2SO_4 was 2:1, the modified PEEK presented island-like structures and nanopore structures, which was similar to that at the ratio of 1:5, while the sizes of most nanopores were above 100 nm.

As shown in Figure 3, when the ratio of HNO_3 to H_2SO_4 was 3:1, a small amount of cracks appeared on the surface of the modified PEEK along the directions of scratches formed by the pretreatment process. When the volume ratio of HNO_3 to H_2SO_4 was 4:1, the surface morphology of the modified PEEK was similar to that at the ratio of 3:1. When the volume ratio of HNO_3 to $H_2SO_4$was 5:1, a large number of cracks were observed on the surface of the modified PEEK along the directions of scratches formed by the pretreatment process.

As shown in Figure 4, after placing PEEK samples in HNO_3 for 5 min, the PEEK surface showed a large number of cracks along the directions of scratches formed by the pretreatment process. After modified with H_2SO_4, PEEK surface presented a three-dimensional pore structure. The original PEEK surface showed a small amount of scratches due to rough grinding and polishing during the pretreatment process.

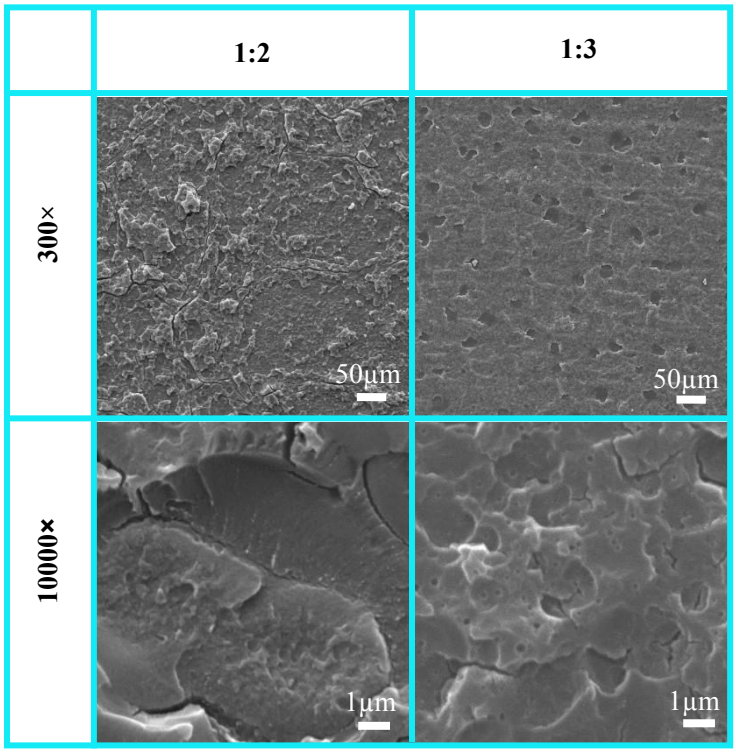

Figure S1. SEM images of PEEK modified with mixed acid (the volume ratios of HNO_3 to H_2SO_4 were 1:2, and 1:3, respectively)

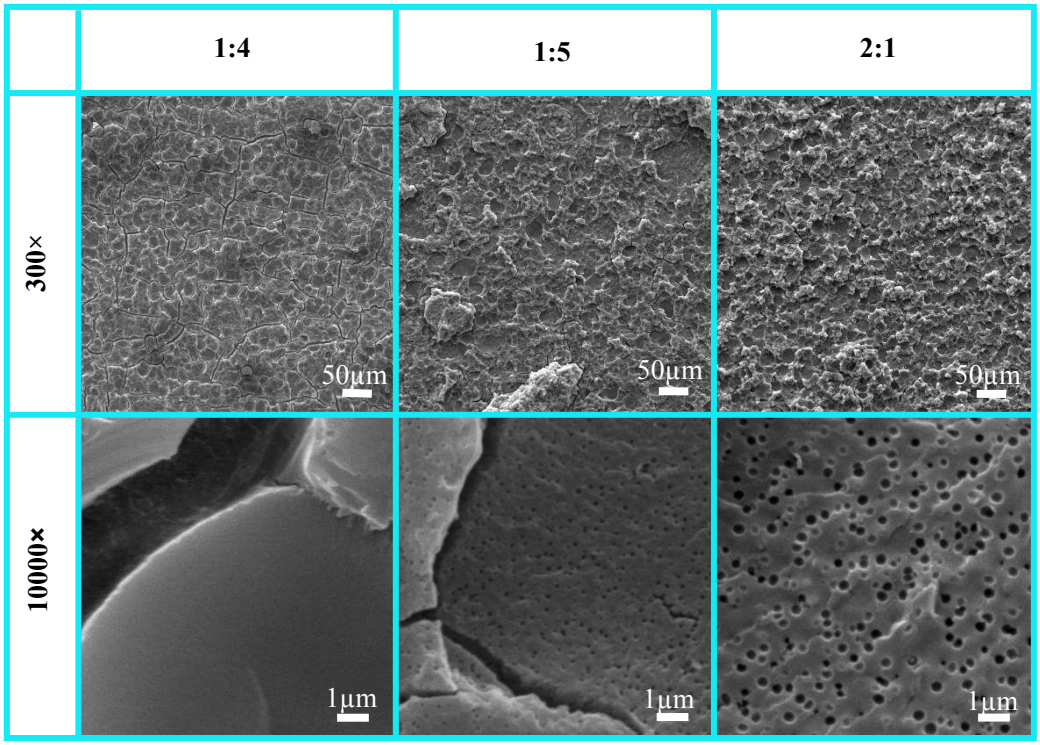

Figure S2. SEM images of PEEK modified with mixed acid (the volume ratios of HNO_3 to H_2SO_4 were 1:4, 1:5and 2:1, respectively)

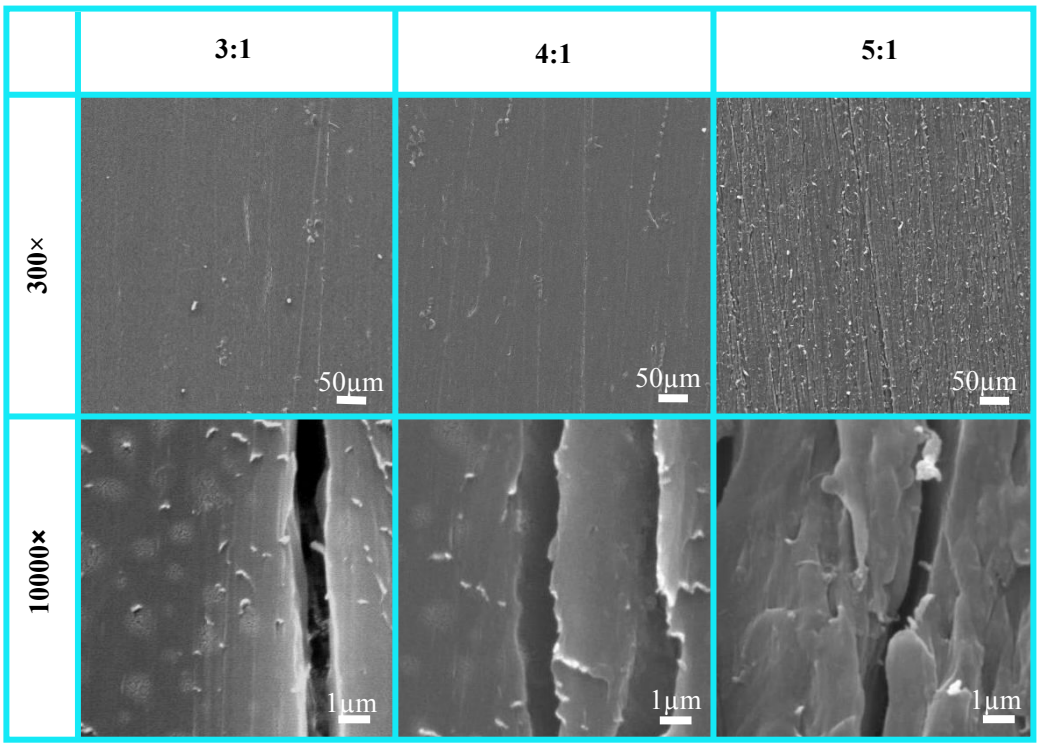

Figure S3. SEM images of PEEK modified with mixed acid (the volume ratios of HNO_3 to H_2SO_4 were 3:1, 4:1and 5:1, respectively)

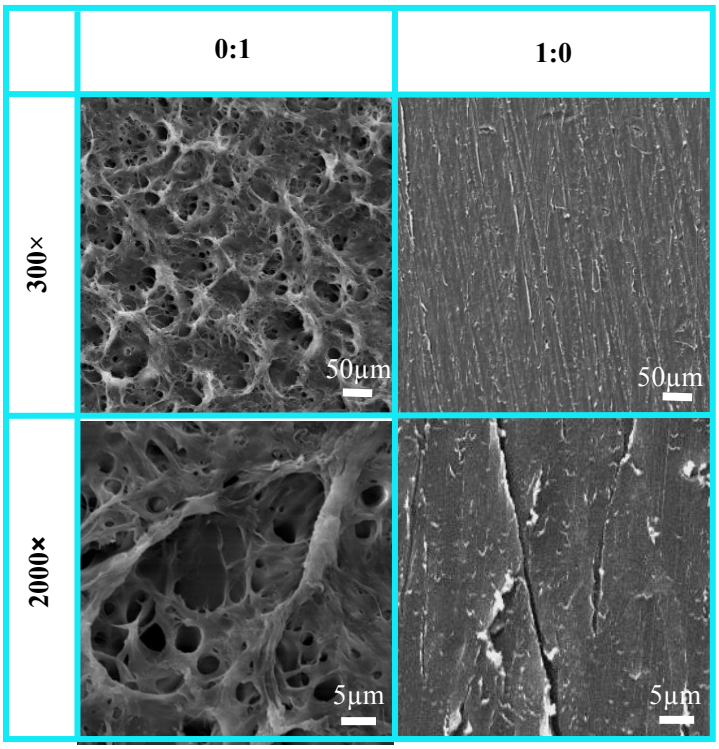

Figure S4. SEM images of the original PEEK and the PEEK modified with H_2SO_4 (0:1) and HNO_3 (1:0), respectively

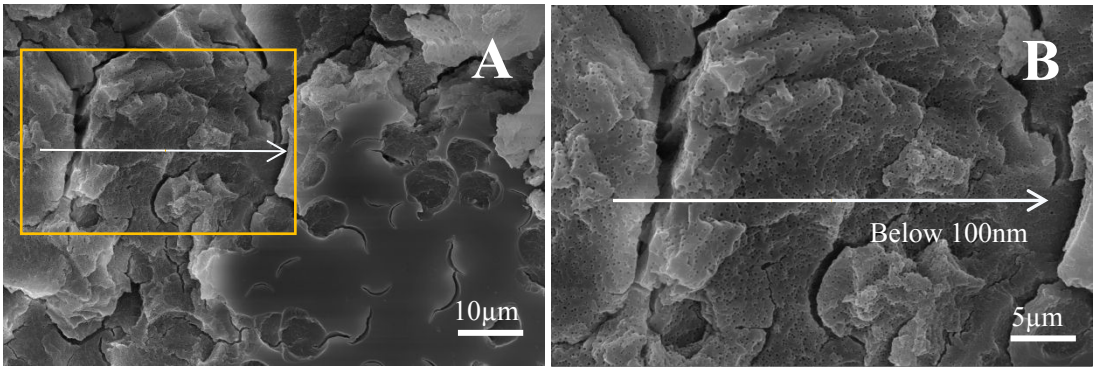

Figure S5. SEM magnified images of PEEK modified with the mixed acid (the volume ratio of HNO_3 to H_2SO_4 was 1:1)