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Surface Treatment of Magnetite Nanoparticle Thin Films by Potassium Phosphate and Their Calcium Phosphate Precipitation Behavior

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Experimental Procedure S1

The synthesis of Mgn NPs were based on the hydrothermal procedure reported by Chen *et al.*^{S1} FeCl₃.6H₂O (8 mmol) and FeCl₂.4H₂O (4 mmol) were dissolved in 100 mL of diethylene glycol (DEG) at 90 °C. Simultaneously, 80 mmol of NaOH was dissolved in the solution, and stirred for 2.5 h. Then, 20 mL of diethanolamine was added to the solution and stirred for 10 min, and the mixture was placed in a Teflon-lined stainless-steel autoclave, which was maintained at 200 °C for 8 h. After cooling to room temperature, the black solid was washed repeatedly with ethanol. The final black product was redispersed in ethanol at the solid concentration of 0.8 wt% as the suspension.

Reference

S1 M. Chen, Y. N. Kim, C. Li and S. O. Cho, J. Phys. Chem. C, 2008, 112, 6710.

Experimental Procedure S2

Hydroxyapatite (HA) nanocrystals were synthesized based on the previously described method.^{S1} The starting materials were dipotassium hydrogen phosphate (K₂HPO₄·3H₂O), potassium hydroxide (KOH), calcium chloride (CaCl₂) and distilled water. K₂HPO₄·3H₂O (24 mmol) and CaCl₂ (40 mmol) were dissolved in distilled water (1 L), respectively. KOH (5 mmol) was added to the K₂HPO₄.3H₂O solution (100 mL) and heated with stirring. When the solution reached 80 °C, 100 mL of the CaCl₂ solution was added to the solution, which was stirred for 30 min. The resultant suspension was washed three times with ultrapure water and the solid product was dried in an oven at 60 °C.

Reference

S1 Y. Wong, S. Zhang, K. Wei, N. Zhao, J. Chen and X. Wang, *Materials Letters*, 2006, **60**, 1484

Experimental Procedure S3

For the preparation of the HA nanocrystal-precipitated Mgn NPs, when the solution containing $K_2HPO_4.3H_2O$ and KOH reached 80 °C, the solution of the ethanolic Mgn NP dispersion liquid was added into the solution. This mixture was stirred at 80 °C for 30 min before the addition of the CaCl₂ solution. From here, the synthesis was completed exactly as described for the synthesis of HA in the **Experimental Procedure S2**. The final solution was separated and washed and dried.

Reference

S1 Y. Wong, S. Zhang, K. Wei, N. Zhao, J. Chen and X. Wang, *Materials Letters*, 2006, **60**, 1484



Figure S1. AFM topographic and MFM images of EPD films on the QCM-D gold sensor surfaces of (a) HA nanocrystals and (b) HA nanocrystal-precipitated Mgn NPs. The blue-colored dotted circles indicated the Mgn NPs shapes.



Figure S2. Photographs of the QCM-D gold sensor surfaces before and after the EPD of the Mgn NPs from the dispersion liquid at the solid weight of 0.8 wt%, and the Mgn NP film surface with the subsequent ultrasonication treatment at the thickness measured by QCM of 71±36 nm (density of Mgn: $5.2 \text{ g} \cdot \text{cm}^{-3}$).



Figure S3. ΔD and Δf curves and ΔD - Δf plots with the adsorption processes (a) 10 vol%FBS/PBS and (b) 10 vol%FBS/ α MEM on Mgn thin film.



Figure S4. AFM phase images of the precipitated surfaces on (a) Mgn, (b) Mgn-KH₂PO₄, (c) Mgn-K₂HPO₄ and (d) Mgn-K₃PO₄ after the immersion into 1.5SBF.