Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information

One-Pod Crystalline ZnO Nanorod Growth in Peptide Mineralization Gels

*Luona Anjia, Zengyan Wei, and Hiroshi Matsui**

When ZnO nanorod (NRD) was formed at pH 7.5 with 0.1 mM CN111-GGGSC (PAGLQVGFAVEVGGGSC) peptide and 1.0 mM $Zn(Ac)_2$, the coating domain of ZnO NPs is most monodisperse and closed-packed with highest crystallinity. When the ZnO NRDs are grown at pH 8.0 instead of pH 7.5 by adding extra amount of NaOH solution, the amount of ZnO NRDs and the size of gels are decreased. At the same time, as pH is increased, more sheet-like microcrystalline $Zn(OH)_2$ starts appearing as shown in **Figure S1**a. SAED at the edge of these $Zn(OH)_2$ sheets shows characteristic diffraction pattern of the peptide nanofiber, ~3.8 Å, in addition to $Zn(OH)_2$ diffraction pattern (Figure S1b). When Zn NRDs are grown at pH9.0, very few of ZnO NRDs are observed. The amount and the size of $Zn(OH)_2$ microcrystalline sheet increase even more at this pH (Figures S1c-d). Again, at the edge of these crystal, the peptide diffraction pattern appears in the SAED along with the $Zn(OH)_2$ diffraction pattern (Figure S1e). And SAED near the center of crystal sheet shows a single crystalline pattern of $Zn(OH)_2$ (Figure S1f). In pH 8.0 and pH 9.0, pH of the growth solution is too high so that overgrown $Zn(OH)_2$ in solution consumes a majority of zinc ions necessary as counter ions to assemble peptide nanofiber bundles in the gel and therefore there observe less ZnO NRDs in the higher pHs.

In a control experiment to mix all growth solutions except the peptide, no ZnO NRDs and gel structures were observed and only the $Zn(OH)_2$ microcrystalline sheets appeared (**Figure S2**). The yield of microcrystalline $Zn(OH)_2$ follow the same trend that observed in experiment with peptide in different pH solutions: microcrystalline $Zn(OH)_2$ gradually increases when pH are increased from pH7.5 to pH9.0.

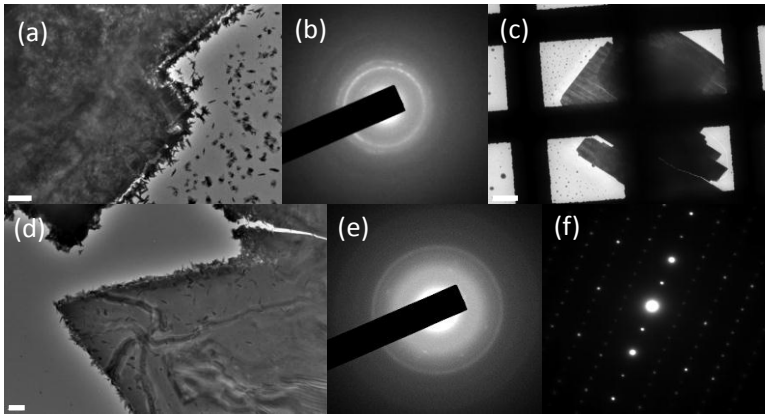

Figure S1. (a) TEM images of sheet-like microcrystalline structure of $Zn(OH)_2$ grown in pH 8.0 solution. Scale bar = 1 µm. (b) SAED of (a). (c) Microcrystalline structure of $Zn(OH)_2$ grown in pH 9.0 solution. Scale bar = 20 µm. (d) The closer-view of (c). Scale bar = 500 nm. (e) SAED at edge of (c). (f) SAED near center of (c).

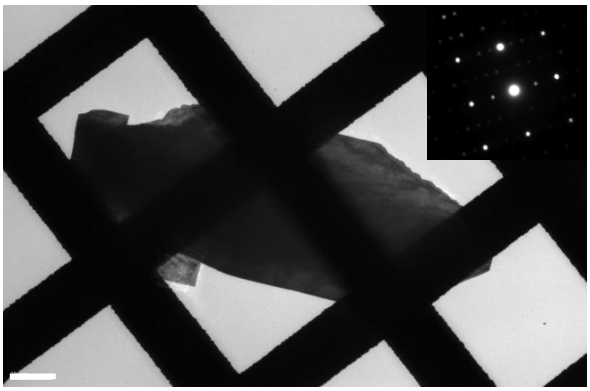

Figure S2. Microcrystalline structure of $Zn(OH)_2$ grown in the same experimental condition in 1.0 mM $Zn(Ac)_2$ and pH 7.5 as in Figure 3, only without the peptide. Inset is the SEAD of microcrystalline $Zn(OH)_2$. Scale bar = 20 µm.

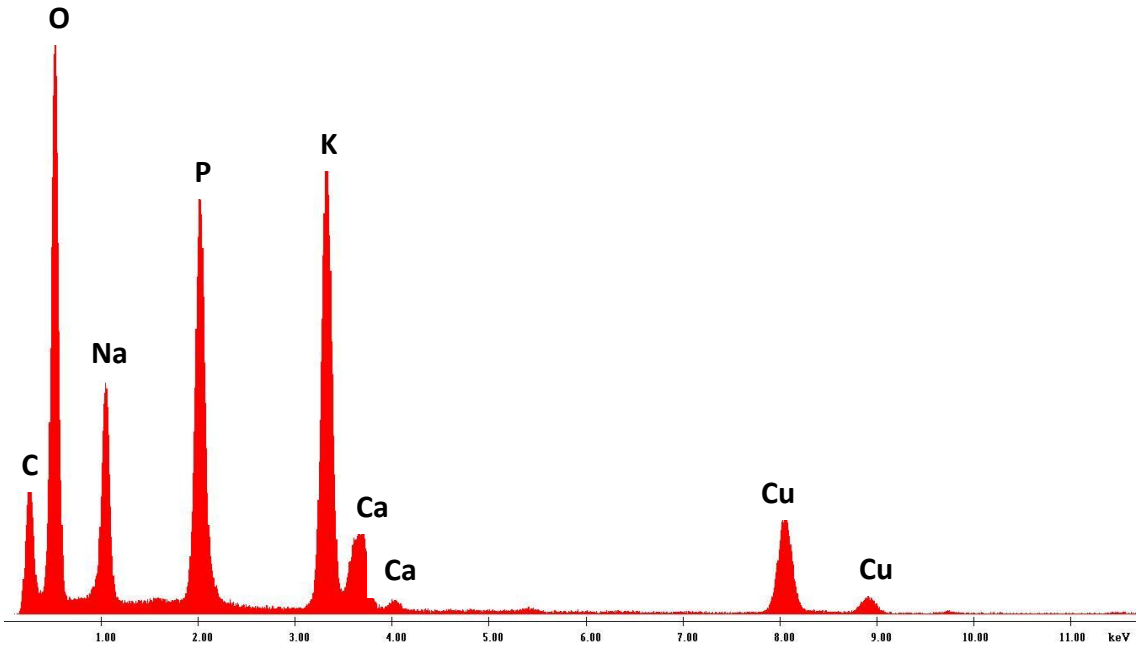

Figure S3. EDS on the Ca^{2+} - peptide spherical gels observed in 0.1 mM peptide with $Ca(NO_3)_2$ in 1.0 mM at pH 7.0.

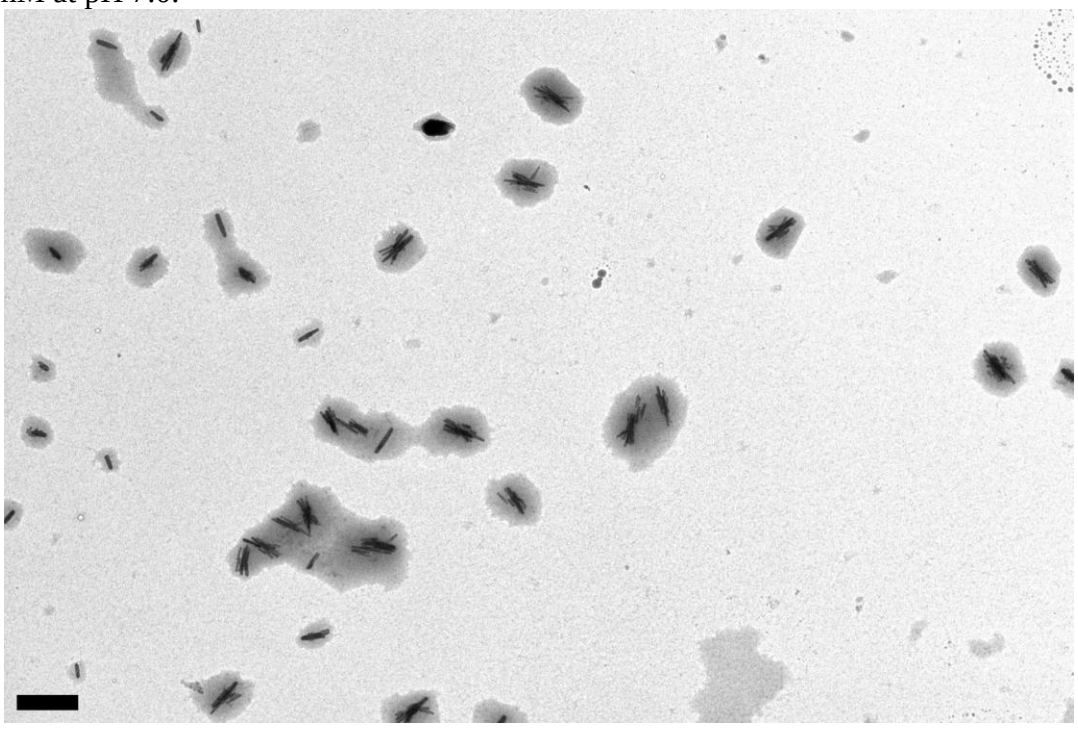

Figure S4. Low magnification TEM image of ZnO-peptide NRDs formed in 1.0 mM $Zn(Ac)_2$ after 4 days. This is the same sample as shown in Figure 3b. Scale bar = 2 μm.

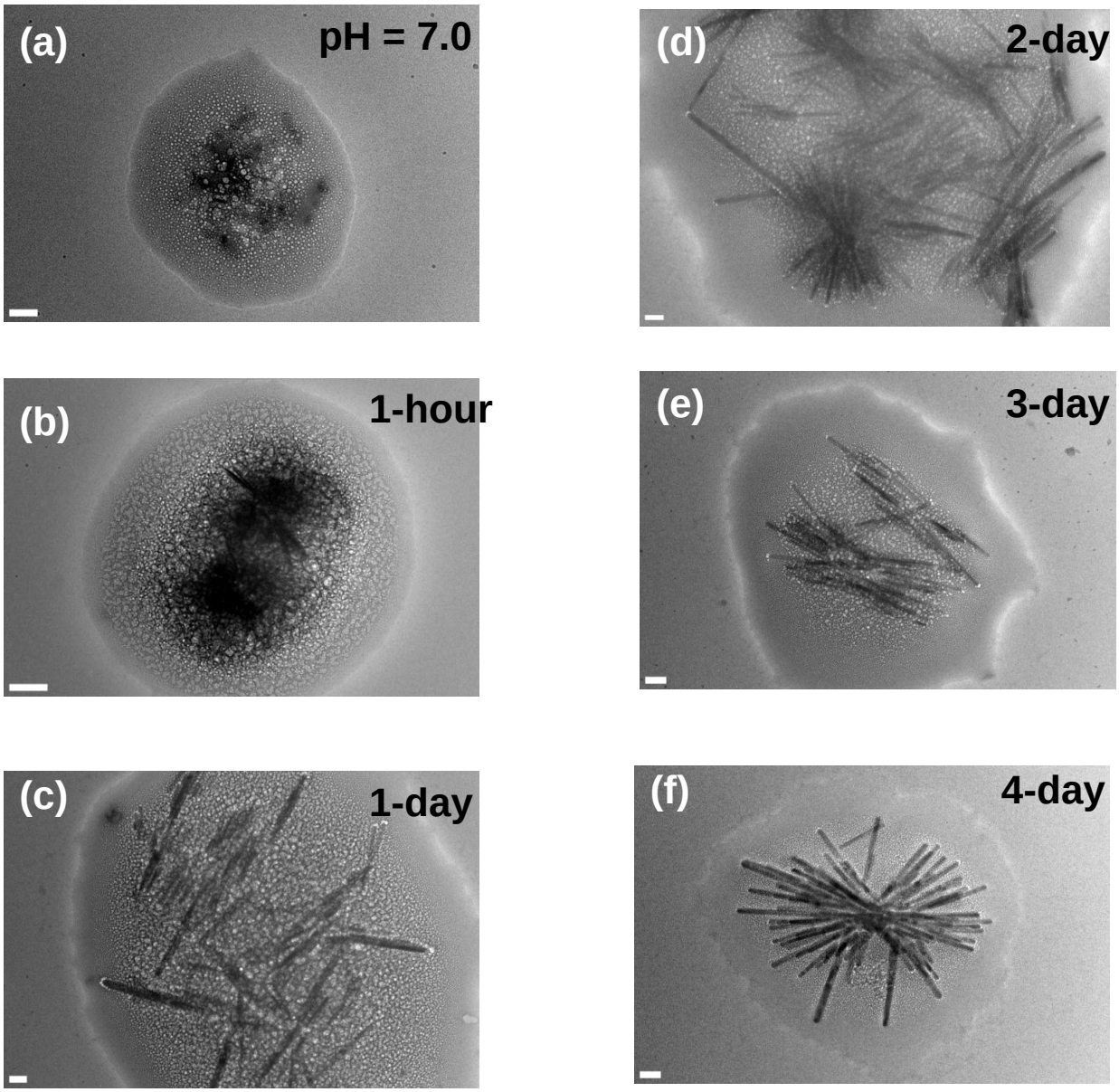

Figure S5. TEM images of ZnO-peptide NRDs. These samples were prepared with in 1.0 mM $Zn(Ac)_2$ before increasing the pH where the pH is 7.0 (a), and after incubation at pH 7.5 for 1-hour (b), 1-day (c), 2-day (d), 3-day (e) and 4-day (f). Scale bar = 200 nm.

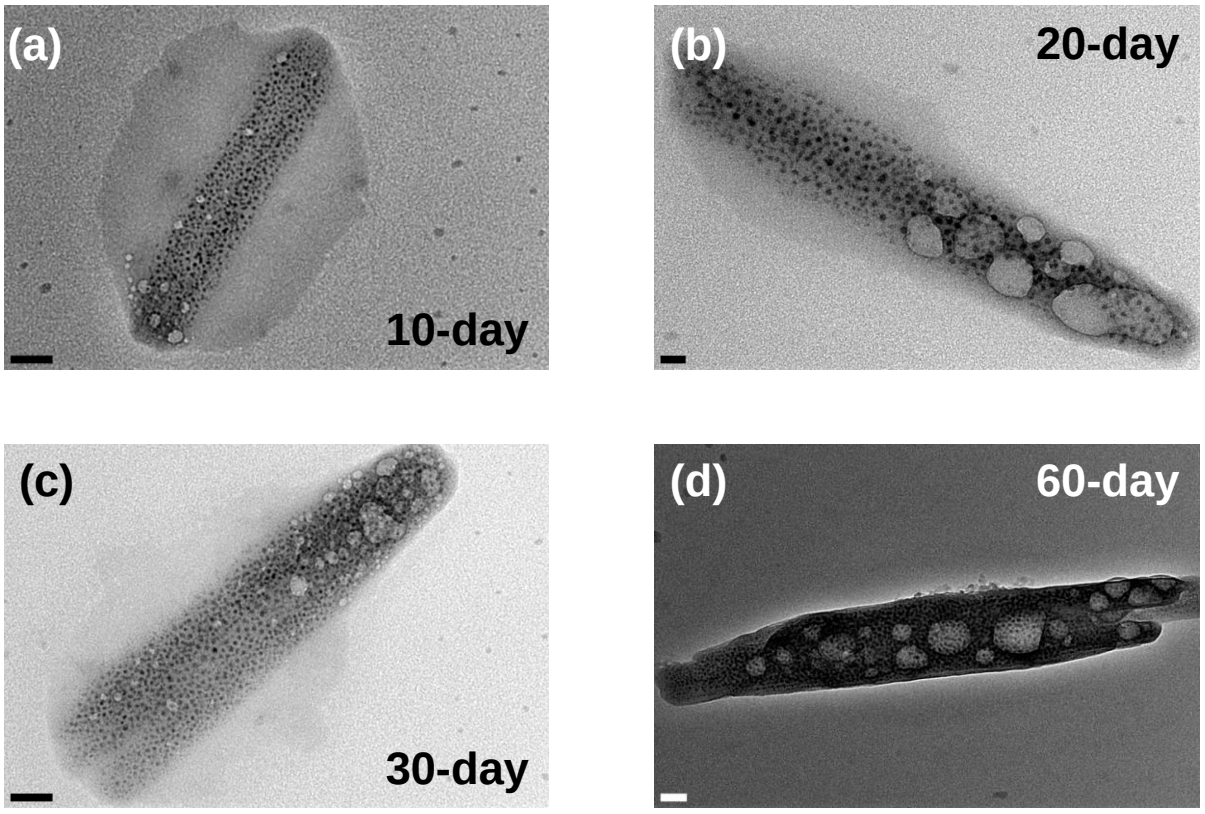

Figure S6. TEM images of ZnO-peptide NRDs with incubation time between 10 days and 60 days. These samples were prepared after 10-day (a), 20-day (b), 30-day (c) and 60-day (d) incubation in 1.0 mM $Zn(Ac)_2$ at pH 7.5. The samples incubated for longer incubation time reduce the size of gel around ZnO NRDs, and after 60days of incubation there observes no gel around ZnO NRDs. In addition, the surface area of ZnO NPs coated on the NRDs increases as the gel shrinks with incubation time. Scale bar = 200 nm.