Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Urchin-like Ni-P microstructures: A facile synthesis, properties and application in the fast removal of heavy-metal ions

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Experimental

1. Preparation of urchin-like Ni-P nanostructures with the room temperature magnetism

All reagents were purchased from Shanghai Chemical Company and used without further purification. In a typical experiment, the appropriate amount of $NiCl_2 \cdot 6H_2O$ (2 mmol, 0.475 g) and $NaH_2PO_2 \cdot H_2O$ (1 mmol, 0.106 g) were dissolved in distilled water to form a solution of 10 mL. Then 10 mL of DMF was added. The mixture was vigorously stirred with a magnetic pulsator at room temperature for 20 min. After the as-prepared solution was poured into a Teflon-lined stainless steel autoclave of 25 mL capacity, the autoclave was sealed and maintained at 160 °C for 16 h, then allowed to cool down naturally. The black precipitates were collected by a magnet, washed with distilled water and absolute ethanol several times to remove the soluble impurities. Finally, the as-prepared sample was dried in vacuum at 60 °C for 6 h.

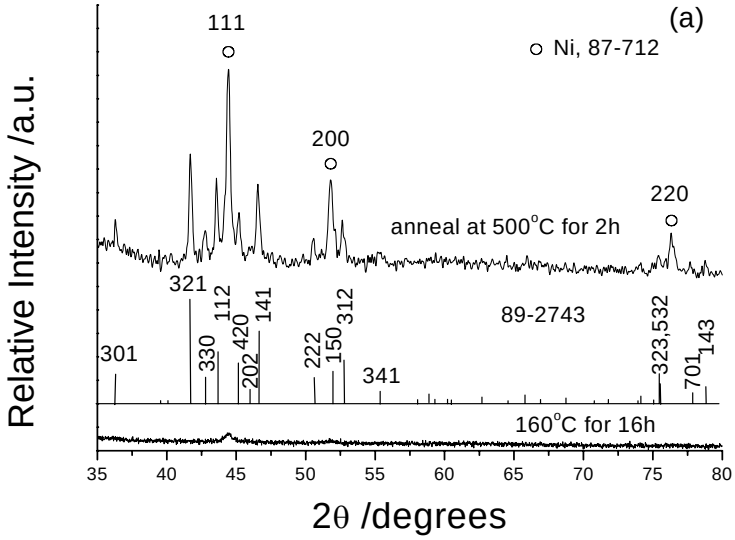
2. Characterization

XRD patterns of the products were recorded on a Japan Shimadzu XRD-6000 X-ray diffractometer equipped with graphite monochromatized Cu Ka radiation (λ= 0.15406 nm), using

a scanning rate of $0.02°s^{-1}$ and 2θ ranges from 35° to 80°. TEM and EDS were obtained on a JEOL-2010 high resolution transmission microscope, employing an accelerating voltage of 200 kV. FESEM images of the products were obtained on a Hitachi S-4800 field emission scanning electron microananlyser, employing the accelerating voltage of 5 kV. The magnetic properties were measured on a vibrating sample magnetometer (VSM) at room temperature. The Brunauer–Emmett–Teller (BET) surface area of the product was measured with an accelerated surface area and porosimetry system (ASAP 2020). X-ray photoelectron spectroscopy (XPS) of the product was obtained on Thermo ESCALAB 250 instrument, employing **monochromic** Al Kα (hν =1486.6 eV) at the power of 150 W.

3. Removal of heavy metal ions

To investigate the capacities of the as-prepared urchin-like Ni-P microstructures for removing heavy metal ions, 10 mg of urchin-like Ni-P microstructures were introduced to a 50 mL solution of Pb^{2+} (or Cd^{2+}) ions with an initial concentration of 10 mg/L at room temperature. The as-obtained mixed system was slowly stirred with a magnetic pulsator for 10 min to ensure sufficient interaction between Ni-P microstructures and heavy-metal ions. The inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 5300DV-ICP, Perkin-Elmer) was employed to analyze the concentration changes of heavy-metal ions before and after adsorption. Then, the adsorbents were collected under the assistance of a magnet and washed by deionized water of 100 mL for three times under the assistance of ultrasonic wave. The data for ion adsorption isotherms are obtained by ICP-AES.



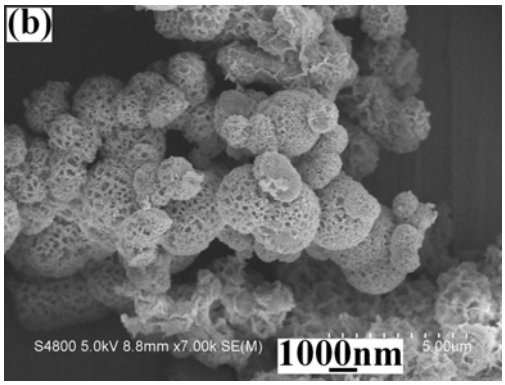


Figure S1. (a) XRD patterns of the products: the below curve is the pattern of the product prepared at 160 °C for 16 h and the upper curve is the one of the product treated at 500 °C for 2 h. (b) A representative SEM image of the product treated at 500 °C for 2 h.

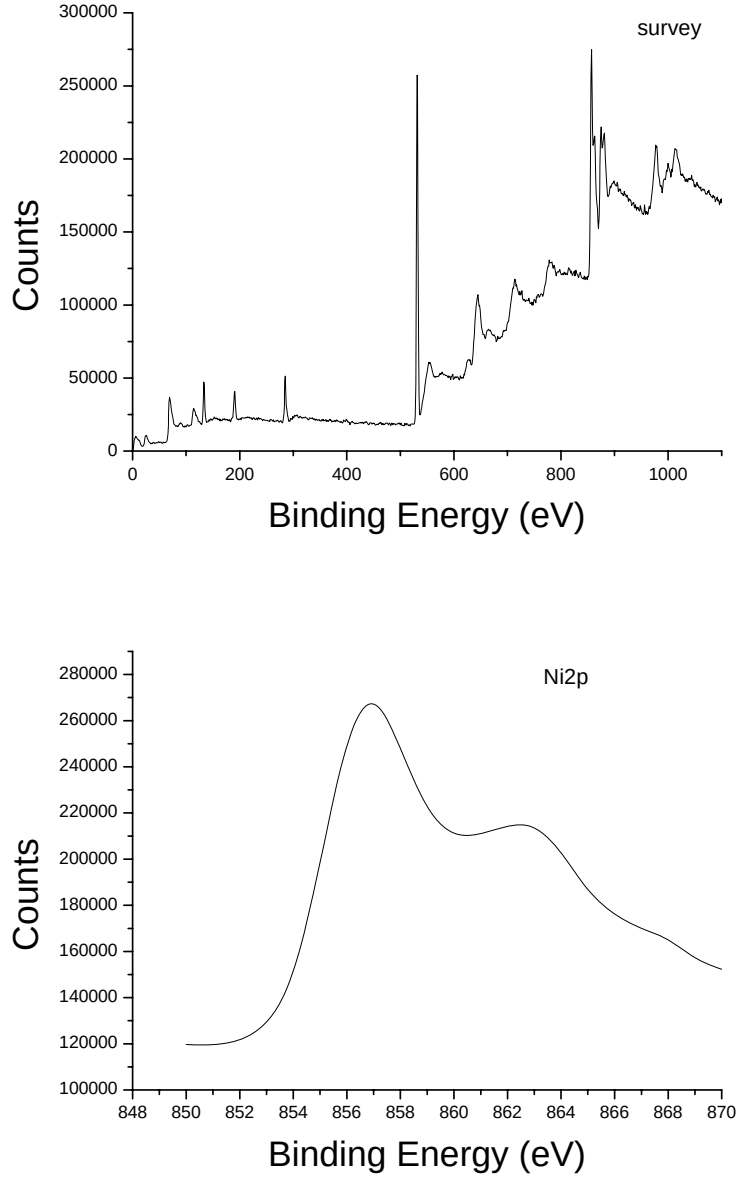


Figure S2 Survey X-ray photoelectron spectra of urchin-like Ni-P microstructures and high resolution XPS of Ni.

Experiments showed that the morphology of the product could be affected by the molar ratio of $Ni^{2+}/H_2PO_2^-$, the volume ratio of water/DMF and the reaction temperature.

Figure S3 shows FE-SEM images of the products prepared from the systems containing various $Ni^{2+}/H_2PO_2^-$ molar ratios at 160°C for 16 h. When the original $Ni^{2+}/H_2PO_2^-$ molar ratio was 4:1, urchin-like Ni-P microstructures could be successfully prepared (Fig.S3a). However, the yield of the product was low. After the molar ratio of 2:1 was employed, large amounts of urchin-like Ni-P microstructures were obtained (see Fig.1). Upon further decreasing the ratio to 1:1, urchin-like microstructures disappeared and a great deal of nanowires was produced (Fig.S3b). When the ratio decreased to 2:3, some microspheres appeared among nanowires (Fig.S3c). When the $Ni^{2+}/H_2PO_2^-$ molar ratio was 1:5, nanowires fully disappeared and the product was heterogeneous microspheres with smooth surfaces (Fig.S3d). The above facts clearly indicate that the high $Ni^{2+}/H_2PO_2^-$ ratio avails to the formation of urchin-like Ni-P microstructures. Xie's research [1] showed that the chemical composition of Ni-P alloys could be influenced by the original $H_2PO_2^-/Ni^{2+}$ molar ratio. The P content in alloys increased with the increase of $H_2PO_2^-$ amount. Similarly, the P content increased with the increase of $H_2PO_2^-$ amount in the current work. As a result of the increase of P content in the product, the shape of the product gradually evolved from urchins, to nanowires, finally to microspheres.

The volume ratio of water/DMF was another important factor affecting the morphology of the final product. As shown in Fig.S4a, when the volume ratio of water/DMF was ~2, the product was aggregated particles with rough surfaces. Contrarily, when the volume ratio of ~1/2 was employed, the product was composed of some retrogressive urchin-like microstructures (see Fig.S4b). The above experiments indicate that the water/DMF volume ratio of 10:10 is optimum in the formation of urchin-like Ni-P microstructures.

The morphology of the final product could be also influenced by the reaction temperature. Fig.S5 depicts FE-SEM images of the final products prepared under the same system at different temperature for 16 h. When the reaction temperature was 140 °C, abundant urchin-like microstructures could be obtained (see Fig.S5a). While 180 °C was employed, only near-spheres particles were produced (Fig.S5b). These imply that the higher temperature is unfavorable for the formation of urchin-like Ni-P microstructures.

Based on our experiments, DMF played a crucial role in the formation of urchin-like Ni-P

microstructures. It is well known that DMF molecules possess strong coordinating ability to Ni^{2+} ions. In the present work, DMF acted as three roles: solvent, pH adjustor and complexant. After 10 mL of DMF was introduced the solution of Ni^{2+} ions, a stable complex of Ni-DMF was formed. Under the lifted temperature, the reaction between Ni-DMF complexes and $H_2PO_2^-$ ions took place and urchin-like Ni-P microstructures were formed under the influence of DMF. However, when small amounts of DMF were employed, abundant free Ni^{2+} ions existed, which led to the formation of aggregated particles with rough surfaces (Fig.S4a). While excess DMF was used, free Ni^{2+} ions dramatically decreased. Herein, though urchin-like microstructures could be still obtained, the shape of the product obviously retrogressed (Fig.S4b). Furthermore, the enhancement of the reaction temperature promoted the decomposition of Ni-DMF complexes, which led to the increase of the reaction rate. At 180 °C, the nucleation and growth rate of the product accelerated; simultaneously, the influence of DMF on the morphology was weakened. Thus, near-spheres particles were produced (Fig.S5b). To ascertain the growth process of Ni-P microstructures, a time-dependent shape evolution was investigated. Fig.S6a depicts a SEM image of the product prepared from the same system at 160 °C for 30 min. The product was comprised of many immature microstructures. After 1 h, the shape of the product hardly changed. Upon further prolonging the time to 4 h, the surfaces of some microstructures started to become compacter (see the arrow direction in Fig.S6b). After that, more microstructures with compacter surfaces appeared with the prolonging of time from 7 h to 13 h (see Fig. S6c, S6d, S6e). After reacting for 16 h, urchin-like Ni-P microstructures were finally obtained (Fig.1). Also, experiments showed that the product could not be produced until the reaction time was 30 min. After that, there was not obvious yield increase with the prolonging of the time, indicating that the reaction to produce Ni-P had completed after 30 min. Zhou's group reported that Ni-P alloy could be prepared at 90 °C for 50 min.[2] Hence, it is probable that Ni-P microstructures are synthesized within a shorter time under a lifted temperature. With the expansion of the time from 30 min to 16 h, immature products gradually converted to mature urchin-like microstructures, implying that Ni-P nanoparticles on the surfaces of the products should undergo a dissolution-recrystallization growth process.

1 H. Xie, B. Zhang, *J. Mater. Process. Technol.* 2002, *124*, 8.

2 S. H. Xie, M. H. Qiao, W. Z. Zhou, G. Luo, H. Y. He, K. N. Fan, T. J. Zhao, W. K. Yuan, *J.*

Phys. Chem. B 2005, *109*, 24361.

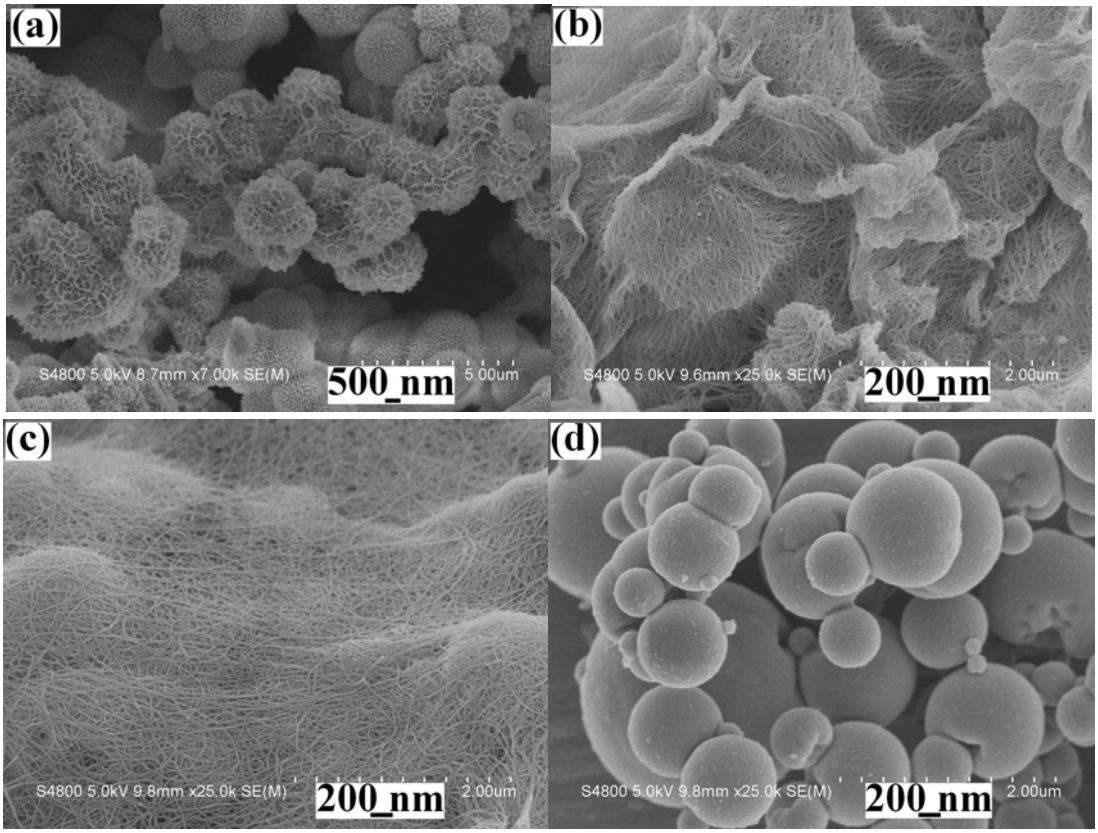


Figure S3. FE-SEM images of Ni-P microstructures prepared from the systems containing various $Ni^{2+}/H_2PO_2^-$ molar ratios at 160°C for 16 h: (a) 4:1, (b) 1:1, (c) 2:3 and (d) 1:5.

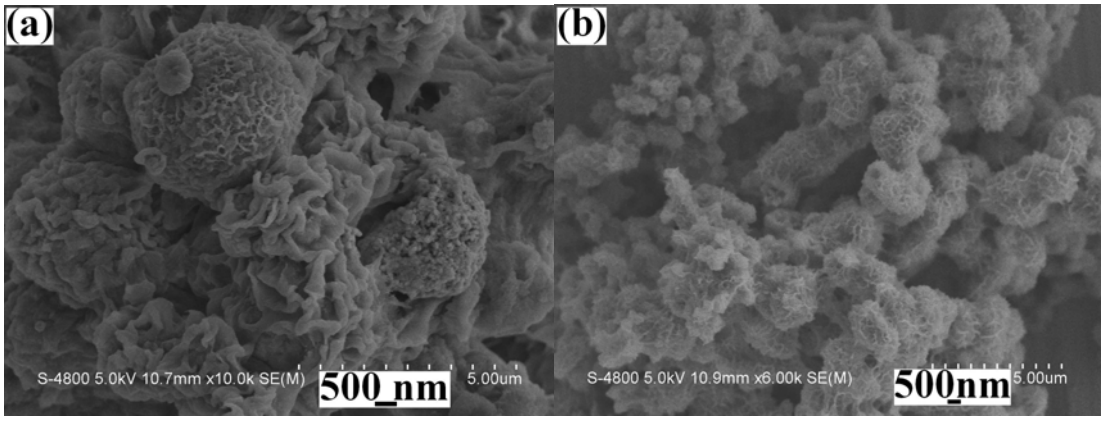


Figure S4. FE-SEM images of Ni-P microstructures prepared from the systems containing various water/DMF volume ratios at 160°C for 16 h: (a) 13.5:6.5 and (b) 6.5:13.5.

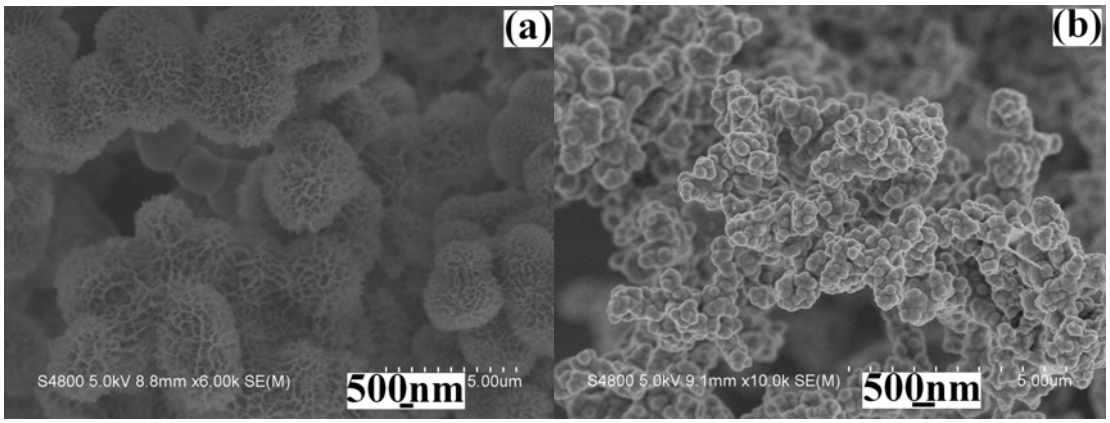


Figure S5. FE-SEM images of Ni-P microstructures prepared under the same system at different temperatures for 16 h: (a) 140°C and (b) 180°C.

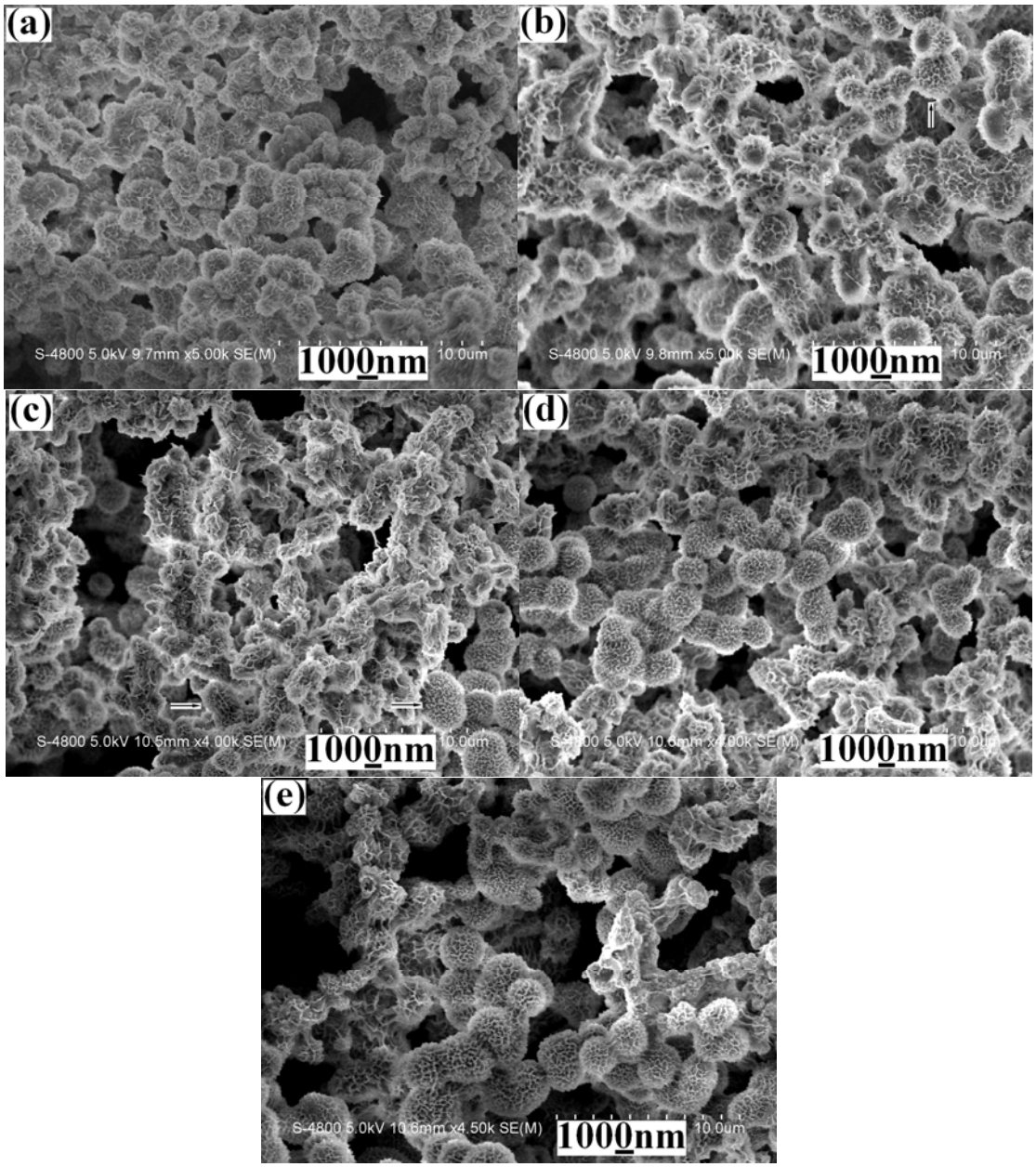


Figure S6. FE-SEM images of Ni-P microstructures prepared under the same system at 160°C for different durations: (a) 30 min, (b) 4 h, (c) 7 h, (d) 10 h and (e) 13h.

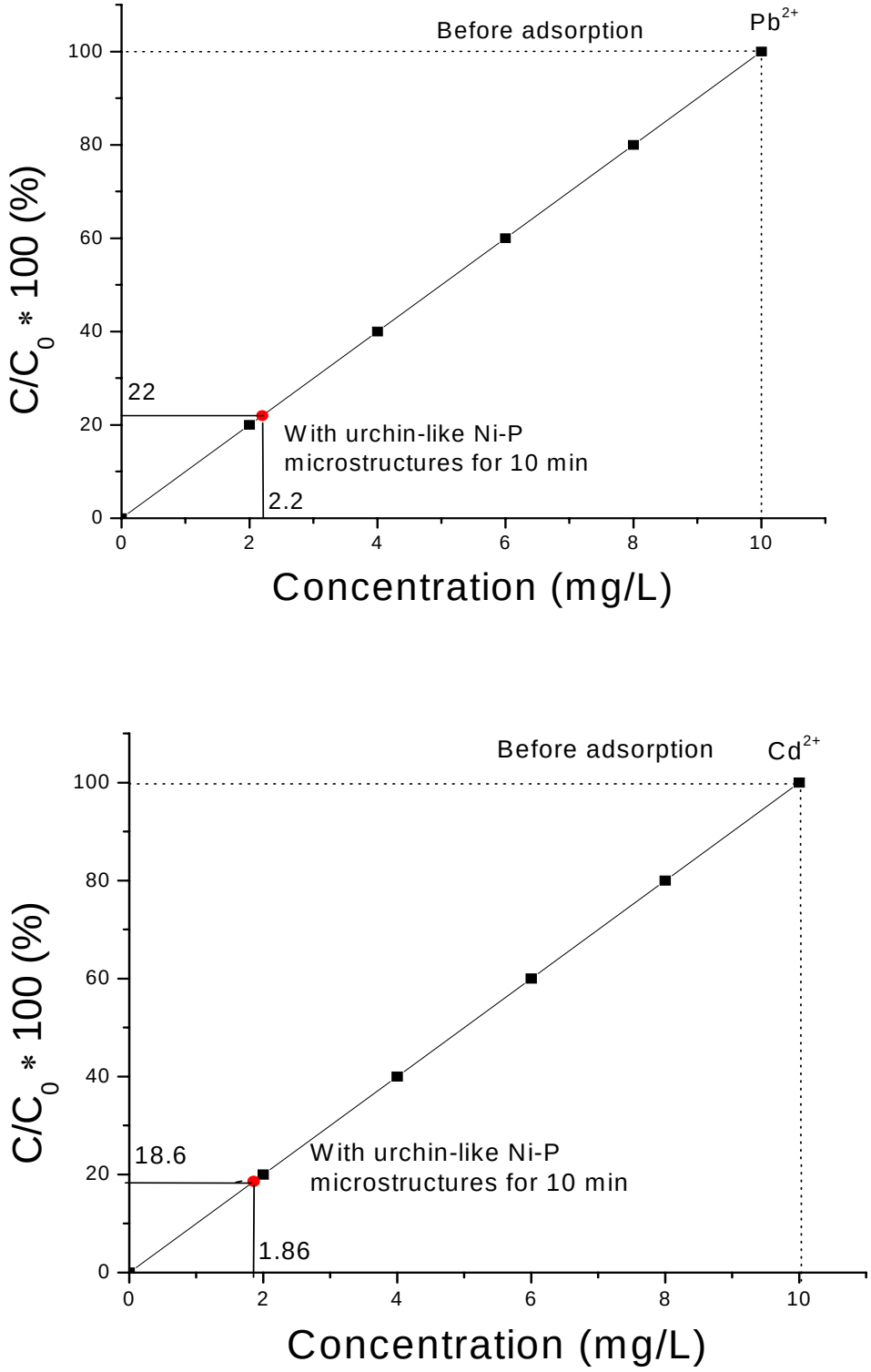


Figure S7. The concentration of the solution containing Pb^{2+}or Cd^{2+}: (—▪—) calibration curve and (……) before and (—) after adsorption with urchin-like Ni-P microstructures for 10 min.