Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

ZIF-67@Co-LDH yolk-shell spheres with micro-/meso-porous structures as vehicles for drug delivery

Liyong Chen*[a,b], Jinfeng Wang[a], Xiaoshuang Shen[c], Yingyue Zhang[a], and Chunying Duan*[a]

[a] *State Key Laboratory of Fine Chemicals, Dalian University of Technology, 2 Linggong RD., Dalian, 116024, China. Email: lychen@dlut.edu.cn cyduan@dlut.edu.cn.*

[b] *Bengbu Medical College, Bengbu, 233030, China.*

[c] *School of Physical Science & Technology, Yangzhou University, Yangzhou, 225002, China.*

Experimental Section

Materials and characterization methods

All chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd, China and used as received.

Transmission electron microscopy (TEM) images were collected from Tecnai F30 operated at 300 kV, and scanning electron microscopy (SEM) images were collected from HITACHI UHR FE-SEM SU8220. A Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu-*K*α radiation (λ = 1.5418 Å) was used to collect X-ray diffraction (XRD) patterns. The content of metal elements was evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Optima 2000DV. N_2 adsorption/desoprtion isotherm at 77 K were carried out an Autosorb-iQ gas sorption analyzer after being degassed in vacuum at 200 ^oC for 12 h. UV-Vis absorption spectroscopy was performed on TU-1900 spectrophotometer. Raman spectroscopy was conducted on a Jobin Yvon LabRAM HR Evolution Raman spectrometer.

Calculation of drug loading capacity and drug loading efficiency

The equations were shown as $drug\ loading\ capacity = \frac{m_{total}^{R6G} - m_{free}^{R6G}}{m_{yolk-shell}} \times 100\%, and$

$drug\ loading\ efficiency = \frac{m_{total}^{R6G} - m_{free}^{R6G}}{m_{total}^{R6G}} \times 100\%$,

where m_{total}^{R6G} is the total mass of R6G used in the drug loading process, m_{free}^{R6G} is the mass of free R6G in solution after loading, and $m_{yolk-shell}$ is the mass of ZIF-67@Co-LDH yolk-shell heterostructures used in the drug loading process.

In the drug loading and release experiments, m_{total}^{R6G} is 0.24 mg, and $m_{yolk-shell}$ is 15 mg. m_{free}^{R6G} is estimated to be 0.051 mg by Lambert-Beer law according to UV-vis spectroscopy of R6G.

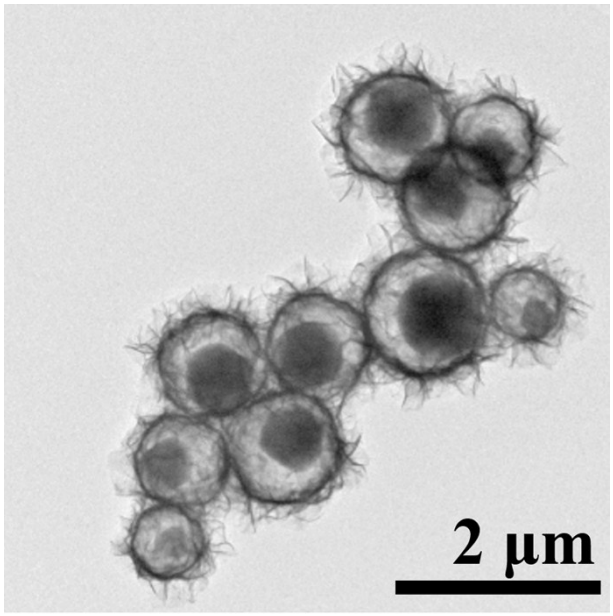

Fig. S1. TEM image of ZIF-67@Co-LDH yolk-shell heterostructures while dropwisely adding of $Co(NO_3)_2$ solution to the synthetic system at a time interval of 10 min.

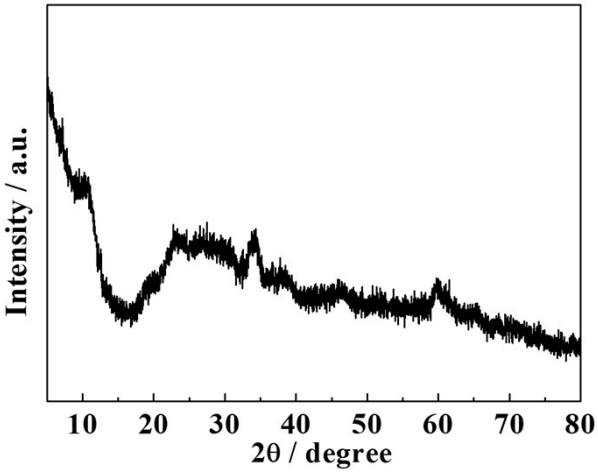

Fig. S2. XRD pattern of ZIF-67@Co-LDH yolk-shell heterostructures incubated into deionized water for 48 h with gently stirring.

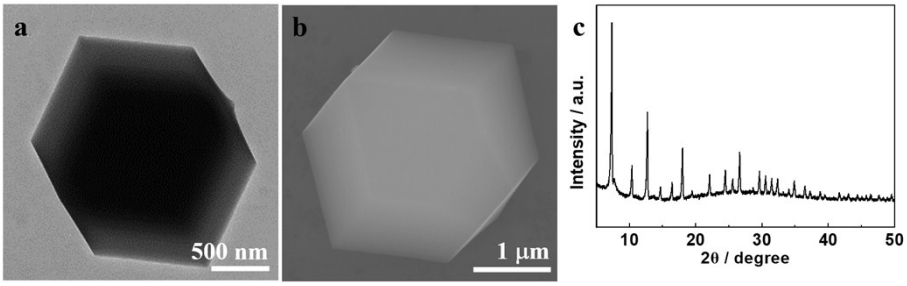

Fig. S3. TEM and SEM images and XRD pattern of the as-made ZIF-67 nanocrystals.

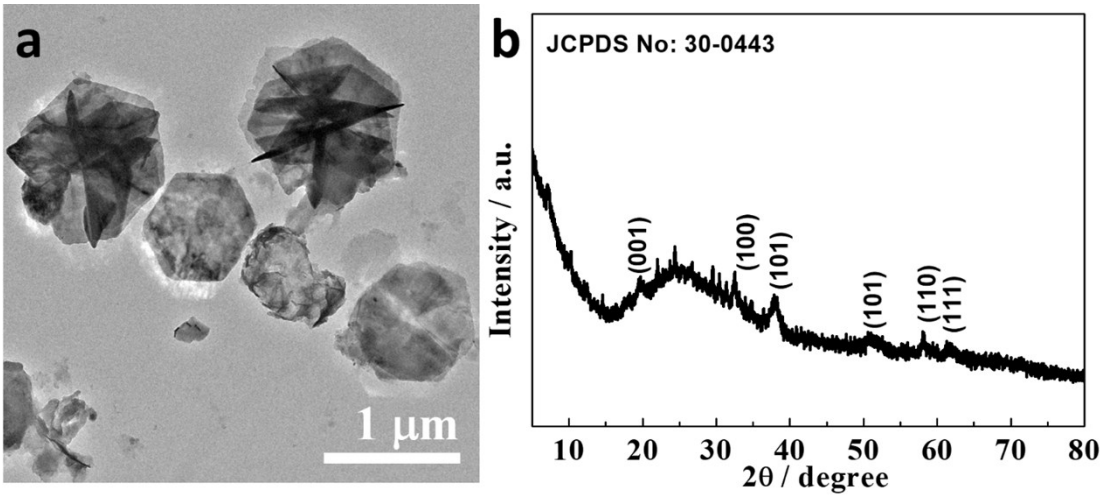

Fig. S4. (a) TEM image and (b) XRD pattern of ZIF-67 nanocrystals incubated in deionized water for 5 h with gently stirring.

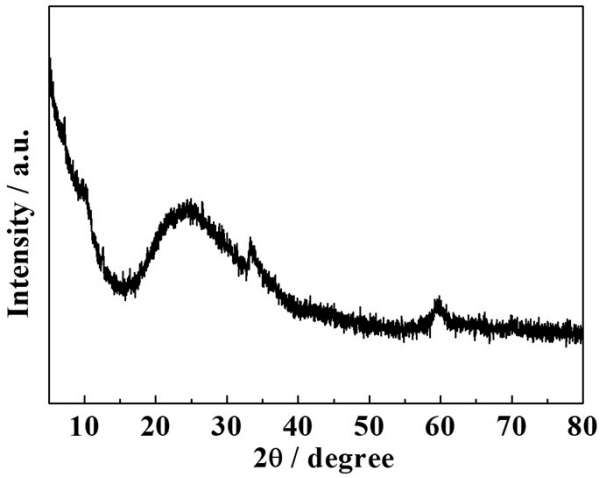

Fig. S5. XRD pattern of ZIF-67@Co-LDH yolk-shell heterostructures incubated in methanolic solution of $Co(NO_3)_2$ for 48 h with gently stirring.

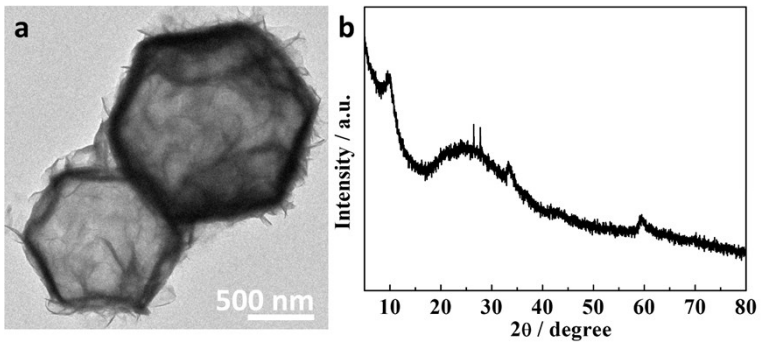

Fig. S6. (a) TEM image and (b) XRD pattern of ZIF-67 nanocrystals incubated in methanolic solution of $Co(NO_3)_2$ for 5h with gently stirring.

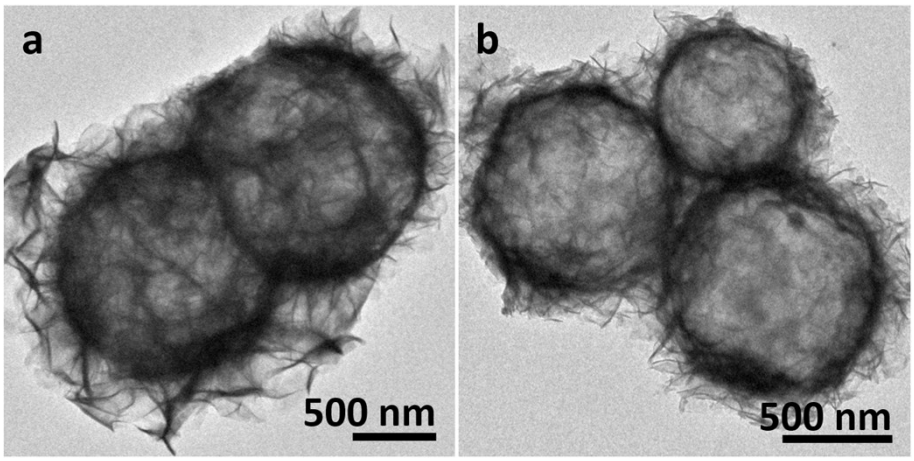

Fig. S7. TEM images of (a) ZIF-67@Co-LDH yolk-shell heterostructures dispersed into methanolic solution $Co(NO_3)_2$ for 5 h with sonication and (b) the yolk-shell heterostructures dispersed into water at 37 ^oC for 24 h.

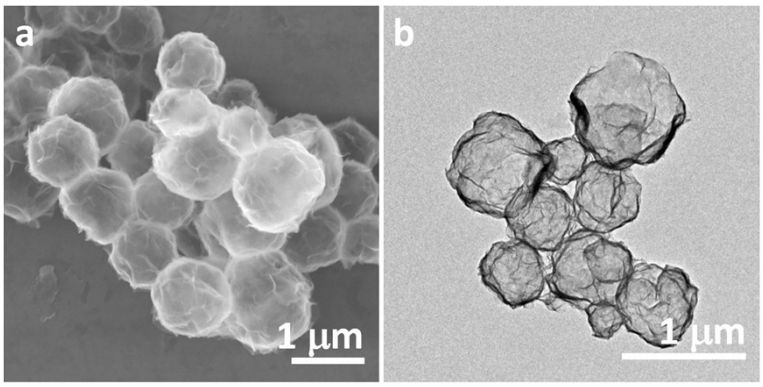

Fig. S8. (a) SEM and (b) TEM images of sample prepared by adding the methanolic solution (5 mL, 0.16M) of $Co(NO_3)_2$ in batches to the methanolic solution of Hmim (5 mL, 0.08 M) at room temperature for another 48 h without disturbance.

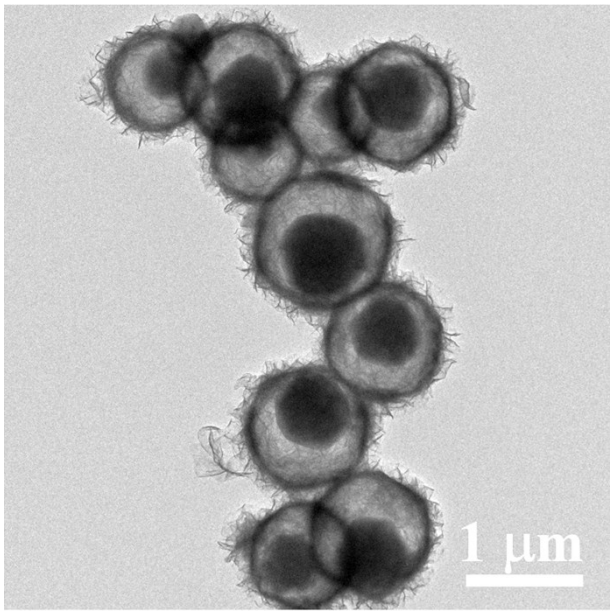

Fig. S9. TEM image of ZIF-67@Co-LDH yolk-shell heterostructures by use of methanolic solution of R6G (10^{-4} M) to replace methanol in the preparation process.

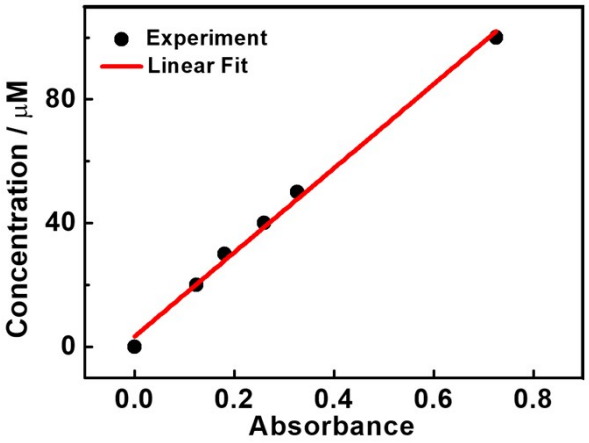

Fig. S10. The correlation between absorbance and concentration of R6G.

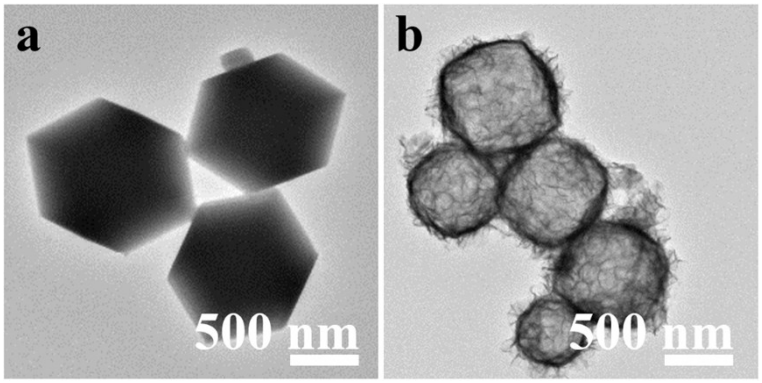

Fig. S11. TEM images of (a) ZIF-67 nanocrystals and (b) Co-LDH hollow spheres by use of methanolic solution of R6G (10^{-4} M) to replace methanol in the preparation process.