Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting Information

Defect Engineering of 2D BiOCl Nanosheets for Photonic Tumor Ablation

Chen Dai†[a], Ruizhi Hu†[a,c], Chunmei Wang†[d], Zhuang Liu[e], Shengjian Zhang[e], Luodan Yu[b], Yu Chen*[b] and Bo Zhang*[a]

[a]Department of Ultrasound, Shanghai East Hospital, Tongji University, Shanghai, 200120, People's Republic of China.Email: zhangbo2016@tongji.edu.cn

[b]State Laboratory of High Performance Ceramic and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China.Email: chenyu@mail.sic.ac.cn

[c]Department of Ultrasound, Shanghai Tenth People's Hospital, Tongji University, Shanghai, 200072, People's Republic of China.

[d]Department of Emergency Medicine and Critical Care, Shanghai East Hospital, Tongji University, Shanghai 200120, People's Republic of China.

[e]Department of Radiology, Fudan University Shanghai Cancer Center, Shanghai, 200032, People's Republic of China.

Calculation of the Extinction Coefficient and Photothermal-Conversion Efficiency.

a. Calculation of the Extinction Coefficient

According to the Lambert-Beer Law, the extinction coefficient $\varepsilon(\lambda)$ of O-BiOCl-PVP nanosheets is obtained:

$$A(\lambda)=\varepsilon LC \quad (1)$$

Where A means the absorbance at a wavelength λ (808 nm), ε means the extinction coefficient, L means path-length (1 cm) and C means the molar concentration of O-BiOCl-PVP nanosheets (in g L^{-1}). The extinction coefficient ε can be acquired by plotting the slope (in Lg^{-1} cm^{-1}) of each linear fit against wavelength. The 808 nm laser extinction coefficient (ε) of OB-1, OB-2 and OB-3 nanosheets can be obtained to be 6.02, 6.64 and 6.93 Lg^{-1} cm^{-1}, respectively.

b. **Calculation of the Photothermal Conversion Efficiency**

Based on previous study[1], the photothermal conversion efficiency (η) of O-BiOCl-PVP nanosheets at 808 nm laser irradiation can bemeasured according to the following equation:

$$\eta = \frac{hS(T_M - T_S) - Q_D}{I\left(1 - 10^{-A_\lambda}\right)} \quad (2)$$

where h is a heat-transfer coefficient, S represents the surface area of the cell, T_M means the maximum equilibrium temperature after laser irradiation until no thermal transmission away from the system, T_S means the surrounding temperature, Q_D represents the lost energy from light absorbed by the cell and is determined independently to be $Q_D = (5.4 \times 10^{-4})I$ (in mW) by using a sample cell containing pure water without O-BiOCl-PVP nanosheets, I means incident laser power (in unit of mW), A_λ means the absorbance of the O-BiOCl-PVP nanosheets at wavelength of 808 nm, In order to acquire hS, a dimensionless driving force temperature θ anda sample system time constant τ_s need to be introduced as the following equations,

$$\theta = \frac{T - T_S}{T_M - T_S} \quad (3)$$

Where T means the temperature of system surface.

$$\tau_s = \frac{\sum_i m_i C_{p,i}}{hS} \quad (4)$$

Where m means the mass of solvent (0.1 g) and C represents heat capacity of solvent (4.2 J g^{-1}).

$$\tau_s = -\frac{t}{\ln \theta} \quad (5)$$

According to the linear curve fitting of temperature cooling period in **Figure 4b-d**, τ_s of OB-1, OB-2 and OB-3 nanosheets were measured to be 216.97, 208.76 and 194.32, respectively. Therefore, *hS* of OB-1, OB-2 and OB-3 nanosheets were measured to be 1.94, 2.01 and 2.16 mW °C^{-1}, respectively. Finally, the photothermal convention efficiency (η) of OB-1, OB-2 and OB-3 nanosheets can be measured to be 5.5%, 11.5% and 13.9%, respectively.

Supplementary figures

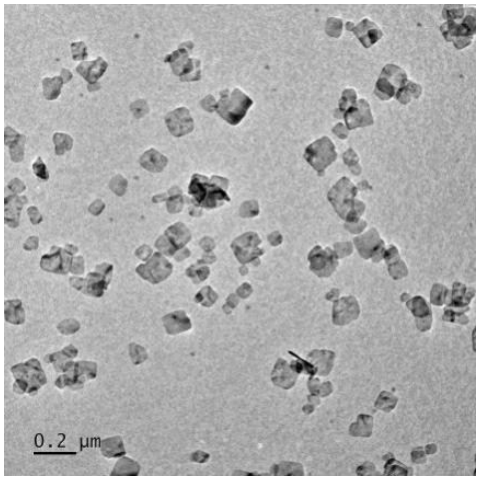

Figure S1. TEM image of BiOCl nanosheets.

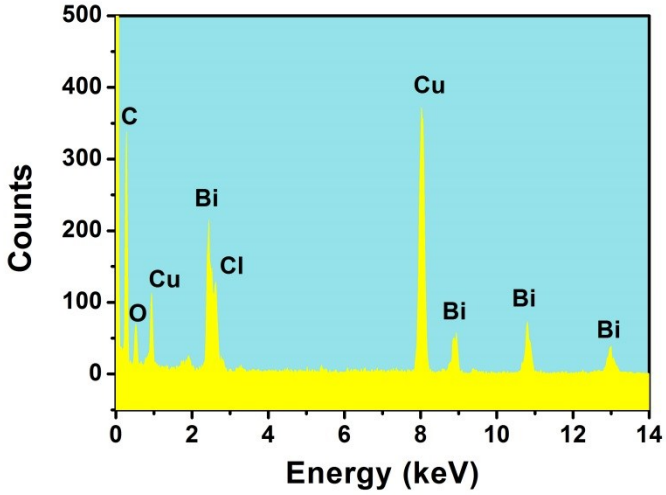

Figure S2. X-ray energy dispersive spectroscopy (EDS) of O-BiOCl nanosheets.

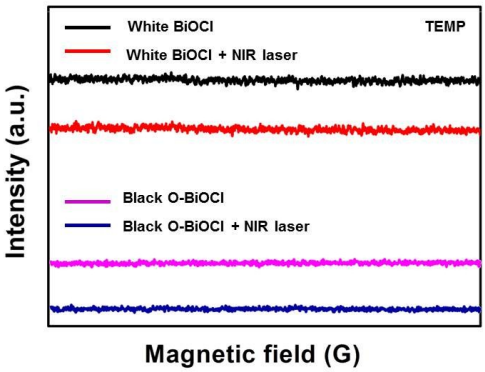

Figure S3. ESR spectra of $^1O_2$ trapped by TEMP in the presence of BiOCl and O-BiOCl nanosheets after NIR laser irradiation (2.0 W cm^{-2} for 300 s).

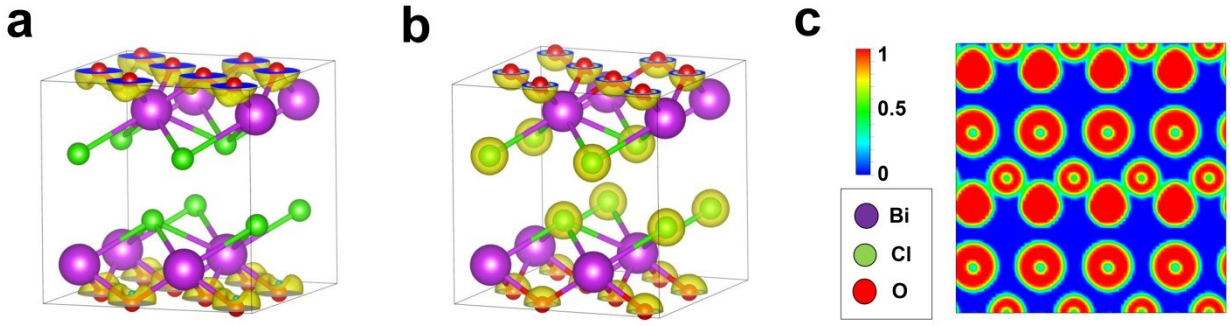

Figure S4. (a) Electron density (ED), (b) electron density difference (EDD) and (c) electron localized function (ELF) of BiOCl.

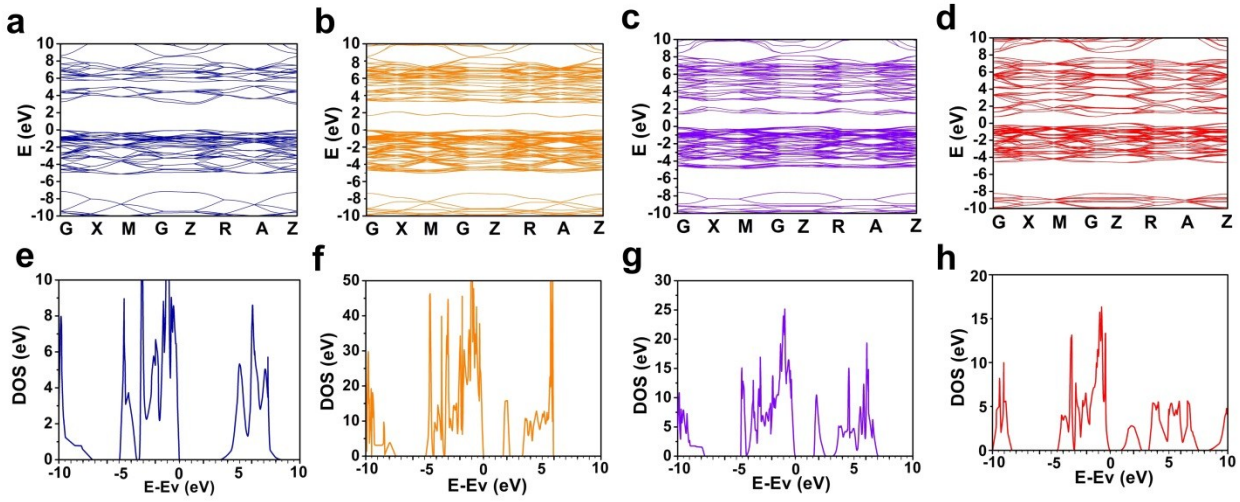

Figure S5. (a-d) Calculated band structure of BiOCl nanosheets with different oxygen-vacancy substitution ratios of 0, 0.125, 0.25 and 0.5. (e-h) Density of states (DOS) of BiOCl nanosheets with different oxygen-vacancy substitution ratios of 0, 0.125, 0.25 and 0.5.

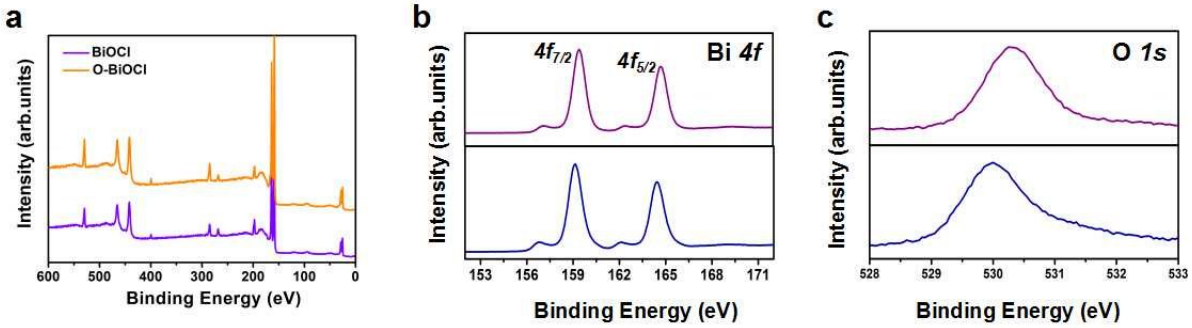

Figure S6. (a) X-ray photoelectron spectroscopy (XPS) of BiOCl and O-BiOCl nanosheets. XPS of BiOCl and O-BiOCl nanosheets in (b) Bi 4f region and (c) O 1s region.

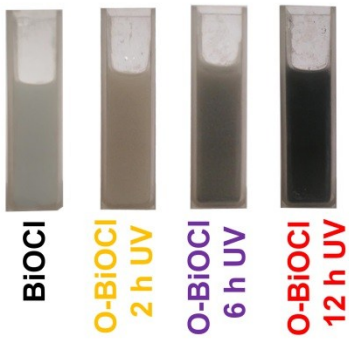

Figure S7. Digital images of BiOCl nanosheets aqueous solutions after the exposure to UV irradiation with extended treatment time durations (2, 6 and 12 h).

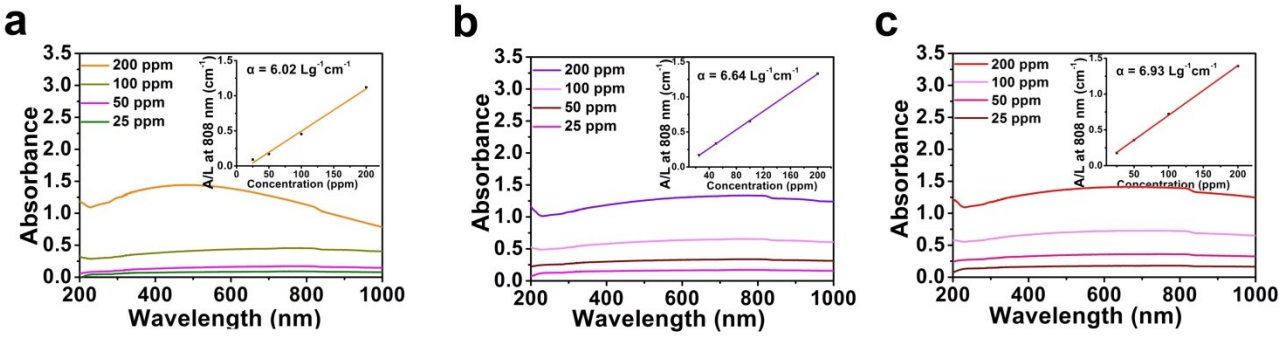

Figure S8. (a, b, c) UV-vis spectra of O-BiOCl nanosheets dispersed in aqueous solution at elevated concentrations (25, 50, 100 and 200 ppm). Inset: Normalized absorbance intensity at λ = 808 nm divided by the characteristic length of the cell (A/L) at elevated concentrations (25, 50, 100 and 200 ppm).

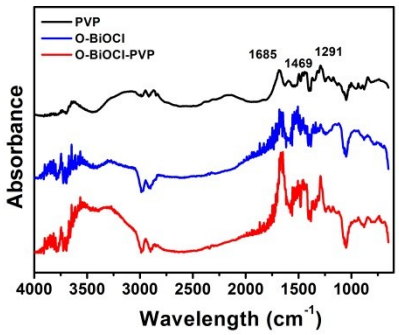

Figure S9. FTIR spectra of PVP, O-BiOCl nanosheets and O-BiOCl-PVP nanosheets.

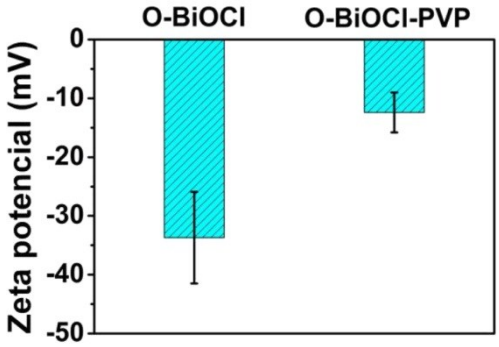

Figure S10. Zeta potential of O-BiOCl and O-BiOCl-PVP nanosheets dispersed in deionized water. n = 3, mean ± s.d.

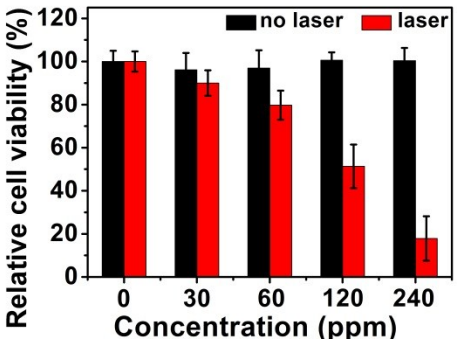

Figure S11. Relative viabilities of 4T1 cells after incubation with O-BiOCl-PVP nanosheets at different Bi concentrations (0, 30, 60, 120 and 240 μg mL^{-1}) followed by NIR laser irradiation at the power density of 2.0 W cm^{-2}.

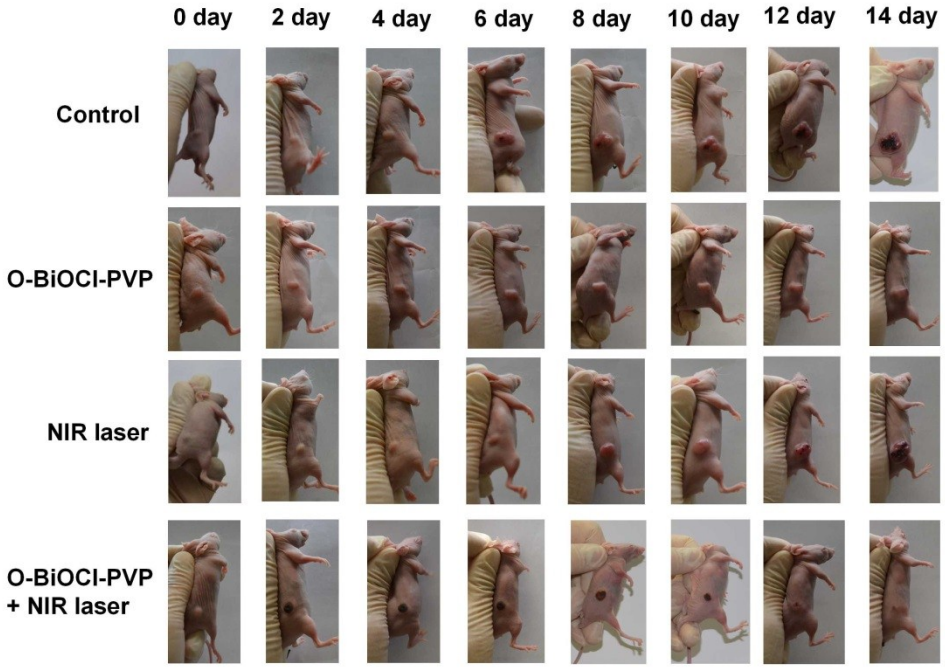

Figure S12. Digital images of tumors from control group, O-BiOCl-PVP group, NIR laser group, and O-BiOCl-PVP + NIR laser group at two weeks after different treatments.

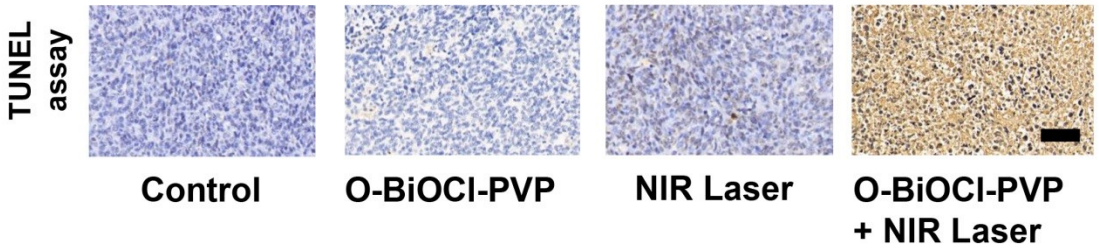

Figure S13. TUNEL staining in tumor tissues from each group after varied treatments. All the scale bars are 50 μm.

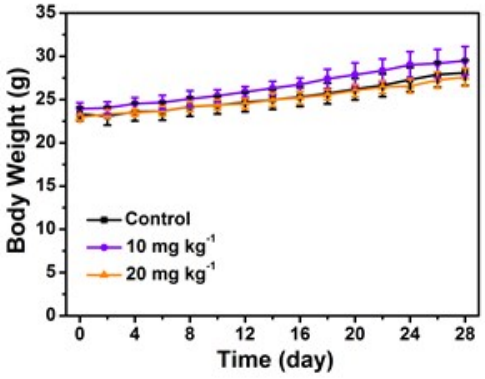

Figure S14. Time-dependent body-weight curves of Kunming mice during one-month period feeding after varied treatments.

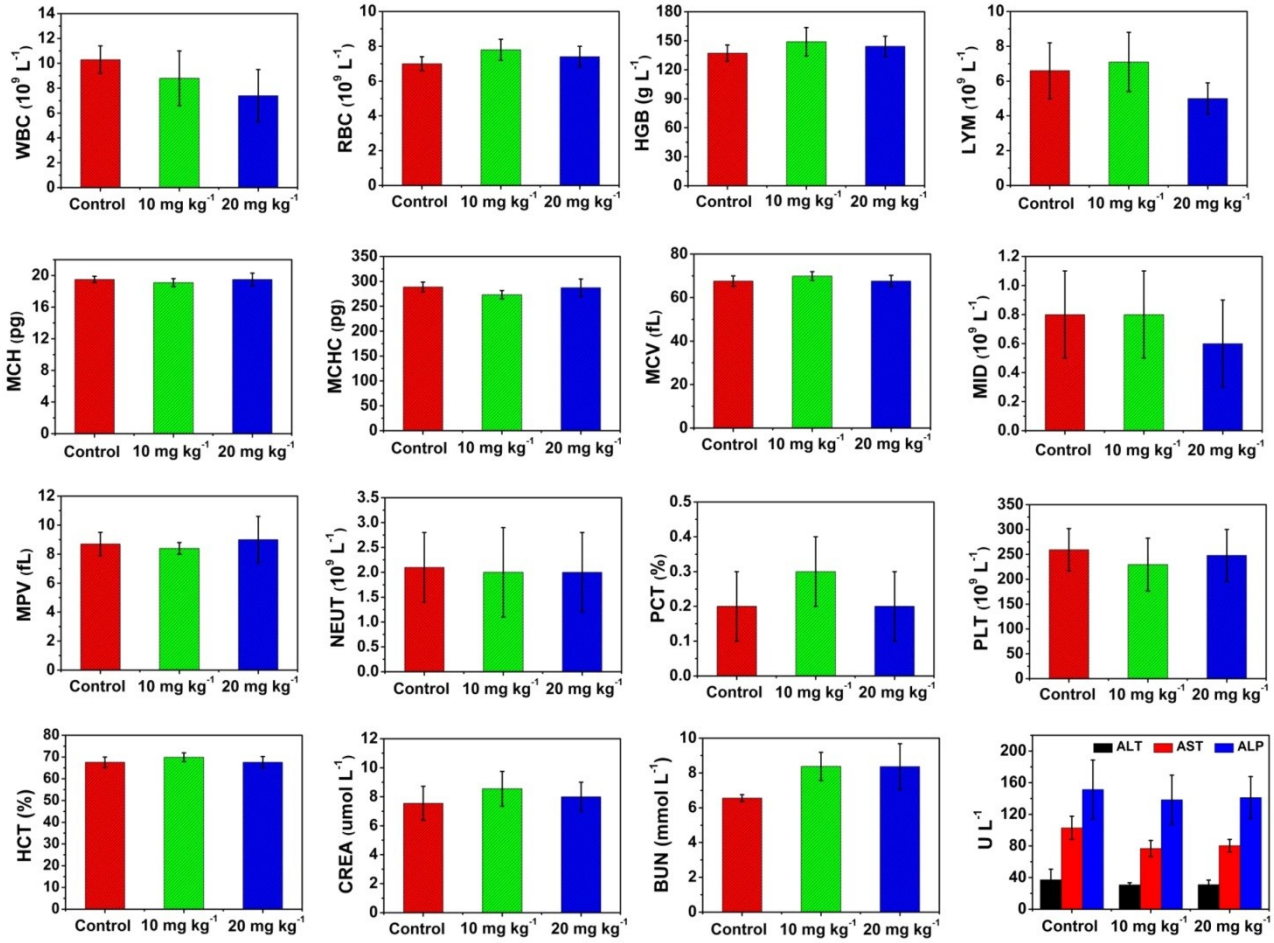

Figure S15. Hematological assay of mice from the untreated control group, O-BiOCl-PVP nanosheets (10 mg kg^{-1}) treated group and O-BiOCl nanosheets (20 mg kg^{-1}) treated group after one month of intravenous administration.

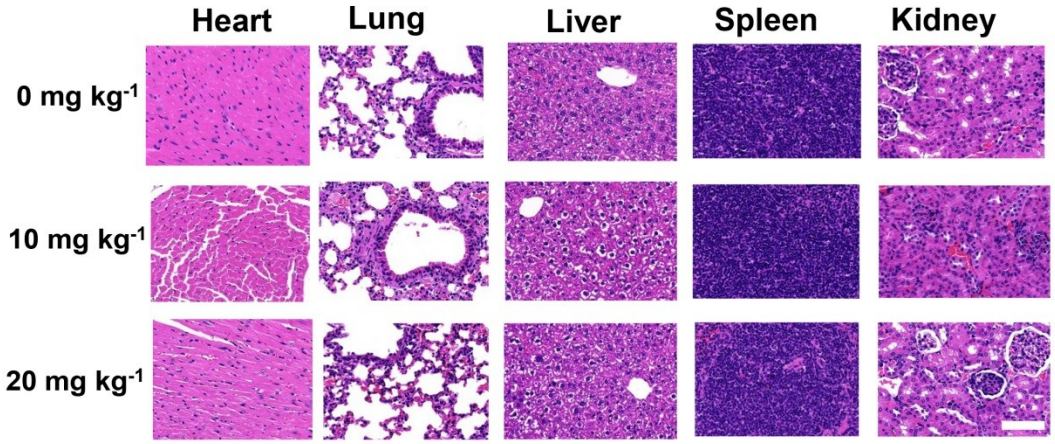

Figure S16. H&E-stained tissue sections of major organs (heart, liver, spleen, lung and kidney) from mice after one month of intravenous injection with saline, 10 mg kg^{-1} of O-BiOCl-PVP nanosheets and 20 mg kg^{-1} of O-BiOCl-PVP nanosheets. All the scale bars are 100 μm.

Reference

[1] D. K. Roper, W. Ahn, M. Hoepfner, *J. Phys. Chem. C* 2007, **111**, 3636.