Electronic Supplementary Material (ESI) for RSC Advances.

MWCNT modified Ni-Fe LDH/$BiVO_4$ heterojunction: Boosted visible-light-driven photoelectrochemical aptasensor for ofloxacin detection

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Experimental

Chemicals and reagents

The reagents used here are at the analytical level; they could be used directly. Sinopharm Chemical Reagent Co., Ltd (www.sinoreagent.com) provided sodium orthovanadate dodecahydrate ($Na_3VO_4 \cdot 12H_2O$), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), ethanol, glucose, MWCNTs (diameters < 8 nm and 0.5–2 μm length). OFL aptamer (5'-SH-ATA CCA GCT TAT TCA ATT AGT TGT GTATTG AGG TTT GAT CTA GGC ATA GTC AAC AGA GCA CGATCG ATC TGG CTT GTT CTA CAA TCG TAATCA GTT AG-3') were provided by the Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China). The stock solution of Na_2HPO_4 was mixed with the stock solution of NaH_2PO_4 to prepare the 0.1 M phosphate buffer (pH 7.0).

Synthesis of materials

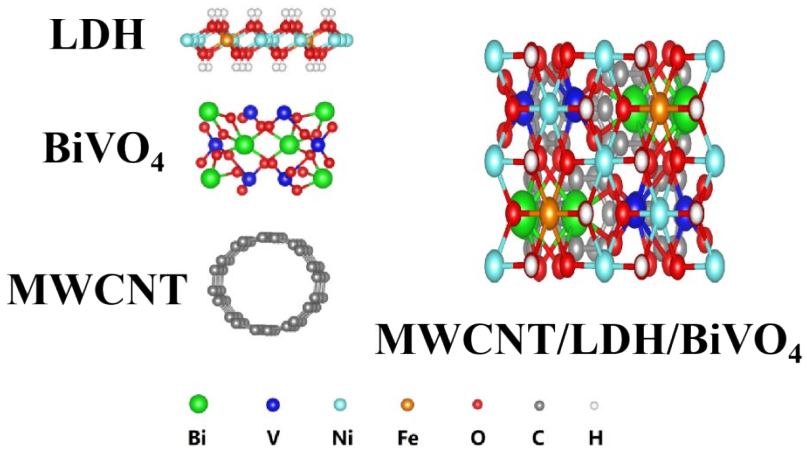
People can synthesize the microstructures of $BiVO_4$ by a single-step and simple hydrothermal method. During the course of a typical building-up process, the amount of $Na_3VO_4 \cdot 12H_2O$ was dissolved in deionized water. After adding the $Na_3VO_4 \cdot 12H_2O$ to another 20 mL of deionized water slowly, the preparation of the solution of $Bi(NO_3)_3 \cdot 5H_2O$ was taken in them. When the step of mixing all the solutions finished, pouring the final mixture solution in Teflon beaker. After that, they were autoclaved in a Teflon lined stainless steel reactor at 160 ℃ and maintained for 10 hours. After the hydrothermal reaction, let the reactor naturally reach indoor temperature. So we can obtain precipitate from materials mentioned above by isolating and filtrating with water and ethanol. And the liquor solid needed to be dried at 60 ℃ in hot air oven.

MWCNT/LDH/$BiVO_4$ microstructures were combined so as to form a more complex product by one-step hydrothermal method. Firstly, $Ni(NO_3)_2 \cdot 6H_2O$ and

$Fe(NO_3)_3 \cdot 9H_2O$ are dissolved in H_2O and continue to take the method of sonication for 0.5 h. Afterwards, the mixture solution was put into $BiVO_4$ and MWCNT, than this solution needed to be stir for 10 minutes. At last, the aforementioned mixture ought to be transferred to a 50 mL Teflon lined autoclave and heated at 150 ℃ for 10 hours in order to get MWCNT/LDH/$BiVO_4$.

Computational physics

First-principles calculations were carried out using density functional theory (DFT) with generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) implemented in the Vienna Ab-Initio Simulation Package (VASP). The valence electronic states were expanded on the basis of plane waves with the core-valence interaction represented using the projector augmented plane wave (PAW) approach3 and a cutoff of 520 eV. Convergence is achieved when the forces acting on ions become smaller than 0.02 eV/Å.



Scheme S1. DFT-optimized composite structure.

Characterization

Performing X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer exposed to Cu Kα radiation. Then conducting the X-ray photoelectron spectroscopy

(XPS) on an ESCALAB 250Xi. And using quinine bisulphate as a reference, gathering together the materials' diffuse reflection spectra (DRS) of and the $BaSO_4$ which can work like a reference on a UV-visible (UV-vis) spectrophotometer. With the help of scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the morphology of the samples was characterized. And finally, testing the conductivity of measurement solutions by using a conductivity meter (AZ 8362).

Electrochemical experiments

A CHI 660E electrochemical workstation which owns a three-electrode system is the operating platform of all these electrochemical experiments. Using the Pt wire and saturated calomel electrode (SCE) to be counter electrode and reference electrode, severally. Then regarding indium tin oxide (ITO) glass as the working electrode and a xenon lamp (PLS-SXE 300, 100 $mW \cdot cm^{-2}$, $\lambda \geq 420$ nm) as the lamp house. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 1 Hz~1 MHz at 0.1 M PBS. It is necessary to wash the ITO electrodes (10×15 mm) by water, acetone and ethanol for 5 minutes, respectively. Then experimenters dispersed 3 mg catalyst powders in the mixture of chitosan and ethanol (0.5 mL) for forming a homogeneous suspension, followed by coating 20 μL of the suspensions on ITO electrodes (0.5 cm^2). Then 20 μL OFL aptamer suspensions (1 μM) were firstly coated on MWCNT/LDH/$BiVO_4$, followed by 12 h of incubation treatment at normal temperature. Subsequently, the electrode received 60 minutes of incubation in MCH solution (20 μL, 1 mM) for constructing a nonspecific binding region specific to electrode. Distilled water was then used to adequately rinse it for the removal of excess aptamer. The fabricated MCH/aptamer/MWCNT/LDH/$BiVO_4$ served for further studies after drying.

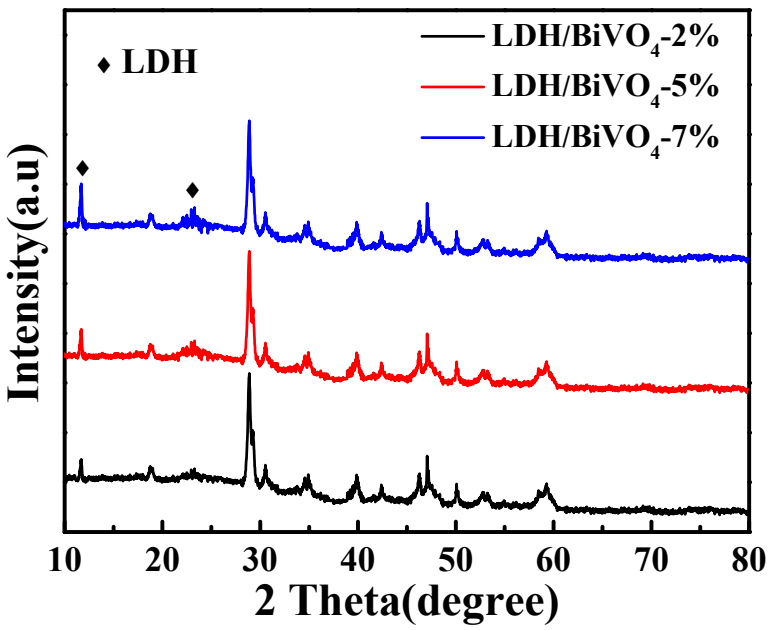


Figure S1 XRD patterns of LDH/$BiVO_4$-X%

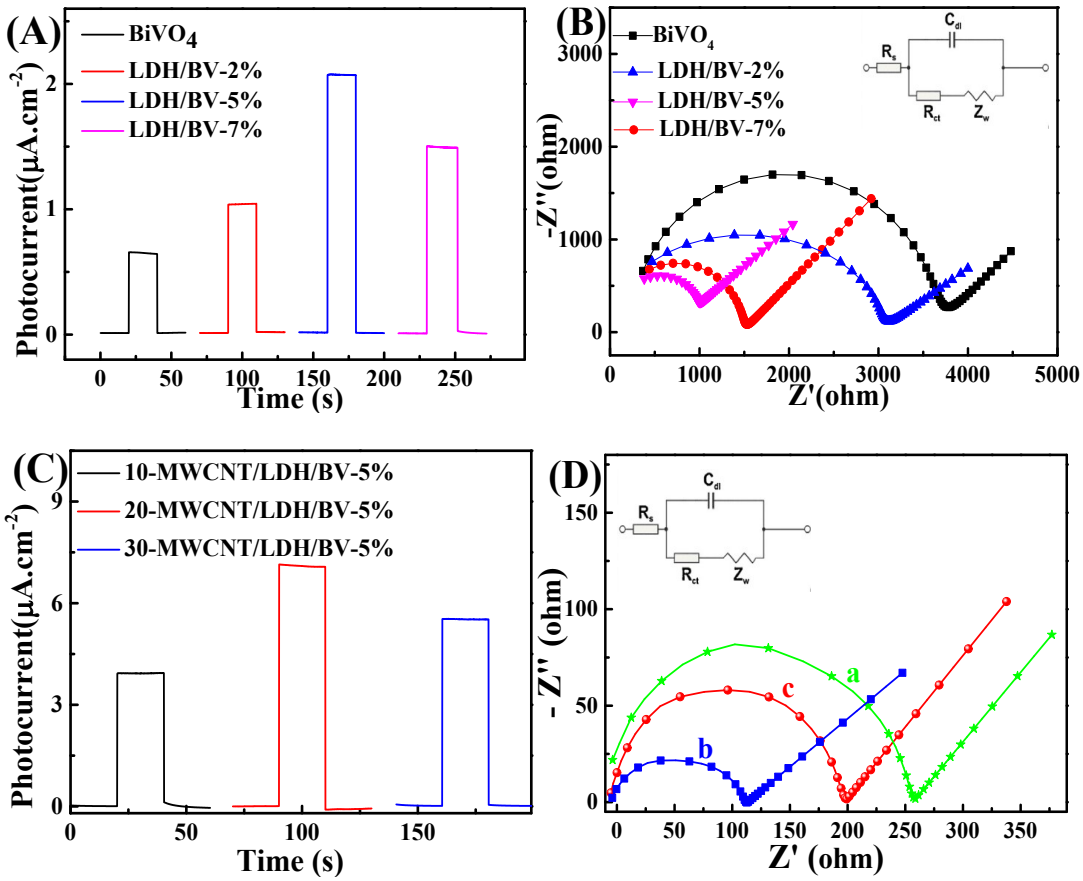


Figure S2 Photocurrent responses (A, C) and EIS spectra (B, D) (a: 10-M/LDH/BV-5%, b: 20-M/LDH/BV-5%, c: 30-M/LDH/BV-5%) of the all samples (with the insets showing the equivalent circuit).

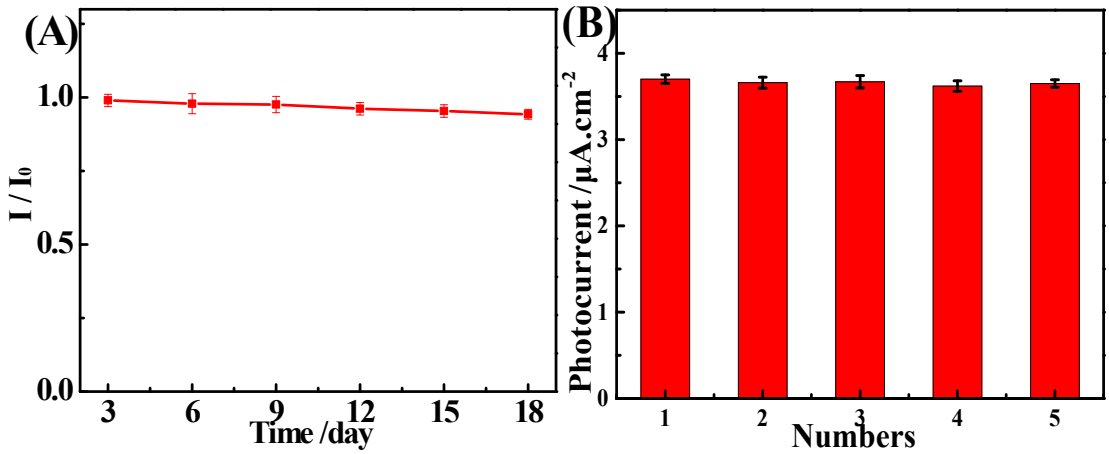


Figure S3 Stability (A) and reproducibility (B) tests of PEC sensor based on MCH/aptamer/20-M/LDH/BV-5% towards OFL.

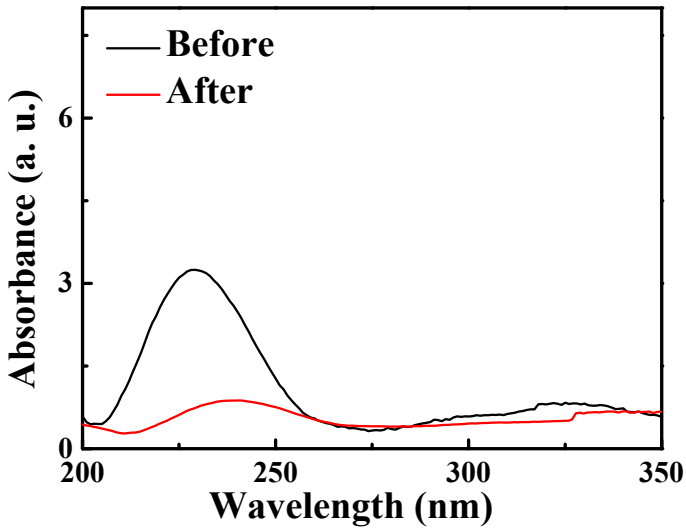


Figure S4 The UV spectrum of AA in before and after test of Electrolyte