Cobalt phosphide nanowires as efficient near-infrared light-driven antibacterial agents with high stability and cytocompatibility

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Abstract

Rapid emergence of antibiotic-resistant bacteria has brought huge threat to global healthcare systems. Alternative strategies are urgently needed to fight against these superbugs. In this study, we synthesized a series of cobalt phosphide nanoarchitectures and characterized their physicochemical properties as well as their antibacterial activities. We found that all nanomaterials showed an impressive photothermal property as indicated by their strong near-infrared (NIR) absorption capacity. In particular, 1D-CoP nanowires exhibited the optimal photothermal efficiency due to their higher aspect ratio. Under NIR light illumination, the temperature of the 1D-CoP nanowires suspension was increased by 45.4 °C within 20 min. In contrast, the temperatures of 2D-CoP nanoplates and 3D-CoP nanocubes were increased by 25.5 °C and 26.9 °C, respectively. The growth of planktonic bacteria can be effectively inhibited by 99% within 30 min under NIR irradiation with the presence of 1D-CoP nanowires in suspension. In comparison, up to 60% of the bacteria could be killed when treated with 2D-CoP nanoplates and 3D-CoP nanocubes. Moreover, all nanomaterials displayed high cytocompatibility. This work emphasizes that the anisotropy plays an important role in governing the photothermal properties of NIR-driven materials. Furthermore, the application of CoP nanowires is a promising strategy to treat antibiotic-resistant bacteria.

1. Introduction

Bacterial contamination has become an alarming public health issue that attracted worldwide attention. The long-period overuse or abuse of antibiotics leads to ever-increasing of the so-called ‘superbacteria’ with multidrug-resistance such as methicillin-resistant Staphylococcus aureus (MRSA), vancomycin-resistant Enterococcus faecium (VREF), and multidrug-resistant Acinetobacter baumannii (MRAB), posing a severe threat to global public healthcare systems [1–3]. Antibiotic resistance, for conservative estimate, causes at least 500,000 deaths every year. If this situation is left untackled, by 2050, the growing antibiotic resistance would lead to 10 million death and a reduction of 2% to 3.5% in the world’s Gross Domestic Product (GDP) each year [4]. Therefore, it is highly desirable and imperative to exploit effective antibiotic-free approaches to combat bacterial infection.

Recent advances in nanotechnology offered new opportunities to address the challenges in microbial infection by killing germs without using antibiotics [4–9]. Inspired by the fundamental principle that an elevated
temperature could accelerate the hyperthermia effects, raising temperature will damage the bacterial membrane and efficiently kill bacteria. Among various reported hyperthermia strategies, antibacterial photothermal therapy (APTT) which can employ photothermal agents (PTAs) to generate hyperthermia, is considered an innovative method in sterilization due to its high therapeutic accuracy, broad-spectrum antibacterial activities and negligible bacterial resistance [10, 11]. The locally increased temperature generated by PTAs under NIR irradiation could rupture the cell membranes, affect their permeability, and lead to bacterial death through hyperthermia-induced denaturation of bacterial proteins and irreversible bacterial destruction [12–14]. PTAs are the essential element for APTT which have witnessed a sharp alternation of several generations over the past decades [15]. A huge number of nanomaterials including noble metal materials (e.g. Ag, Au, Pd) [16–19], inorganic compounds (e.g. CuS, WS₂ and MoS₂) [20–24] and carbon-based materials (e.g. carbon nanotubes and graphene oxides) [25–27] have been successfully fabricated and employed as effective PTAs. However, certain intrinsic limitations of the currently developed PTAs, such as high costs, complicated synthetic procedures, uncontrollable size and morphology, insufficient photothermal conversion efficiency, poor photothermal stability and unreliable biocompatibility, have raised great concerns and it is still highly desirable to find better alternatives.

Previous investigations indicated that cobalt-based chalcogenides (e.g. Co₃S₄, CoS, CoS₂, etc.) display strong optical absorption in the NIR region and excellent photothermal properties, which endow them with bright application potential in PTT and other related applications [28–31]. Moreover, it is noteworthy that cobalt chalcogenides, with tunable morphology including nanowires, nanosheets, and nanospheres always demonstrate anisotropy-dependent PTT performances. Recently, cobalt phosphides (e.g. CoP, CoP₂, CoP₃, etc.), as typical transition metal-based pnictides (TMPs), stand out and have been extensively explored for environment remediation, energy conversion and storage as well as biological agents because of their higher acid-base stability compared to metal chalcogenides [32]. Meanwhile, cobalt phosphide materials with different morphology and structures, such as nanoparticles [33–35], nanorods [36, 37], nanowires [38, 39], nanosheets [40, 41] and nanotubes [42] have been developed to meet the requirement of different applications. Moreover, cobalt phosphides have wider photoabsorption region suggesting their possibility of better photothermal therapy. However, the performance of cobalt phosphides as PTAs especially anisotropy-dependent PTAs to combat bacterial infection remains unexplored.

In this work, CoP nanostructures with different morphology (1D-CoP nanowires, 2D-CoP nanoplates and 3D-CoP nanocubes) have been synthesized through a combined approach of template-free hydrothermal and subsequent phosphorization process. The aim of the study is to systematically investigate the relationship between anisotropy of the CoP nanostructures and their antibacterial performance. In this paper, the properties of the as-prepared materials were characterized by transmission electron microscopy (TEM), x-ray diffraction (XRD), UV−vis−NIR spectroscopy and x-ray photoelectron spectroscopy (XPS). The correlation between the morphology of CoP nanomaterials and their antibacterial activities were carefully investigated using colony counting, scanning electron microscopy (SEM) images and live/dead fluorescence staining methods. Furthermore, the biocompatibility of the CoP nanomaterials were evaluated in MC3T3—E1 murine osteoblas —like cells by LIVE/DEAD Viability/Cytotoxicity Kit and Cell Count Kit-8 (CCK-8).

2. Materials and methods

2.1. Materials

All the initial reagents for synthesis and analysis in the experiments were commercially available and used directly without any further treatment. Cobalt chloride tetrahydrate (CoCl₂·4H₂O), cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O) and urea (H₂NCONH₂; H₂NCONH₂ ≥ 99.0%) were purchased from Sinopharm Chemical Regent Co., Ltd (Tianjin, China). Sodium chloride (NaCl), sodium hydroxide(NaOH) and sodium dihydrogen phosphate (NaH₂PO₄) were acquired from Shanghai Aladdin Bio-Chem Technology Co., Ltd (Shanghai, China). Absolute ethanol (CH₃CH₂OH; ≥ 99.7%) was purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai China). Brain heart infusion (BHI) and Luria–Bertani broth (LB) medium were available from Qingdao Hope Bio–Technology Co. Ltd (Qingdao, Shandong, China). ViaQuant™ Viability/ Cytotoxicity Kit for Bacteria Cells was purchased from GeneCopoeia™ (Rockville, MD, USA). LIVE/DEAD Cell Imaging Kit (488/570) was obtained from Invitrogen (Carlsbad, CA, USA). Cell counting kit-8 was acquired from Dojindo Molecular Technologies (Rockville, MD, USA). High purity water (18.2 MU cm) was obtained from a Milli-Q system (Bedford, MA, USA).
2.2. Sample preparation

2.2.1. Synthesis of Co₃O₄ nanowires (1D-Co₃O₄ nanowires)

1.75 mmol of CoCl₂·4H₂O and 3.5 mmol of NaCl were dissolved in 70 ml of deionized water. After being stirred for 10 min, 3.5 mmol of urea was added into the above mixture. Subsequently, the resulted solution was sealed into a 100 ml Teflon-lined stainless steel autoclave and heated at 100 °C for 12 h. After naturally cooling down to room temperature (RT), the precipitates were rinsed with deionized water and ethanol for several times and then separated by centrifuging. The precipitates were vacuum dried at 80 °C for 24 h for further use.

2.2.2. Synthesis of Co₃O₄ nanoplates (2D-Co₃O₄ nanoplates)

For the synthesis of 2D-Co₃O₄ nanoplates, 7.5 mmol of Co(NO₃)₂·6H₂O was dissolved into 60 ml deionized water under stirring to form a clear homogeneous solution. A small amount of NaOH solution (2 M, 10 ml) was added and then obtained suspension was vigorously stirred for 1 h. Subsequently, the result was transferred into a autoclave, and heated at 100 °C for 12 h. After cooling to room temperature the synthesized products were rinsed with water and ethanol and dried at 80 °C for 24 h for further use.

2.2.3. Synthesis of Co₃O₄ nanocubes (3D-Co₃O₄ nanocubes)

For the synthesis of 3D-Co₃O₄ nanocubes, 30 mmol of Co(NO₃)₂·6H₂O and 3.75 mmol of sodium hydroxide were dissolved in 15 ml of deionized water. After being magnetic stirred for 20 min, the suspensions were sealed in a 20 ml Teflon-lined autoclave and heated at 200 °C for 4 h. Later, the suspensions were cooled down to room temperature naturally and washed with deionized water and ethanol for several times. Finally, the precipitates were dried at 80 °C for 24 h for further use.

In order to synthesize CoP nanostructures with different morphology, the obtained Co₃O₄ precursors and sodium dihydrogen phosphate were placed in two consecutively connected crucibles respectively and heated at 450 °C for 1 h under N₂ atmosphere. The resulted products were denoted as 1D-CoP nanowires, 2D-CoP nanoplates and 3D-CoP nanocubes, respectively.

3.3. Morphological and nanostructural characterization

The crystal structure of the resultant products was characterized by x-ray diffraction (XRD, Rigaku D/max-γB, Tokyo, Japan), equipped with Cu-Kα radiation source (λ = 1.5406 Å). Field emission scanning electron microscope (FE-SEM, SU-70, Hitachi, Tokyo, Japan), transmission electron microscope (TEM, JPN Thermo Fischer Talos F200x, Thermo Fisher Scientific, Waltham, USA) and ImageJ processing program were used to evaluate the morphology and the particle sizes. The surface composition and chemical states of the obtained samples were investigated by x-ray photoelectron spectroscopy (XPS, Kratos Analytical Co., Ltd, Manchester, UK) with a monochromatic Al Kα (1486.68 eV) source. The UV-vis-NIR absorbance spectra were recorded using UV-Visible spectrometer (UV-Vis, Thermo Scientific™ Evolution 201, Carlsbad, USA).

4.4. Photothermal performance measurement

Photothermal performance was measured using laser and thermal imager. Briefly, aqueous suspension containing CoP nanomaterials (100 μg ml⁻¹) was exposed to an 808 nm laser with a power of 1.5 W cm⁻² for 20 min. The temperature changes was monitored every 30 s using a thermal imager camera (E8 XT, FLIR Corp., USA). Water was used as a blank control.

4.5. In vitro antibacterial examination

Gram-positive S.aureus (ATCC 25923) and Gram-negative E.coli (ATCC 25922) were employed as the models to assess the in vitro antibacterial activity of various CoP nanomaterials. S.aureus and E.coli were cultured in fresh Brain heart infusion (BHI) or Luria–Bertani broth (LB) medium in a shaking incubator (220 r.p.m.) at 37 °C and harvested at the logarithmic growth phase. And then, the logarithmic growth phase bacterial was diluted with fresh medium which supplemented with 100 μg ml⁻¹ of samples (1D-CoP nanowires, 2D-CoP nanoplates and 3D-CoP nanocubes) with laser (808 nm, 1.5 W cm⁻²) or kept in the dark for 30 min. The bacterial cells without materials in the dark were used as control.

For CFU assay, 50 μl of the appropriate diluted bacterial suspension were coated and incubated on standard BHI or LB agar plates with a spreader for overnight at 37 °C. Assessment of colony forming unit (CFU) quantization was implemented by arithmetic on the basis of CFUs emergence As mentioned earlier [43]. Bacterial colonies were counted by Image J 1.47v and the survival rate was assessed by the following equation:

Survival rate (%) = C₀/C × 100

Where C₀ and C represent the numbers of bacteria (CFUs) in the control group (PBS) without NIR and in the experimental group, respectively.
To further investigate the antibacterial effect, the bacterial suspension were then stained for 15 min in the dark at room temperature with the ViaQuant™ Viability/Cytotoxicity Kit for Bacteria Cells comprised of NucBeacon GREEN and propidium iodide (PI). The cells were imaged using a confocal laser scanning fluorescence microscope.

For bacterial morphology observation, bacterial strains exposed to 100 μg ml⁻¹ CoP nanomaterials were observed by SEM. After 30 min. NIR irradiation or kept in dark, the bacterial suspension was collected by centrifuging, fixed with 4% paraformaldehyde and dehydrated in graded ethanol series (30%–100%). The suspensions were then dropped onto a clean aluminum foil and dried naturally for SEM observation.

2.6. In vitro cytocompatibility evaluation

The cytotoxicity induced by CoP nanomaterials was determined by live/dead staining. Briefly, MC3T3-E1 murine osteoblast-like cells (5 × 10⁴ cells ml⁻¹) purchased from the Cell Bank of Chinese Academy of Sciences were seeded on 24-well plates and exposed to different CoP nanomaterials at various concentrations (0–500 μg ml⁻¹) dispersed in the complete cultured medium for 48 h. Cells were then stained with LIVE/DEAD Cell Imaging Kit (488/570) following the manufacturer’s protocol and imaged via fluorescence microscopy to determine whether they were live (green) or dead (red). Images were then processed with Image J 1.47v. The proliferation rates of MC-3T3-E1 cells were also assessed using a cell counting kit-8 (CCK-8 kit). Briefly, MC-3T3-E1 cells were seeded 24 h before the assay in 96-well plates at a density of 1 × 10⁴ cells/well. The cells were exposed to CoP nanomaterials at various concentrations (0–500 μg ml⁻¹). At the scheduled time period (24 h and 48 h), 100 μl of serum-free DMEM containing 10% (v/v) CCK-8 was replaced and subsequently incubated at 37 °C for 2 h. The optical density (OD) was measured at λ = 450 nm using a spectrophotometer (SPECTROstar Nano, BMG Labtech Inc.). The absorption of the nanomaterials incubated cells was normalized to the absorption of control cells (untreated), which represents 100% cell viability. Each sample was prepared in triplicate, and each experiment was repeated at least three times.

2.7. Statistics

Student’s t-test was used to determine significance among the small groups. All experiments were repeated for at least three times and the results are displayed as mean ± standard deviation (SD). Standard deviation is indicated by the error bars. Statistical significance was considered at P < 0.05 (⁎).

3. Results and discussion

3.1. Structure and morphology

According to the procedures shown in Scheme 1, CoP nanostructures with different morphology (e.g., nanowires, nanoplates and nanocubes) have been obtained through a combined approach of template-free hydrothermal and subsequent phosphorization process. XRD was used to characterize the crystal structures of the different CoP nanomaterials. Subsequent phosphorization of Co₃O₄ precursor under N₂ atmosphere led to the complete conversion of Co₃O₄ powders to major CoP (JCPDS card No. 29-0497) and minor Co₃P (JCPDS card No. 32-0306) products (figure 1). It can be noted from XRD results, the relative intensity of the main peaks varied in the three samples with different preferred growth orientation. 1D-CoP nanowires and 3D-CoP nanocubes showed a preferential growth trend along the (211) plane, while 2D-CoP nanoplates showed a preferential growth trend along the (111) plane. The difference in XRD spectra between 2D-CoP nanoplates and other nanomaterials may be attributed to the difference in their structure and morphology. The peak along (211) is suppressed for the sample of 2D-CoP nanoplates indicating a decrease in the exposure of the crystal plane which might be attributed to the space confinement of the 2D structure during the growing process of crystal plane [44].

The morphology and structure details of as-prepared CoP nanomaterials were characterized by SEM. The 1D-CoP nanowires present wire-like shape with an average diameter of around 200–400 nm and length of 10 μm (figures 2(a), (d)). The 2D-CoP nanoplates exhibit plate-like shape with the width of around 200–400 nm (figures 2(b), (e)). And the as-prepared 3D-CoP nanocubes display cube-like shape with uniform size of around 200 nm (figures 2(c), (f)). It can be noted from SEM results, the relative aspect ratios varied in the three samples and the 1D-CoP nanowires and the 3D-CoP nanocubes showed a higher aspect ratios.

The microstructures of as-prepared CoP nanomaterials were further characterized by TEM. A parallel array of nanowires without homologues crossing over can be observed in figure 3(a). Lattice fringes in high resolution TEM (HRTEM) images showed that both the (211) crystal planes with d-spacing of 0.189 nm with interfacial angle of 60° appeared on 1D-CoP nanowires (figures 3(b) and (c))[45]. In addition, the corresponding FFT image spot array could be indexed as [111] zone axis (figure 3(d)). As shown in figure 3(e), the 2D-CoP nanoplates showed the plate-like shape, which were well matched with the SEM images. HRTEM images
Figures 3(f) and (g) of 2D-CoP nanoplates showed well-resolved lattice fringes with an interplanar distance of 0.247 nm, corresponding to the (111) plane of CoP, of which the spacing distances agree well with the XRD results [35]. The TEM and HRTEM images of 3D-CoP nanocubes were illustrated in figures 3(i)–(l). It can be seen TEM images of 3D-CoP nanocubes from figure 3(i), which were in constant with the SEM results. The lattice fringe space of 0.189 nm, corresponding to the (211) crystal planes and an interfacial angle of 45° can be distinctly observed [45].

The surface chemical states of the as-synthesized CoP nanomaterials were further characterized by the XPS (figure 4). As illustrated in figures 4(a), (c), (e) the Co 2p core-level spectra of CoP nanomaterials displayed two
major peaks at 797.5 eV and 781.6 eV attributed to the typical Co2p1/2 and Co2p3/2 orbitals, respectively [46]. In the P 2p spectra, the binding energy at 129.2 eV and 133.7 eV are originated from the peaks of P3− species (figures 4(b), (d), (f)) [47]. The above analysis indicated that CoP nanomaterials with nanowires, nanoplates and nanocubes morphology were successfully synthesized.

3.2. Photothermal measurement
The UV–Vis-NIR spectra of various synthesized CoP nanomaterials was recorded in the range from 250 to 1100 nm. As shown in figure 5(a), the 1D-CoP nanowires exhibits the lowest value of percentage transmittance which gives the
The strongest absorbance in the infrared regions. The strong absorbance in the NIR region inspired us to measure their photothermal performance. As illustrated in Figure 5(b), deionized water showed only a 0.8 °C temperature increase under irradiation of an 808 nm NIR laser (1.5 W cm⁻²) for 20 min. In sharp contrast to water, the temperature of the aqueous suspension of 1D-CoP nanowires, 2D-CoP nanoplates and 3D-CoP nanocubes were drastically increased by 45.4 °C, 25.5 °C and 26.9 °C with a concentration of 100 μg ml⁻¹ (Figure 5(b)), respectively. These results indicated that all CoP nanomaterials are able to convert light energy into heat efficiently via photo-absorption at 808 nm. Most of all, the 1D-CoP nanowires exhibit the best photothermal conversion ability which could be ascribed to its higher aspect ratio. In addition, the photothermal conversion efficiency and cycling stability for 1D-CoP nanowires were also observed. The photothermal conversion efficiency for 1D-CoP nanowires was calculated to be 51.6% based on a previously reported method [20], which was relatively higher than that of black phosphorus quantum dots (28.4%, 808 nm laser) [48], hollow CuS nanocubes (30.3%, 808 nm laser) [49] and gold nanorods (21%, 808 nm laser) [50]. To investigate the photothermal stability of 1D-CoP nanowires, four cycles of LASER ON/OFF experiments were conducted. As shown in Figure 5(c), the 1D-CoP nanowires showed high stability and photostability with no obvious deterioration under four on/off cycles of 20 min irradiation. All these results demonstrated that the synthesized 1D-CoP nanowires show efficient photothermal behavior and good stability.

3.2.1. In vitro antibacterial activity

Based on the photothermal effect of CoP nanomaterials, we evaluated the antibacterial activity of CoP nanomaterials against S.aureus and E.coli through CFU assay with calculating bacterial survival rates. Most pathogenic bacteria are mesophilic and thrive at temperatures between 33 °C and 41 °C. Elevated temperatures inhibit bacterial proliferation and mobility [51]. As illustrated in Figure 6, CoP nanomaterials have no antibacterial effect without NIR laser against S.aureus and E.coli with the survival rate of more than 95%. Under NIR laser irradiation, the bacteria survival rates were still above 95% in the absence of CoP nanomaterials, indicating that NIR laser alone was harmless to both bacterial strains. After treatment with NIR light, the hyperthermia generated by CoP nanomaterials enlargements the membrane permeability of bacteria and simultaneously promoted the antibacterial ability [10, 32, 53]. The survival rates of 2D-CoP nanoplates-treated S.aureus and E.coli decreased to 33% and 36%. While 3D-CoP nanocubes lead to 65% and 68% decrease in viabilities for S.aureus and E.coli, respectively. 1D-CoP nanowires exhibited the highest bactericidal efficacy,
killing 99% of \textit{S.aureus} and \textit{E.coli}, which could be ascribed to the superior photothermal effect through the locally elevated temperature.

The antibacterial effect of CoP nanomaterials was further proved by fluorescence-based cell viability assay. The fluorescence images under different treatments are shown in figure 7. Propidium iodide (PI) was used to stain dead bacteria with red fluorescence through destroyed membrane whereas NucBeacon GREEN labeled live bacteria with green fluorescence. There were almost no red spots observed in dark for PBS, 1D-CoP nanowires, 2D-CoP nanoplates and 3D-CoP nanocubes suggesting that germs were not affected by CoP nanomaterials without NIR irradiation. In PBS with NIR laser group, there was almost no dead bacteria because most of \textit{S.aureus} and \textit{E.coli} survived. For 1D-CoP nanowires group with laser irradiation only few green fluorescence was observed indicating that 1D-CoP nanowires with NIR irradiation caused serious damage to cell membranes. Whereas, more green spots were visualized when exposed to 2D-CoP nanoplates and 3D-CoP nanocubes indicating their strong antibacterial efficiency toward \textit{S.aureus} and \textit{E.coli} under NIR irradiation. All these results clearly demonstrated that the 1D-CoP nanowires had the best antibacterial efficacy which could act as a powerful photothermal agent to mediate efficient photothermal ablation of bacteria.

To further affirm the antibacterial behavior, morphological changes of germs interacting with the synthesized CoP nanomaterials are qualitatively evaluated by SEM (figures 8(a) and (b)). As shown in figure 8, germs showed perfect sphere-shaped or rod-shaped morphology with an integrated membrane without NIR irradiation. Under the exposure of NIR light for 30 min, 1D-CoP nanowires show obvious destruction effect on the bacteria. Most of the cell membrane destroyed and leakage of intracellular material leading to bacterial surface collapse indicating their effective bacteria killing abilities. But for 2D-CoP nanoplates and 3D-CoP nanocubes group, most of cell walls became wrinkled, distorted and even partly lysed after treatment for 30 min with NIR irradiation. All the results of bacterial morphology were consistent with the results of bacterial live-dead staining.
Figure 6. S. aureus and E. coli treated with four groups: PBS, CoP nanowires, CoP nanoplates and CoP nanocubes with or without NIR at the same concentration. Bacterial colonies of S. aureus (a) and E. coli (c). Survival rate of S. aureus (b) and E. coli (d). *P < 0.05.

Figure 7. Confocal fluorescent images of live or dead S. aureus (a) and E. coli (b) after treated with different groups with or without NIR light. Scale bar is 100 μm.
3.3. *In vitro* cytotoxicity evaluation

The biocompatibility of CoP nanomaterials was evaluated in MC-3T3 E1 cells by LIVE/DEAD Viability/Cytotoxicity Kit and Cell Count Kit-8 (CCK-8). As shown in figure 9(a), cells treated with different concentrations of CoP nanomaterials exhibited negligible cell death. The cytotoxicity of CoP nanomaterials was further investigated *in vitro* through CCK8 assay. Figures 9(b) and (c) showed the cell viability curve of CoP nanomaterials against MC-3T3 E1 cells. After 24 h and 48 h incubation, most of the cells remained viable under different concentrations of CoP nanomaterials. The cellular viability was estimated to be higher than 90% after 48 h in the presence of CoP nanomaterials with concentrations of 500 $\mu$g ml$^{-1}$. These results revealed that the CoP nanomaterials were suitable for biomedical applications owing to their good biocompatibility.

All in all, as PTAs, the CoP nanomaterials were suitable for APTT treatment attributed to their good photothermal effect. Bacteria will be destroyed by the hyperthermia lysis and the 1D nanowires have excellent photothermal antibacterial activity. CoP nanomaterials caused a significant antibacterial effect on both Gram-positive and Gram-negative bacterial strains. Similar to our results, previous studies have reported the antibacterial activities of Cr$_2$S$_3$–Co$_3$O$_4$ nanoparticles [54], Co$_2$O$_4$ nanoparticles and CoS nanoparticles [55]. It has also been observed that CoP nanowires have the advantages in destroying pathogens over other cobalt-based antibacterial agents due to its higher efficiency (compare with Co$_2$O$_4$) simple composition and stable properties (compare with Co$_3$O$_4$ nanoparticles and CoS nanoparticles).

4. Conclusions

In summary, CoP nanomaterials with different morphology (e.g., nanowires, nanoplates and nanocubes) were successfully prepared via a combined approach of template-free hydrothermal and subsequent phosphorization process. Materials characterization showed that CoP nanomaterials with nanowires, nanoplates and nanocubes morphology were successfully synthesized. All these CoP nanostructures have demonstrated to be effective antibacterial photothermal agents under NIR light irradiation. The 1D-CoP nanowires displayed pronounced photothermal properties. It is found that 1D-CoP nanowires as a rapid (within 30 min) and effective (99% killing efficiency) photothermal agent against both gram-positive bacteria (*S. aureus*) and gram-negative bacteria (*E. coli*) by the NIR-induced hyperthermia. Additionally, the CoP nanomaterials with various morphology showed excellent biocompatibility in contact with the mammalian cells even after 24 h and 48 h of incubation. It could be concluded that the 1D-CoP nanowires may find a great potential platform as a robust and effective sterilization for biomedical applications.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Authors contributions

Yixin Yin performed most of the experiments, collected the data, and drafted the manuscript. Linmao Ma, Yuanyuan Yan and Luning Zheng performed some of the biological experiments. Hecheng Han performed some of the materials science experiment. Xiaoyan Li interpreted the experimental results and edited the manuscript for intellectual content. Xin Xu provided advice and revised the manuscript. All authors approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.
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