Few-layered tungsten selenide as a co-catalyst for visible-light-driven photocatalytic production of hydrogen peroxide for bacterial inactivation†

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Sustainable and “green” technologies for hydrogen peroxide (H2O2) production have aroused increasing interest, yet challenges prevail in production of H2O2 for environmental applications. In this study, tungsten selenide (WSe2) with a few-layered microstructure was used as a new co-catalyst to synthesize H2O2 under visible light irradiation. The ultrathin WSe2 nanosheets were anchored onto a g-C3N4 surface by in situ growth solvothermal methods. The as-prepared WSe2/g-C3N4 showed remarkably enhanced H2O2 production efficiency without organic electron donors, which was 11.8 times higher than that of pristine g-C3N4. H2O2 was generated via O2 reduction mediated by photogenerated e−, and dissolved O2 could be generated by water oxidation and in situ used to produce H2O2 under anaerobic conditions. The introduction of WSe2 not only promoted visible light absorption, but also facilitated the charge transfer efficiency by forming a Z-scheme rather than a type II heterojunction. The photogenerated e− was enriched onto WSe2, leading to the high H2O2 production activity. Moreover, the in situ generated H2O2 could be directly used for pathogenic bacteria inactivation through Fenton reactions without external H2O2 addition. This work is expected to open an avenue for developing novel photocatalysts towards sustainable H2O2 production for water disinfection and related environmental applications.

Environmental significance
H2O2 as a “green” oxidant is of vital importance to advanced oxidation processes (AOPs) in the environmental field. However, large-scale application of H2O2-based Fenton processes is restrained by the high-cost production of H2O2 and the difficulties in the transfer and storage of liquid H2O2. This study presented the utilization of solar energy for direct production of H2O2 through the introduction of photocatalysts by applying few-layered WSe2 as co-catalysts. The generated H2O2 can also be combined with iron catalysts to construct in situ Fenton systems without addition of external H2O2, thus solving the problem of H2O2 production and storage. The newly constructed in situ Fenton systems are expected to be used for various environmental applications including pollutant degradation and inactivation of pathogenic microorganisms, such as bacteria and viruses.

1. Introduction

Hydrogen peroxide (H2O2) as an environmentally benign oxidant has been widely used in organic pollutant degradation and pathogenic bacteria inactivation.1-3 However, H2O2 is traditionally produced using the anthraquinone process, which suffers from high energy consumption.4 In addition, the direct synthetic routes using H2 and O2 in the presence of noble metal catalysts involve high risk, due to the explosive nature of the H2/O2 mixture.5 Therefore, safer and “green” methods for the production of H2O2 are highly desired and have recently attracted increasing attention worldwide.6 The semiconductor photocatalytic reaction has been regarded as one of the most promising technologies for H2O2 synthesis due to the utilization of sustainable sunlight as the energy source.7 In a photocatalytic process, O2 is captured by an excited semiconductor, photogenerated electrons from an excited semiconductor, and undergoes a two-electron reduction process to produce H2O2,6 avoiding the use of conventional methods of the explosive H2/O2 mixture. However, the most widely used
photocatalyst for H$_2$O$_2$ production is TiO$_2$, which is only active under UV irradiation. In addition, noble metals are often used as co-catalysts.\textsuperscript{9} For example, Tsukamoto \textit{et al.} have reported that the H$_2$O$_2$ production rate by pure TiO$_2$ is low, and can be significantly enhanced by loading with Au–Ag alloys.\textsuperscript{10} Moreover, H$_2$O$_2$ also suffers from decomposition under UV irradiation.\textsuperscript{11} In this regard, visible-light driven (VLD) photocatalysts for H$_2$O$_2$ production have been an intensively pursued topic in recent years. Among these identified VLD photocatalysts, graphitic carbon nitride (g-C$_3$N$_4$), being widely used as a prospective photocatalyst for pollutant degradation,\textsuperscript{12} water disinfection,\textsuperscript{13–15} H$_2$ production,\textsuperscript{16} and CO$_2$ reduction,\textsuperscript{17} has also been found to possess high activity towards H$_2$O$_2$ production.\textsuperscript{18,19} For example, Shiraishi \textit{et al.} have found a superior efficiency of H$_2$O$_2$ production over g-C$_3$N$_4$ to TiO$_2$, due to the formation of 1,4-endoperoxide species on g-C$_3$N$_4$, which facilitates the subsequent H$_2$O$_2$ production.\textsuperscript{20} However, in most of the photocatalytic H$_2$O$_2$ production systems including g-C$_3$N$_4$, sacrificial agents are always needed and H$_2$O$_2$ is often produced with electron donors (i.e. ethanol, isopropanol, etc.).\textsuperscript{20–26} The use of earth-abundant water replacing alcohols for photocatalytic H$_2$O$_2$ synthesis will fulfill the concept of clean and sustainable production. However, developing highly efficient photocatalytic systems which can produce H$_2$O$_2$ in pure water is still a challenge.\textsuperscript{27} To this end, it is very attractive to develop alternative noble-metal-free co-catalysts to promote the H$_2$O$_2$ production in pure water systems.

Recently, transition metal dichalcogenides (TMDs) have attracted boosting interest worldwide due to their layered crystal structure, high chemical stability and excellent electrochemical properties.\textsuperscript{28} Tungsten selenide (WSe$_2$), as a typical TMD widely used in solar cells\textsuperscript{29} and gas sensors,\textsuperscript{30} has also found great applications in photocatalytic water splitting\textsuperscript{31} and CO$_2$ reduction.\textsuperscript{32} Lin \textit{et al.} reported that WSe$_2$ as a co-catalyst could improve the photocatalytic performance for photocatalytic water splitting by promoting electron–hole separation.\textsuperscript{33} Duan \textit{et al.} further found that WSe$_2$ exhibits tunable band gaps when the thickness is varied from bulk to a single layer.\textsuperscript{34} The unique properties of small band gaps and layered crystal structures facilitate the high VL absorption and substance adsorption.\textsuperscript{35,36} Unfortunately, it is still unknown whether WSe$_2$ nanostructures could be used as co-catalysts for photocatalytic H$_2$O$_2$ production.

Meanwhile, pathogenic bacterial inactivation has been taken as a priority to improve water quality, as huge mortality occurred as a result of microbial contaminated water especially in developing countries. Bacterial inactivation using advanced oxidation processes (AOPs) as alternative disinfection methods has attracted increasing attention. In particular, the Fenton process is one of the most widely studied AOPs.\textsuperscript{37} However, the traditional Fenton technology requires external oxidant (\textit{i.e.} H$_2$O$_2$) addition, which inevitably increases the operation costs. Therefore, it would be interesting to utilize H$_2$O$_2$ generated by photocatalytic processes to continuously supply the oxidant needed in the Fenton process. This synergistic effect for bacterial inactivation has not been investigated in previous studies.

Herein, WSe$_2$ with different layers was used as a co-catalyst for H$_2$O$_2$ production in a g-C$_3$N$_4$ photocatalytic system. In order to achieve efficient photocatalytic H$_2$O$_2$ production in pure water under VL irradiation, few layered WSe$_2$ was loaded onto g-C$_3$N$_4$ by a facile solvothermal method. The photocatalytic H$_2$O$_2$ generation efficiencies in pure water and alcohols were also compared, and the role of WSe$_2$ in the photocatalytic process was studied in detail. Moreover, a photo-Fenton system was constructed by using the \textit{in situ} generated H$_2$O$_2$ combined with Fe(II) for bacterial inactivation without external addition of H$_2$O$_2$. To the best of our knowledge, there is no report about VL photocatalytic H$_2$O$_2$ production using WSe$_2$ as a co-catalyst for bacterial inactivation. This work is expected to shed light on the design and fabrication of WSe$_2$-based photocatalysts for H$_2$O$_2$ production, thus advancing the areas of cleaner production \textit{via} green and sustainable routes for environmental applications.

2. Experimental

2.1 Chemicals

Melamine (99%, Aladdin), sodium tungstate dihydrate (Na$_2$WO$_4$·2H$_2$O, 99.5%, Aladdin), N,N-dimethylformamide (DMF, 99.5%, Aladdin), selenium (99.9%, Aladdin), N,N-diethyl-p-phenylenediamine sulfate salt (DPD, C$_{15}$H$_{45}$N$_2$·H$_2$SO$_4$, 98%, Aladdin), sodium borohydride (NaBH$_4$, 98%, Aladdin), peroxidase from horseradish (POD, >200 units per mg, Aladdin) and ethanol (99.7%) were used as received without further purification.

2.2 Materials synthesis and characterization

Pristine g-C$_3$N$_4$ was prepared by thermal polymerization of melamine. 10 g melamine was placed in a crucible with a lid of Fe and covered by a Fe layer, then transferred into a 100 mL Teflon-lined autoclave and heated at 121.6 mg) and Na$_2$WO$_4$·2H$_2$O (0.772 mmol, 254 mg) was dissolved in 60 mL N,N-dimethylformamide (DMF) solution, followed by adding 100 mg NaBH$_4$ under vigorous stirring for 2 h. Subsequently, 2.5 g of pristine g-C$_3$N$_4$ was added to the above solution. The mixtures were vigorously stirred for 1 h, and then transferred into a 100 mL Teflon-lined autoclave and heated at 240 °C for 24 h. After cooling down to room temperature, the product was collected, washed with ethanol and distilled water several times, and dried in a vacuum at 60 °C for 24 h. Then the product was annealed at 300 °C for 5 h under an Ar atmosphere, and the final WSe$_2$/g-C$_3$N$_4$ product was obtained and denoted as CNW-4. To optimize
the efficiency, WSe$_2$/g-C$_3$N$_4$ samples with different weight ratios of WSe$_2$ (5.5%, 7.1%, 8.7%, 12% and 13.7%) were also synthesized by the same process, and denoted as CNW-1, CNW-2, CNW-3, CNW-5 and CNW-6, respectively.

To test whether the treatment with NaBH$_4$ in the preparation procedure would affect the photocatalytic properties of pristine g-C$_3$N$_4$, control experiments were added to synthesize bare g-C$_3$N$_4$ by the similar method in which only NaBH$_4$ was added (without Se powder and Na$_2$WO$_4$-2H$_2$O), and the obtained bare g-C$_3$N$_4$ product was denoted as BCN. In addition, pure WSe$_2$ was also synthesized by the similar method without the addition of pristine g-C$_3$N$_4$. The as-prepared samples were characterized by XRD, FTIR, SEM, TEM, BET, PL and electrochemical tests. Rotating disc electrode (RDE) tests were employed to investigate the number of electron transfer for O$_2$ reduction. The details of the synthetic procedure for WSe$_2$ and the characterization methods can be found in the ESI.

2.3 Photocatalytic H$_2$O$_2$ production experiments

In a typical test, 50 mg of the as-prepared WSe$_2$/g-C$_3$N$_4$ was dispersed in 50 mL pure distilled water in a container with a cooling water jacket outside, followed by ultrasonic treatment for 1 min. The aqueous suspension was stirred in the dark for 20 min, and then irradiated by a 300 W Xe lamp with a UV cutoff filter (λ > 420 nm), while being continuously bubbled with an O$_2$ flow. The light intensity was fixed at 50 mW cm$^{-2}$ which was determined using a photometer (FZ-A, PerfectLight, China), and the reaction temperature was maintained at 25 °C during the experiments. At given time intervals, aliquots of the suspensions were taken from the reaction cell, and the produced concentrations of H$_2$O$_2$ were determined by the DPD/POD method according to the previous literature. Briefly, 400 μL of phosphate buffer, 1120 μL of water, 1000 μL of the filtered sample, 50 μL of DPD solution and 50 μL of POD solution were mixed and kept under vigorous stirring for 90 s. Then, the concentration of H$_2$O$_2$ was obtained by analyzing the absorbance at 551 nm with an excitation wavelength of 460 nm with an emission wavelength of 332 nm.

3. Results and discussion

3.1 Structure and morphology characterization

The XRD patterns in Fig. 1(A) show that the pristine g-C$_3$N$_4$ has two typical diffraction peaks centered at 13.1° and 27.6° respectively, which can be assigned to the (1 0 0) and (0 0 2) crystal facets of g-C$_3$N$_4$ respectively, in agreement with previous studies. In addition, the XRD peaks of the obtained WSe$_2$ can be well indexed to the typical hexagonal structure of WSe$_2$ [JCPDS No. 38-1388], suggesting that pure WSe$_2$ was successfully synthesized by the present solvothermal method without other impurities. For the as-prepared WSe$_2$/g-C$_3$N$_4$ composite samples, the positions of the diffraction peaks remained unchanged, indicating that the basic structure of g-C$_3$N$_4$ was not changed after loading with WSe$_2$. No characteristic diffraction peaks of WSe$_2$ can be observed, which is attributed to the weak crystallization and high dispersion of the anchored WSe$_2$ nanoparticles. In the FT-IR spectra (Fig. 1(B)), the pure WSe$_2$ shows almost no sharp peaks in the range of 650–3700 cm$^{-1}$, in agreement with a previous study. For pristine g-C$_3$N$_4$, the sharp peak observed at 808 cm$^{-1}$ is attributed to typical vibration of triazine rings, while the strong characteristic peaks in the range of 1100–1700 cm$^{-1}$ can be assigned to the stretching vibration of the C–N bond and C≡N bond in heterocyclic g-C$_3$N$_4$ compounds. In addition, the peaks located in the 3100–3400 cm$^{-1}$ region are attributed to the –NH$_2$ groups in the g-C$_3$N$_4$ structure. It was noted that the peak positions of BCN (g-C$_3$N$_4$ treated with NaBH$_4$) were similar to those of pristine g-C$_3$N$_4$, suggesting that g-C$_3$N$_4$ alone would not change the molecular structure of g-C$_3$N$_4$. In addition, the as-prepared WSe$_2$/g-C$_3$N$_4$ composites also exhibited similar FT-IR spectral profiles with much lower peak intensity than those of pristine g-C$_3$N$_4$ and BCN, which could be obviously ascribed to the presence of black WSe$_2$ absorbing infrared light. The light harvesting properties were further studied by UV-vis absorption spectroscopy (Fig. 1(C)). Evidently, the pristine g-C$_3$N$_4$ and BCN exhibited typical absorption spectra with limited light absorption in the VL region (λ < 450 nm). Interestingly, the VL absorption wavelength was extended to 800 nm after loading with WSe$_2$ nanosheets on the surface of g-C$_3$N$_4$, due to the high VL absorption properties of WSe$_2$. With the increase of WSe$_2$.
loading amounts, the color of g-C\textsubscript{3}N\textsubscript{4} was gradually changed from yellow to a dark color (Fig. 1(C) upper image), further confirming the existence of WSe\textsubscript{2} in the composites. The significantly enhanced light absorption would be beneficial to the photocatalytic H\textsubscript{2}O\textsubscript{2} production efficiency.

The typical SEM image of the WSe\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} composites shows that many ultra-thin WSe\textsubscript{2} nanosheets are grown on the surface of g-C\textsubscript{3}N\textsubscript{4}, indicating the successful fabrication of WSe\textsubscript{2} on g-C\textsubscript{3}N\textsubscript{4} (Fig. 1(D)). The particle size of WSe\textsubscript{2} nanosheets attached onto the surface was much smaller than that of layered g-C\textsubscript{3}N\textsubscript{4}. In contrast, pure WSe\textsubscript{2} exhibits a hierarchical flower-like structure self-assembled from ultra-thin nanosheets, while pristine g-C\textsubscript{3}N\textsubscript{4} and BCN exhibit a similar layered structure (Fig. S1†). To further confirm the existence of WSe\textsubscript{2} nanosheets on the surface of g-C\textsubscript{3}N\textsubscript{4}, TEM was conducted as shown in Fig. 2(A). Self-assembled nanosheets of WSe\textsubscript{2} were anchored onto the edge of g-C\textsubscript{3}N\textsubscript{4}, and the sizes of g-C\textsubscript{3}N\textsubscript{4} nanosheets were observed to be much larger than that of WSe\textsubscript{2} nanosheets, in agreement with the above SEM image. The HR-TEM image in Fig. 2(B) further confirms 6 layers of nanosheets with an interlayer spacing of ∼0.67 nm, which corresponds to the (002) planes of WSe\textsubscript{2} according to ref. 47. The HAADF image and corresponding element mapping analysis demonstrate the presence of C, N, W and Se elements in the composites (Fig. 2(C)–(G)), and the amounts of W and Se were obtained to be 0.66 atom% and 1.34 atom%, respectively. The elemental ratio of W to Se was close to 1:2, confirming the successful synthesis of WSe\textsubscript{2} nanosheets onto g-C\textsubscript{3}N\textsubscript{4} to form heterojunctions of binanosheets.

### 3.2 Photocatalytic H\textsubscript{2}O\textsubscript{2} production

The photocatalytic H\textsubscript{2}O\textsubscript{2} production experiments were conducted in pure water without any electron donors. As shown in Fig. 3(A), all the as-prepared samples exhibit different photocatalytic activities towards H\textsubscript{2}O\textsubscript{2} production. In general, the H\textsubscript{2}O\textsubscript{2} amounts increase with reaction time, and gradually slow down and tend to reach equilibrium, due to the simultaneous decomposition of H\textsubscript{2}O\textsubscript{2}.\textsuperscript{5} The pristine g-C\textsubscript{3}N\textsubscript{4} and pure WSe\textsubscript{2} show a rather limited activity, and only about 6.85 μmol L\textsuperscript{-1} and 10.71 μmol L\textsuperscript{-1} H\textsubscript{2}O\textsubscript{2} were generated within 2 h. Interestingly, the CNW composites exhibit remarkably higher activity than pristine g-C\textsubscript{3}N\textsubscript{4} and pure WSe\textsubscript{2}. Fig. 3(B) compares the H\textsubscript{2}O\textsubscript{2} generation concentration within 2 h under VL irradiation. It was found that with
increasing WSe2 loading amount, the H2O2 generation efficiency was first increased and then decreased, probably because the excess WSe2 would block light penetration to reach g-C3N4 and decrease the active sites of the catalyst. The highest activity was achieved for the CNW-4 sample, and the H2O2 generation could reach 81.24 μmol L⁻¹, which was 11.8 times higher than that of pristine g-C3N4.

A previous study has reported that the NaBH4 treatment of g-C3N4 can lead to enhanced photocatalytic H2O2 production activity of g-C3N4 by creating N vacancies.⁵⁸ To verify whether the improvement of H2O2 production is caused by WSe2 loading or by NaBH4 treatment, control experiments were conducted using the bare g-C3N4 treated with NaBH4 (BCN). Results show that BCN exhibits an enhanced H2O2 production concentration within the same 2 h (19.50 μmol L⁻¹) compared with pristine g-C3N4, but the efficiency is still much lower than CNW-4 (81.24 μmol L⁻¹). This result confirms that the in situ loading of WSe2 as a co-catalyst is crucial to obtain the high H2O2 production efficiency. These results indicate that WSe2 nanosheets could be new noble-metal-free co-catalysts for photocatalytic H2O2 production.

Table S1† compares the photocatalytic H2O2 production efficiency in different systems reported in this work as well as in early reported references. The CNW composites show superior H2O2 production efficiency to most of the reported photocatalytic systems, especially in pure water, suggesting their great potential for practical use. Moreover, the wavelength-dependent photocatalytic H2O2 production was also studied using monochromatic light irradiation. Results showed that the VL responsive wavelength could be extended to 450 nm, which coincides with the VL absorption cutoff wavelength of WSe2/g-C3N4 (Fig. S2†). The calculated apparent quantum yield (AQY) at 420 nm was 7.18% and 0.69% for WSe2/g-C3N4 and pristine g-C3N4, respectively. Obviously, the AQY of photocatalytic H2O2 production over WSe2/g-C3N4 is 10.4 times as high as that over pristine g-C3N4, which is also higher than the reported value (6.5%) obtained on polyoxometalate/g-C3N4.⁴⁹ It was also found that the H2O2 production efficiency could be further promoted by adding electron donors. As shown in Fig. 3(C), the H2O2 production is increased from 81.24 μmol L⁻¹ (pure water) to 151.77 μmol L⁻¹ within the same 2 h when adding 10% ethanol as the electron donor. This value was further increased to 240.08 μmol L⁻¹ when absolute ethanol (99.8%) was used, nearly 3.0 times higher than using pure water. This result also confirmed that H2O2 was produced via O2 reduction by photogenerated e⁻ from the conduction band (CB) of the photocatalyst, which was different from some studies that H2O2 could be produced by photogenerated h⁺ from the valence band (VB).⁵⁰ Therefore, O2 should be a crucial factor for the production activity of H2O2. However, it was interesting to find that the H2O2 generation was only slightly inhibited under simulated anaerobic conditions with N2 aeration (Fig. 3(C)), suggesting that external O2 is not so important in this photocatalytic system. This can be rationalized that the CNW composites can also serve as photocatalysts for O2 evolution, since the VB potential of g-C3N4 is high enough to generate O2.⁵¹,⁵² To support this assumption, dissolved O2 in a sealed reactor was monitored during the reaction, and a steady increase in O2 content was observed (Fig. S3†), suggesting that the CNW composites can really generate O2 in situ which can be used for subsequent H2O2 production. These results suggest that the novel CNW system has potential to be used under anaerobic conditions to produce H2O2, thus further greatly expanding its application range in environmental remediation. To test the photostability, the used photocatalysts were recycled by centrifugation, washing and drying, and then three successive repeated experiments were examined. Fig. 3(D) shows that no obvious decline of H2O2 production efficiency over CNW-4 is observed within 50 min of VL irradiation during three cycles of H2O2 production. In addition, the crystal structure of CNW-4 remains unchanged before and after the reaction (Fig. S4†), indicating its good photostability and durability.

3.3 Enhanced mechanisms of H2O2 production

It is well known that the surface area plays a significant role in determining the photocatalytic activity. Therefore, the Brunauer–Emmett–Teller (BET) surface areas of the pristine g-C3N4, BCN and CNW-4 composite samples were evaluated. However, the BET surface areas of the three samples were less than 10 m² g⁻¹, which indicates that the excellent photocatalytic performance of CNW-4 did not originate from
higher surface area. The nitrogen adsorption–desorption isotherms of pristine g-C_3N_4, BCN and CNW-4 are also shown in Fig. S5.† The three samples exhibited type-IV isotherms with a hysteresis loop. Additionally, the pore volumes of pristine g-C_3N_4, BCN and CNW-4 were obtained to be 0.038733 cm^3 g^{-1}, 0.039347 cm^3 g^{-1} and 0.065480 cm^3 g^{-1}, respectively. These results indicate that the surface area and porosity have little influence on the enhanced activity of the CNW composites.

The spatial charge separation ability of the CNW-4 composite was also studied by a photoelectrochemical study. Fig. 4(A) presents the photocurrent response of the samples under VL irradiation. It was clear that the CNW-4 sample displays a much higher photocurrent density than pristine g-C_3N_4 and BCN, suggesting that WSe_2 nanosheets could accelerate the spatial charge separation of g-C_3N_4. Electrochemical impedance spectroscopy (EIS) was conducted and the results are shown in Fig. 4(B). The Nyquist plots were fitted with a Randles circuit (inset of Fig. 4(B)) which was composed of charge transfer resistance (R_{ct}), electrolyte resistance (R_s), and constant phase elements (CPE). The smaller arc radius of the EIS pattern suggested the more efficient separation of photogenerated e^-–h^+ pairs. It can be observed that the arc radius of CNW-4 is smaller than that of pristine g-C_3N_4 and BCN, further confirming that the introduction of WSe_2 nanosheets can increase the interfacial charge-transfer efficiency. In addition, the charge separation efficiency was also examined by the photoluminescence (PL) technique. As presented in Fig. 4(C), for pristine g-C_3N_4 and BCN, the spectrum shows a strong emission peak at 460 nm, which originates from the band-to-band recombination of electrons and holes. Nevertheless, the intensity of PL was dramatically decreased when loading WSe_2 nanosheets on the surface of g-C_3N_4, which means that the recombination of electrons and holes was effectively inhibited. To further obtain more information about spatial charge separation and transfer, the time-resolved PL spectra were investigated and the results are shown in Fig. 4(D). It was found that the average PL lifetime was decreased from 5.39 ns to 3.82 ns after incorporating with WSe_2 as the co-catalyst. The decreased lifetime suggested that the radiative recombination of charge pairs was suppressed, and the depopulation of the excited states in the CNW composites occurred more readily through nonradiative pathways, leading to enhanced charge transfer and separation.\textsuperscript{21} Furthermore, the charge transfer efficiency can be calculated from the following equation (eqn (2)).\textsuperscript{53}

\[
E = 1 - \frac{\tau_{DA}}{\tau_D}
\]
where $\tau_{DA}$ and $\tau_D$ are the average PL lifetimes of g-C$_3$N$_4$ with and without WSe$_2$, respectively. The calculated charge transfer efficiency in the CNW composites was obtained to be 29.13%.

To gain insights into the reaction pathway of O$_2$ reduction, rotating disk electrode (RDE) studies were performed.$^{54,55}$ The linear sweep voltammetry (LSV) measurements indicate that the diffusion-limited current density is increased as the rotation rate changes from 100 to 1800 rpm due to the enhanced diffusion of the electrolyte (Fig. S6(A) and (B)$^\dagger$). The number of electrons involved in the process of O$_2$ reduction that is calculated from the Koutecky–Levich equation is $2.1 - 2.54$ and $2.35 - 2.76$ for g-C$_3$N$_4$ and CNW-4, respectively (Fig. S6(C) and (D)$^\dagger$). This indicates that O$_2$ reduction over both catalysts is dominated by the 2e$^-$ pathway. The relatively higher electron-transfer numbers over CNW-4 can be attributed to the enhanced charge transfer at the heterojunction interfaces.$^{54}$

To further reveal the effects of the CNW heterojunctions on the separation of photogenerated e$^-$/h$^+$ pairs, the band structures of g-C$_3$N$_4$ and WSe$_2$ were studied by analyzing Mott–Schottky plots (Fig. S7(A) and (B)$^\dagger$). As shown, both g-C$_3$N$_4$ and WSe$_2$ present positive slopes of the Mott–Schottky plots, indicating that both samples are typical n-type semiconductors.$^{56}$ Therefore, the CB of g-C$_3$N$_4$ and WSe$_2$ is located at about $-0.88$ V and $-1.07$ V vs. NHE, respectively. Given that the bandgap of g-C$_3$N$_4$ and WSe$_2$ is about 2.70 eV and 1.60 eV,$^{57}$ the valence band (VB) potential of g-C$_3$N$_4$ and WSe$_2$ nanosheets can be calculated to be 1.82 V and 0.53 V vs. NHE, respectively. Obviously, the potential of OH/$\cdot$OH (+1.99 V) is more positive than the VB of g-C$_3$N$_4$ and WSe$_2$ nanosheets. Since the H$_2$O$_2$ produced from the VB is believed to be mediated by coupling of $\cdot$OH (eqn (3)),$^5$ the lack of $\cdot$OH indicates that the H$_2$O$_2$ generation cannot be triggered by photogenerated $h^+$ from the VB. However, H$_2$O$_2$ is mainly produced via the reduction of O$_2$ by photogenerated e$^-$ from the CB (eqn (4)). It should be noted that the CNW composites have a similar CB potential to g-C$_3$N$_4$ (Fig. S8$^\dagger$), which suggests that anchoring of WSe$_2$ nanosheets would not change the band structure of bulk g-C$_3$N$_4$.

$$\text{HO}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (3)$$

$$\text{O}_2 + e^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \quad (4)$$

According to above results, the CB of WSe$_2$ nanosheets is more negative by approximately $-0.1$ V than the $V_{fb}$ in n-type semiconductors.$^{56}$ Therefore, the CB of g-C$_3$N$_4$ and WSe$_2$ is located at about $-0.88$ V and $-1.07$ V vs. NHE, respectively. The CB of g-C$_3$N$_4$ and WSe$_2$ is more positive than the VB of g-C$_3$N$_4$ and WSe$_2$ nanosheets. Since the H$_2$O$_2$ produced from the VB is believed to be mediated by coupling of $\cdot$OH (eqn (3)),$^5$ the lack of $\cdot$OH indicates that the H$_2$O$_2$ generation cannot be triggered by photogenerated $h^+$ from the VB. However, H$_2$O$_2$ is mainly produced via the reduction of O$_2$ by photogenerated e$^-$ from the CB (eqn (4)). It should be noted that the CNW composites have a similar CB potential to g-C$_3$N$_4$ (Fig. S8$^\dagger$), which suggests that anchoring of WSe$_2$ nanosheets would not change the band structure of bulk g-C$_3$N$_4$.
transfer mode (Fig. S7(D)†) under VL illumination. It has been reported that g-C₃N₄ meets the thermodynamic requirements for photocatalytic water oxidation, since its VB potential is located at a value more positive than the H₂O to O₂ oxidation potential (1.23 V vs. NHE).⁵⁸ The photocatalytic water oxidation for O₂ evolution over g-C₃N₄ has also been widely reported in previous studies.⁵⁹–⁶³ In contrast, the VB potential of WSe₂ is insufficient for water oxidation to O₂ evolution. In the present study, the CNW composites can produce O₂ by photocatalytic water oxidation (Fig. S3†). Therefore, the photogenerated h⁺ is expected to oxidize water at the VB of g-C₃N₄ rather than WSe₂. In this scenario, the charge transfer should follow the Z-scheme mode rather than the type II transfer mode. In other words, both g-C₃N₄ and WSe₂ nanosheets can be excited with VL irradiation, and then photogenerated e⁻ migrates from the CB of g-C₃N₄ to the VB of WSe₂ forming a Z-scheme type of electron transport. WSe₂ acts as the electron sinker which traps the photogenerated e⁻ from g-C₃N₄. H₂O₂ is then produced at the reduction site of WSe₂, and water oxidation occurs at the oxidation site of g-C₃N₄. The loading of WSe₂ not only facilitates the charge separation, but also promotes the electron energy level at the reduction site, resulting in enhanced photocatalytic H₂O₂ production activity.

3.4 Application in bacterial inactivation

Fig. 5(A) shows E. coli inactivation efficiency using the as-prepared samples as photocatalysts under VL irradiation. It was found that both pristine g-C₃N₄ and CNW-4 exhibited very limited activity towards E. coli inactivation within 180 min. Surprisingly, the bacterial inactivation efficiency was increased dramatically with the addition of Fe(II). Complete inactivation of 7.0 log cells could be achieved within 150 min in the CNW-4/Fe(II) system, while only 4.0 log-reduction was obtained within 180 min in the g-C₃N₄/Fe(II) system. The inactivation efficiencies coincided with the H₂O₂ production concentrations, suggesting that the generated H₂O₂ was in situ activated by added Fe(II) to construct homogeneous Fenton systems which can be used for bacterial inactivation. To confirm the in situ activation of H₂O₂, production of 'OH was monitored using coumarin as the trapping agent. As shown in Fig. 5(B) and S9,† the fluorescence intensity of 7-hydroxycoumarin ('OH trapping products) increased linearly with reaction time, suggesting that 'OH was really produced and led to the inactivation of bacterial cells. In contrast, no 'OH was detected in the CNW-4 sample without Fe(II). This result further confirmed that the produced H₂O₂ could be directly used for bacterial inactivation via constructing in situ Fenton systems without external addition of H₂O₂.

Based on the above discussion, a possible mechanism for photocatalytic H₂O₂ production for bacterial inactivation over the WSe₂/g-C₃N₄ composite is proposed in Fig. 6. The few layered WSe₂ nanosheets play a critical role in the present photocatalytic H₂O₂ production system, which can efficiently boost the spatial charge separation and suppress the recombination between photogenerated e⁻ and h⁺. The photogenerated e⁻ of g-C₃N₄ transfers to the VB of WSe₂, which improves the enrichment of e⁻ on WSe₂ for H₂O₂ production activity.

![Fig. 6](https://example.com/fig6.png)
production. In addition, the high VL absorption of WSe$_2$ could facilitate the utilization of photon energy, further improving the H$_2$O$_2$ generation efficiency. Moreover, O$_2$ can be produced by the CNW composite via water oxidation, and then can be further used for H$_2$O$_2$ production, especially under anaerobic conditions. The produced H$_2$O$_2$ can be used for various environmental applications, such as the bacterial inactivation demonstrated in this study, through constructing in situ Fenton systems.

4. Conclusions

In summary, few-layered WSe$_2$ nanosheets were in situ anchored onto g-C$_3$N$_4$ to construct a binanosheet structure by a solvothermal method. For the first time, the WSe$_2$/g-C$_3$N$_4$ composites were found to be excellent photocatalysts for H$_2$O$_2$ production in pure water under VL irradiation. The highest produced H$_2$O$_2$ concentration could reach 81.24 $\mu$mol L$^{-1}$ within 2 h in the absence of organic electron donors, which was 11.8 times higher than that of pristine g-C$_3$N$_4$. In addition, the generated H$_2$O$_2$ could be directly combined with iron catalysts (Fe(II)) to construct in situ Fenton systems for bacterial inactivation without addition of external H$_2$O$_2$. Complete inactivation of 7.0 log $E. coli$ cells could be achieved within 150 min under VL irradiation. These results highlight the potential of using few-layered WSe$_2$ nanosheets as a general co-catalyst for photocatalytic H$_2$O$_2$ production from pure water, thus developing new external oxidant-free Fenton systems for various environmental control applications, for example the degradation of refractory organic pollutants and the inactivation of pathogenic microorganisms, such as bacteria and viruses.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (41425015 and 21607028), the Science and Technology Planning Project of Guangzhou, China (202002030177), the Science and Technology Project of Guangdong Province, China (2017A050506049), the Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017BT01Z032), and the Leading Scientific, Technical and Innovation Talents of Guangdong Special Support Program (2016TX03J094). The authors are very grateful to Prof. Zhao-Qing Liu (Guangzhou University) for his assistance in conducting the RDE measurements.

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