Supporting Information

Graphene oxide modified LaVO₄ nanocomposites with enhanced photocatalytic degradation efficiency of antibiotics

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1. Material characterization

The crystal structure of samples was determined on a Shimadzu XRD-6000 X-ray diffractometer (using Cu Kα radiation) with a scanning rate of 7° min⁻¹ in the 2θ range of 10 - 80°. The Raman spectra were recorded by a micro-Raman spectrometer (Renishaw Invia) with 532 nm laser at room temperature. The morphologies and structures of different samples were characterized by a field emission scanning electron microscope (SEM, JEOL JSM-7800F), which equipped with an energy dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM, JEOL JEM 2010, 200 kV). X-ray photoelectron spectroscopy (XPS) was performed on ESCALab MKII X-ray photo-electron spectrometer with Mg Kα radiation to
explore the elements of the surface and the valence state. Diffuse reflection spectra (DRS) were analyzed by a UV-2450 Shimadzu UV-vis spectrophotometer in the range of 200 - 800 nm, where BaSO$_4$ powder used as internal reflectance standard. The photoluminescence (PL) spectra of the as-prepared samples were investigated on a Varian Cary Eclipse Fluorescence spectrometer with an excitation wavelength of 360 nm. The electron spin resonance (ESR) spectra were taken on an ESR spectrometer (JES-FA200) with DMPO (Sigma Chemical Co.) as the spin-trap reagent dispersed in water and methanol, respectively. The mass spectrometer (MS) was determined on Finnigan MAT900 mass spectrometer (Bremen, GR) and equipped with an ESI source and operating in positive ionization mode. Nitrogen (99.99% purity) was used as the desolvation gas. The flow rate of nitrogen sheath and auxiliary gas were 40 and 5 (arbitrary units), respectively. MS experiments were performed on mass-selected precursor ions in the range of m/z 100-500.

2. Photoelectrochemical measurements

The photocurrent performance and electrochemical impedance spectroscopy (EIS) analysis were performed on an electrochemical analyzer (CHI 660B Chenhua Instrument Company) to determine the separation and transfer rate of the charges in pure LaVO$_4$ and 0.01% GO/LaVO$_4$ composites. Firstly, we need to prepare the working electrodes. In details, 5 mg of as-prepared samples and 0.5 mL of EG were mixed to produce a suspension, followed by coating 20 μL of the suspension on a ITO glass electrode (an area of 0.5 * 1 cm$^2$). A saturated Ag/AgCl and a platinum wire
were used as reference and counter electrode, respectively. 500 W Xe arclamp was used as the photosource. Meanwhile, phosphate buffered saline (0.1 mol/L, pH=7.0) was utilized as the electrolyte during photocurrent measurement. The EIS measurement was performed in a 0.1 M KCl solution containing 5 mM Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$.

3. Photocatalytic activity measurements

The photocatalytic activities of pure LaVO$_4$ and different GO/LaVO$_4$ composite materials were evaluated by the degradation of antibiotic TC and naproxen (NPX) under visible light irradiation. The photocatalytic experiment was taken with a circulating water system maintaining the temperature at 30℃ to avoid the thermal catalytic effects and a 300 W Xe lamp with a 420 nm cutoff filter as light source. In details, 70 mg as-prepared samples and 70 mL antibiotic TC (20 mg/L) were transferred into a Pyrex photocatalytic reactor. The mixed solution was putted in a box, where an air pump as the constant supply of oxygen, and then magnetically stirred for 30 min in the dark to achieve the absorption-desorption equilibrium both the pollutant and catalyst, after which the light was opened, the reaction solution was irradiated for 3 h with about 4 mL reaction liquid taken out in each 30 min and centrifuged to obtain supernatant. The concentration of TC was determined on a UV-vis spectrophotometer (Shimadzu, UV-2450). The photodegradation experiment for NPX is similar to the process of TC, the irradiation time is 6 h with about 4 mL reaction liquid taken out in each 1 h. The concentration of NPX was also determined
on a UV-vis spectrophotometer (Shimadzu, UV-2450) with a wavelength of 230 nm.

4. Antibacterial tests

E. coli were used as the target bacterium to evaluate the antibacterial tests. Before experiment, all glass apparatuses and culture medium solution used in the experiments were autoclaved at 121°C for 20 min. The bacterial cells were grown in nutrient broth at 37°C for 20 h under agitating at 200 rpm to yield a cell count of approximately 10^9 colony forming units (cfu)/mL. Subsequently, the sample was washed three times with sterilized saline (0.85% NaCl) solution by centrifugation for 10 min. Then the cell pellet was resuspended in the 0.85% NaCl saline solution. The final cell concentration in the test was adjusted to 10^7 cfu/mL. After that, 2 mL of TC reaction solutions were obtained before and after different photodegradation for 1 h, 2 h and 3 h, and then filtered through 0.22-μm Millipore filter to remove catalysts. 100 μL of the diluted E. coli suspension was transferred to the obtained 2 mL filtrate. Then, 50μL the above mixture solution was uniformly dispersed on the agar plate. The agar plate was incubated at 37 °C for 24 h.

5. Figures and tables
Fig. S1 Photocatalytic activities of pure LaVO$_4$ and 0.01% GO/LaVO$_4$ materials for the photodegradation of NPX under visible light.

Fig. S2 (A) SEM image of 0.1% GO/LaVO$_4$ material; (B) TEM image of 0.1% GO/LaVO$_4$ material.
Fig. S3 EDS spectrum of 0.1% GO/LaVO4 material.

Fig. S4 Survey XPS spectra of pure LaVO4 and 0.05% GO/LaVO4 materials.
Fig. S5 Nitrogen adsorption-desorption isotherm of pure LaVO₄ and 0.1% GO/LaVO₄ composite.

Fig. S6 The absorption activity of 0.01% GO/LaVO₄ composite material for TC in the dark.
Fig. S7 The maximum energy edge of the valence band (VB) of LaVO₄.

Fig. S8 Plots of \((\alpha \nu)^{1/2}\) versus \(\nu\) of pure LaVO₄ and different GO/LaVO₄ composites.
Table. Comparison of photocatalytic performance with other previously reported photocatalysts for degradation of TC in recent years

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TC concentration (mg L(^{-1}))</th>
<th>Degradation (%)</th>
<th>pathways analysis</th>
<th>Toxicity analysis</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu-CN@BiVO(_4)</td>
<td>20</td>
<td>92.1%</td>
<td>No</td>
<td>No</td>
<td>[S1]</td>
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<td>h-BN/g-C(_3)N(_4)</td>
<td>10</td>
<td>79.7%</td>
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<tr>
<td>Co(_2)SnO(_4)-SnO(_2)/GC</td>
<td>10</td>
<td>83%</td>
<td>Yes</td>
<td>No</td>
<td>[S3]</td>
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<tr>
<td>Bi(_3)O(_4)Cl/g-C(_3)N(_4)</td>
<td>10</td>
<td>76%</td>
<td>Yes</td>
<td>No</td>
<td>[S4]</td>
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<tr>
<td>g-C(_3)N(_4) aggregates</td>
<td>10</td>
<td>97.9%</td>
<td>No</td>
<td>No</td>
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<tr>
<td>Bi(_2)O(_3)@g-C(_3)N(_4)</td>
<td>10</td>
<td>80.2%</td>
<td>No</td>
<td>No</td>
<td>[S6]</td>
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<td>CdTe/TiO(_2)</td>
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<td>78%</td>
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<td>t-Se/BiOCl</td>
<td>10</td>
<td>87%</td>
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<td>No</td>
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<td>g-C(_3)N(_4)/Bi(_3)TaO(_7)</td>
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<td>89.2%</td>
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<td>Ag(_2)O/Ta(_3)N(_5)</td>
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<tr>
<td>GO/LaVO(_4)</td>
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<td>83%</td>
<td>Yes</td>
<td>Yes</td>
<td>this work</td>
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</table>

References:


