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Graphene Oxide Coated Coordination Polymer Nanobelt Composite Material: a New Kind of Visible Light Active and High Efficient Photocatalyst for Cr (VI) Reduction

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Abstract

A visible light active photocatalyst was synthesized successfully through the coating of graphene oxide (GO) on coordination polymer nanobelt (CPNB) with a simple colloidal blending process. Compared with neat CPNB, the resulted graphene oxide coated coordination polymer nanobelt composite material (GO/CPNB) exhibits excellent photocatalytic efficiency on the reduction of K$_2$Cr$_2$O$_7$ under visible light irradiation. In composite material, GO performs two functions. At first, it cuts down band gap ($E_g$) of photocatalyst and extends its photoresponse region from ultraviolet to visible light region. Secondly, GO exhibits excellent electron transportation ability and impedes its recombination with hole, which can enhance photocatalytic efficiency. For GO, on its surface, the number of functional group has great influence on photocatalytic performance of the resulted GO/CPNB composite material and an ideal GO “coater” to obtain high efficient GO/CPNB photocatalyst has been obtained. As a photocatalyst which may be used in the treatment of Cr(VI) in wastewater, GO/CPNB exhibited outstanding stability during the reduction of this pollutant.
Introduction

As a mutagenic, carcinogenic and notoriously toxic, hexavalent chromium (Cr(VI)) is widely disturbed in wastewater all over the world, since it is indispensable during many industrial processes.\textsuperscript{1,2} Nowadays, the dire consequences caused by Cr(VI) pollution makes its cost-effective and low energy expending treatment highly desired.\textsuperscript{3,4} In this aspect, photocatalytic reduction has been proved to be a promising method for the hypotoxic reduction product of this process, Cr(III).\textsuperscript{5} Up to now, several semiconductor photocatalysts have been employed for photocatalytic reduction of Cr(VI) and researchers are exploring photocatalysts with more excellent performance.\textsuperscript{6} As a type of new photocatalyst, coordination polymers (CP), especially nanoscale coordination polymers (NCP) have attracted considerable attention, owing to their potential application in green photocatalytic reduction of Cr(VI) and other pollutants.\textsuperscript{7,8} Although a few ultraviolet-light-active NCP photocatalysts have been reported, the design and fabrication of visible-light-active NCP photocatalysts with high photocatalytic efficiency still remains a challenge, which suffers from drawbacks of wide band gap and flash electron-hole recombination rate during the photocatalysis process.\textsuperscript{9-12}

For wide band gap photocatalysts such as NCP, to improve their photocatalytic activity, the combination with carbonaceous material is a feasible strategy because the formation of chemical bonds between NCP and carbonaceous material can decrease band gap and extend photoresponse region.\textsuperscript{13} Furthermore, for its excellent electrical conductivity, carbonaceous material can transport electron in time and impede its recombination with hole. In the family of carbonaceous material, GO is an ideal choice.\textsuperscript{14} Firstly, the functional groups (such as -COOH and -OH) on its surface can form chemical bonds with metal ion of NCP.\textsuperscript{15} Secondly, as other carbonaceous
substance, **GO** is an excellent electron transporter, which can take electron away and shields it from hole. Thirdly, the large surface area and outstanding absorption capability make **GO** an ideal carrier for the fabrication of composite material. To our knowledge, **GO** has been employed to improve the photocatalytic activity of some wide band gap photocatalysts and achieved satisfactory results. Hence we speculate photocatalytic activity of **NCP** can also be improved through its combination with **GO**.

Our imagination was confirmed to be reasonable by a composite material, named as **GO/CPNB**, which was fabricated by the coating of **GO** on nanobelt of a new coordination polymer, \([\text{Zn}(\text{cca})_2(\text{bipy})]_n\cdot n(\text{bipy})\) (CP) (cca = 4-carboxycinnamic dianion; bipy = 2,2'-bipyridine). Photocatalytic reduction of \(\text{K}_2\text{Cr}_2\text{O}_7\) was investigated under visible light irradiation and the results indicated the coating of **GO** on **NCP** could enhance **NCP**’s photocatalytic activity effectively. For **GO**, the number of functional group had great effects on its physical and chemical properties, which may further influence photocatalytic activity of **GO/CPNB**. Here, on **GO**, the number of functional group was controlled by the mass of oxidant. The influence of functional group on photocatalytic property had been discussed in detail.

**Experimental Section**

**Materials and Synthesis**

All purchased chemicals were of reagent grade and used without further purification. The morphology was observed on an ultra plus field emission scanning electron microscope (ZEISS, Germany). PXRD patterns were recorded on D8 X-ray diffractometer, employing monochromatized Cu Ka incident radiation. FTIR spectra were recorded in the range 4000-400 cm\(^{-1}\) on an Alpha Centaur FTIR spectrophotometer using KBr pellets. The X-ray photoelectron spectroscopy (XPS)
measurements were carried out on a Thermo Scientific ESCALAB 250 instrument with a monochromatic AlKα source. Raman spectrum was carried out on the Renishaw in Via Raman system 1000 with a 532 nm Nd:YAG excitation source. Diffuse reflectance spectra (DRS) were recorded on a Shimadzu-2501PC spectrometer using BaSO₄ as a standard. Photoluminescence spectra were measuring using a FL-2T2 instrument (SPEX, USA) with 450-W xenon lamp monochromatized by double grating (1200 gr/mu). Electrochemical experiments were conducted on CHI 660B electrochemical workstation. The UV-visible adsorption spectrum was recorded using a Hitachi U-3010 UV-visible spectrometer. The conductivity measurement was performed by the conventional four-probe technique.

**Synthesis of [Zn(cca)(bipy)]ₙ·n(bipy) (CP)**

CP was prepared from the mixture of Zn(OAc)₂·4H₂O (0.030 g, 0.1 mmol), H₂cca (0.019 g, 0.1 mmol), bipy (0.016 g, 0.1 mmol) and H₂O (5 mL), the pH value of the mixture was adjusted to 5 with 1M NaOH. After being stirred for another 10 minutes, the mixture was transferred to a 23 mL Teflon-lined stainless steel bomb and kept at 160°C under autogenously pressure for 5 days. A large amount of colorless crystals of CP were found. Yield: 82% (based on Zn). Anal. Calcd for C₄₀H₂₂N₄O₄Zn: C, 63.47%; H, 3.90%; N, 9.87%. Found: C, 63.65%; H, 3.79%; N, 9.93%. IR: 3208 (s), 3019 (s), 1594 (s), 1536 (s), 1012 (s), 983 (s), 869 (s), 754 (s), 464 (s).

**Synthesis of CPNBs**

The crystals of CP were grinded for 3 hours with an agate mortar and pestle. The resulted powder was dissolved in methanol and placed in a Teflon autoclave, which was heated in a microwave oven at 300 W for 3 hours. The CPNB was separated by centrifugation, rinsed with water and then dried in a vacuum drier at 80 °C for 24 hours.
Synthesis of GO

Initially, GO was synthesized from graphite using a modified Hummers method. 1.0 g graphite was added to 70 ml H2SO4 (98%) with stirring in an ice bath. Then 0.5 g NaNO3 was added and stirred for 5 minutes. Consequently, a certain amount of KMnO4 was added gradually to the dark mixture, and the reaction mixture was maintained at that temperature and stirred for 3 hours. After that, 70 ml deionized water and 20 mL H2O2 was added respectively and the resulted reaction system was maintained for 30 minutes. After the addition of hydrogen peroxide, the color of the solution turned brown, which indicated fully oxidized graphite. The as-obtained graphite oxide slurry was sonicated for 4 hours at 70 °C and exfoliated to generate GO nanosheets. At last, the mixture was separated by centrifugation, washed repeatedly with 0.5M HCl and deionized water, and dried in a vacuum oven at 60 °C for 24 hours. In this experiment, the mass of KMnO4 is 3.0 g, 4.5 g, 6.0 g and 7.5 g. Resulted products were labeled as GO(A), GO(B), GO(C) and GO(D) respectively.

Synthesis of GO/CPNB and GO/CPNBM

The composite materials were prepared by one-step colloidal blending process using CPNB and GO in H2O. At first, GO (1 mg/mL) was dissolved in 10 mL water. Then, CPNB (1.0 g) was dispersed in 40 mL water and dropped into the solution of GO. The resulted mixture was sonicated for 1 hour and further stirred for 5 hours at room temperature to obtain a homogeneous solution. The product was separated and dried in a vacuum drier at 70 °C for 12 hours. From GO(A) to GO(D), the resulted composite materials were denoted as GO(A)/CPNB, GO(B)/CPNB, GO(C)/CPNB and GO(D)/CPNB respectively. GO/CPNBM was obtained from the mixture of CPNB and GO (with mass ration 100:1), which was grinded for 1 hour with an agate mortar and pestle. The product was separated and dried in a vacuum.
Wetting behavior test of GO

A droplet of GO suspension in ethanol was placed on a cleaned glass substrate fixed on a spin coater at a rotating speed of 2000 rpm for 3 minutes, and a film would be formed after drying. The wettability of the as-prepared films was characterized by measuring the water contact angle (CA) with a contact angle meter. A 2 µL water droplet was placed on this particle array film for water CA measurement. CA values were obtained by averaging five measurements on different areas of the sample surface.

Photocatalytic activity study

The photocatalytic activities of the samples were evaluated by the reduction of $\text{K}_2\text{Cr}_2\text{O}_7$ in the aqueous solution. The sample was composed of 80 ml 10 ppm $\text{K}_2\text{Cr}_2\text{O}_7$ aqueous solution and 20 mg catalysts. After the suspension containing $\text{K}_2\text{Cr}_2\text{O}_7$ and photocatalyst being magnetically stirred in dark for 40 minutes till an adsorption-desorption equilibrium was established, it was exposed to illumination. A 300 W medium pressure mercury lamp served as an ultraviolet light source and a 300 W Xe lamp with a cutoff filter ($\lambda \geq 420$ nm) served as a visible light source. Samples were then taken out regularly from the reactor and centrifuged immediately for separation of any suspended solid. The concentration of Cr(VI) was determined colorimetrically at 540 nm with diphenylcarbazide (DPC) by a UV-vis spectrometer.

Langmuir-Hinshelwood (L-H) equation ($r_0 = k_0 C_0 / (1 + K_0 C_0)$) was employed to quantify the reduction reaction of $\text{Cr}_2\text{O}_7^{2-}$ ($r_0$ represents the initial rate, $k_0$ represents the kinetic rate constant and $K_0$ represents the adsorption coefficient of the reactant $\text{Cr}_2\text{O}_7^{2-}$). As the value of $C_0$ is too small, $K_0 C_0 \ll 1$, the L-H rate expression can be simplified to the first-order rate expression: $r_0 = \frac{dC_0}{dt} = k_0 C_0$. This equation can be solved to obtain $\ln(C/C_0) = -k_0 t$. Based on Lambert-Beer law, $C/C_0 = I/I_0$, the equation
can be reduced to $\ln(I/I_0) = -k_0t$ finally.

**Electrochemical measurements**

Photoelectrochemical tests were carried out with a conventional three-electrode system in quartz cell filled with 0.1 M Na$_2$SO$_4$ electrolyte (100 mL), with the CPNB/ITO or GO/CPNB/ITO serving as the working electrode, a Pt plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A 300 W Xe lamp with a cutoff filter ($\lambda \geq 420$ nm) was used as the excitation light source for visible irradiation. Electrochemical impedance spectra (EIS) were recorded in potentiostatic mode. The amplitude of sinusoidal wave was 10 mV, and the frequency of the sinusoidal wave ranged from 100 kHz to 0.05 Hz. The Mott-Schotty plot was measured at a frequency of 100 Hz in the dark.

**X-ray crystallography**

Suitable single crystal of CP was carefully selected under an optical microscope and glued on glass fiber. Structural measurement was performed on a Bruker AXS SMART APEX II CCD diffractometer at 293 K. The structure was solved by the direct method and refined by the full-matrix least-squares method on $F^2$ using the SHELXTL 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Carbon-bound hydrogen atoms were placed in geometrically calculated positions; Oxygen-bound hydrogen atoms were located in the difference Fourier maps, kept in that position and refined with isotropic temperature factors. The X-ray structural analysis is listed in Table S1. Selected bond lengths and angles are listed in Table S2. Further details of the crystal structure have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication, which can be obtain free of charge (CCDC 1004144). The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Structure and morphology of CPNB

Single-crystal X-ray diffraction analysis reveals there exists only one crystallographically independent Zn atom in the fundamental unit of CP, which adopts distorted octahedral coordination mode with four oxygen atoms from two cca ligands and two nitrogen atoms from a chelating bipy ligand. In CP, adjacent Zn atoms are connected by cca ligands and results in zigzag chains. To our interests, there exists strong C-H···O hydrogen bonds between neighboring chains, with C7-H7a···O1 bond distance 3.11 Å and bond angle 139.07°. This forms 2D undulating layers with additional bipy ligands dangling alternately on both sides. Besides hydrogen bond, π-π interactions are also apparent in CP between the 2D layers, which further extend the 2D layers to a 3D supramolecular network with 1D channel. Furthermore, there exist some guest bipy molecules reside in this channel (Fig. 1a). TGA illustrates CP keeps stable at 300 °C (Fig. S1). The morphology of CPNB is studied with SEM (Fig. 1b). It could be observed the lengths and widths vary from 6 to 10 µm and 1 to 3 µm, respectively. The thickness of CPNB can also be measured clearly, which ranges from 40 to 60 nm. Furthermore, the surface of CPNB seems very smooth.

Morphology and structure of GO

For GO, the number of functional group has great effect on photocatalytic property of GO/CPNB composite material. Here, this factor is controlled by the mass of KMnO₄ used in synthesis process of GO. Although morphologies of GO are similar, their surface element contents are of great difference (Fig. 2). The discrepancy of functional groups can be illustrated clearly from surface wettabilities. The contact angles (CA) of GO are 47.4°, 40.8°, 34.9° and 28.6° respectively (Fig. 2, inset). The decreasing of CA illustrates with addition of KMnO₄, the number of functional group
increases and hydrophilic property of GO is improved. This will initiate supramolecular interactions (such as hydrogen bonds and π-π interactions) and the synergy effect between CPNB and GO.

To study the structure of GO in detail, XPS and Raman spectra were employed (Fig. 4). In GO, the peaks appear at 532.3 and 284.7 eV can be ascribed to O1s and C1s respectively. C 1s spectra reveal there exist three kinds of carbon bonds in GO, which are C-C (284.8 eV), -C=O (287.6 eV) and -COOH (289.2 eV) respectively (Fig. S2a to 2d). This can also be confirmed by O 1s spectra (Fig. S2e to 2h). Furthermore, from GO(A) to GO(D), the intensity ratio between O1s and C1s peaks increase slowly, which indicates the increasing of functional groups on surface of GO (Fig. S2i to 2l). The results of Raman spectra also suggest this point (Fig. S3). For GO, its D and G bands can be assigned to the defects or disordering atomic arrangement of sp\(^3\) hybridized carbon atoms and plane vibration sp\(^2\) hybridized carbon atoms in 2D layer of GO respectively. So the higher I\(_D\)/I\(_G\) value can indicates more defects and disorders exist on the GO. From GO(A) to GO(D), the I\(_D\)/I\(_G\) value increases from 1.05 to 1.19, which further indicates the addition of functional groups on the surface of GO with the increasing of KMnO\(_4\).

**Morphology and structure of GO/CPNB composite materials**

The morphologies of GO/CPNB were studied with SEM (Fig. 3). It can be seen obviously GO coats eventually on the surface of CPNB. In these composite materials, CPNB exhibit similar dimension and element content with pure CPNB. PXRD was applied to study structures of CPNB and GO/CPNB. CPNB and GO/CPNB both exhibit similar diffraction patterns with CP, which illustrates in CPNB and GO/CPNB the structure of CP is well retained (Fig. S4a and 4b). Furthermore, the peaks belonging to GO are not observed, which can be ascribed to the content of GO.
may be too small to determine its existence (Fig. S4c). To study the interactions
between CPNB and GO, FTIR spectra were employed. For CPNB, the peaks
appearing at about 1594 to 1536 cm\(^{-1}\) can be ascribed to the asymmetric and
symmetric stretching vibrations of carboxlyate groups in the cca ligand (Fig. S4d and
4e). Compared with CPNB, in the GO/CPNB, these peaks shift to a higher
wavenumber region (Fig. S4f). The movements reveal the effective interactions
between CPNB and GO, which can be ascribed to the existence of hydrogen bond or
π-π interaction.\(^{22}\)

The structures of GO/CPNB composite materials were investigated in detail with
XPS (Fig. 4). CPNB shows two peaks located at 1022.2 and 1045.2 eV, which are
assigned Zn 2p\(_{3/2}\) and Zn 2p\(_{1/2}\) respectively. From GO(A)/CPNB to GO(D)/CPNB,
the Zn 2p\(_{3/2}\) and Zn 2p\(_{1/2}\) peaks shifted to higher energy levels and appeared at 1024.9,
1048.8 eV; 1025.1, 1048.2 eV; 1025.3, 1048.3 eV and 1024.8, 1047.9 eV respectively.
The movements of these peaks can be attributed to the generation of Zn-O bonds
between CPNB and GO. Because compared with zinc, carbon is a highly
electronegative element, which can withdraw the electron from Zn.\(^{17a}\) As a result,
compared with Zn in CPNB, the binding energy of Zn increases in GO/CPNB
composite materials.

**Optical and electrochemical analysis**

The diffuse reflectance spectra (DRS) of CPNB and GO/CPNB composite
materials were studied. Compared with CPNB, composite materials exhibit much
stronger absorptions in visible light region, which suggest the coating of GO on
CPNB is a feasible strategy to improve its photoresponse in visible light region (Fig.
5a). To illustrate this point in detail, band gaps (E\(_g\)) of CPNB and GO/CPNB were
obtained from Tauc equation. From GO(A)/CPNB to GO(D)/CPNB, band gaps are
2.79, 2.62, 2.32 and 2.41 eV respectively, while for CPNB, its band gap is 3.65 eV, which is much wider than above composite materials. This further indicates CPNB is active only in ultraviolet light region, while GO/CPNB composite materials can be irradiated in both ultraviolet and visible light region. To clarify the fate of electron and hole, photoluminescence spectra was employed (Fig. 5b). For CPNB, the main emission peak appears at 480 nm, which can be ascribed to π-π* or π-n transitions of cca ligand. Furthermore, the emission intensity of CPNB is strong, which illustrates after irradiation, a large amount of electrons and holes recombine and result in photoluminescence. On the contrary, the photoluminescence of composite materials is much weaker than CPNB; in particular, GO(C)/CPNB gives the lowest photoluminescence intensity among these four composite materials. This results indicate the coating of GO on CPNB is an effective strategy to impede the recombination of electron and hole.

The optical research results are also supported by electrochemical analysis. Here, the interface charge separation efficiency was investigated by photocurrent spectra (Fig. 5c). Under visible light irradiation, CPNB is inactive, while for GO/CPNB, upon irradiation, the photocurrent appeared promptly and then reached a relatively steady state, when the illumination was shut down, the current fell to zero immediately. Furthermore, their reproducibility and stability are excellent as the illumination was turned on and off. The highest photocurrent was achieved with GO(C)/CPNB, which is about one and an half times than GO(A)/CPNB. To study the charge separation and transfer process in detail, EIS was employed (Fig. 5d). The typical EIS spectra were presented as Nyquist plots. It can be observed obviously, the introduction of GO, through in small amount, is able to lead to dramatic decrease in arc radiuses as compared with CPNB. This indicated a decrease in the solid state
interface layer resistance and the charge transfer resistance of the surface, which facilitates the transportation of electron and impede its recombination with hole.\textsuperscript{25}

Based on optical and electrochemical analysis results, extension of photoresponse region as well as enhancement of electron-hole pair separation efficiency both benefit from the introduction of GO. However, excessive increasing of functional groups on GO exhibits a negative effect on the efficiency of photocatalyst.

**Photocatalytic property study**

The photocatalytic reduction of Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2-} over CPNB and GO/CPNB composite materials were evaluated (Table 1). Compare with visible light inactive CPNB; composite materials exhibit more excellent photocatalytic activities under irradiation of visible light (Fig. S5). Moreover, it is clear, for GO, the number of functional groups exhibits great influence on photocatalytic efficiency of GO/CPNB composite materials. As functional groups increased, photocatalytic activity of composite material does not raise monotonously (Fig. 6a). The reason for this tendency can be explained as follows: with the increasing of functional group, GO is coated on CPNB more tightly, so the transportation of electron is speeded up and electron-hole pair can be separated more adequately, which enhances the photocatalytic efficiency of the photocatalyst. But as functional group raise continually, more defects may appear on its surface, the extensively conjugated π system and layer structure can be damaged. This will decrease electron transportation property of GO and impede the separation of electron-hole pair, which stems further enhancement of photocatalytic efficiency.

The suggestion is proved to be truth by the conductivity of GO (Fig. 6b). For a photocatalyst, during photocatalytic reduction of Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2-}, the repeatability and stability are crucial factors for its practical applications. For GO(C)/CPNB, after recycled for five times, the activity only decreased about 3%, which indicates it
possessed favorable recycling property (Fig. 6c). Moreover, GO(C)/CPNB also
displayed excellent stability during reduction of Cr$_2$O$_7^{2-}$, which was confirmed by
PXRD pattern and FTIR (Fig. 6d and 6e). This indicates the structure of
GO(C)/CPNB is not destroyed during the reduction process of Cr(VI).

In composite materials, the improvement of photocatalytic activity originates from
the synergy between GO and CPNB. To illustrate this point clearly, GO/CPNBM
(the mechanically blended product of GO and CPNB) were used as the reference to
evaluate the photocatalytic efficiency (Fig. 6f). It is notable that their photocatalytic
efficiency is considerably less than GO/CPNB. This result indicates that the synergy
between GO and CPNB plays the dominating role in the enhancement of
photocatalytic activity. The synergy is introduced by supramolecular interaction
between GO and CPNB, which facilitates the transportation of photogenerated
electron and achieve efficient separation of hole and electron. To quantify the extent
of synergy effect between GO and CPNB, a parameter, named as synergy factor (R)
was introduced, which is defined as $k_{GO/CPNB}/k_{GO/CPNBM}$. From GO(A)/CPNB to
GO(D)/CPNB, R values are 1.55, 1.95, 4.56 and 2.63 respectively, which suggests
the coating of GO on CPNB does create an obvious synergetic effect in composite
material. In these composite materials, synergetic effect of GO(C)/CPNB is the most
obvious and this lies in the particular structural feature of GO(C).

**Mechanism study**

For GO/CPNB composite material, to illustrate the reason why its photocatalytic
activity is improved so greatly, the analysis of CPNB’s energy bands is necessary.
The conductive band (CB) potential of CPNB, obtained with Mott-Schotty
measurement is -0.65 eV (vs SCE) and the positive slope of $C^2/E$ plot illustrates
CPNB is a typical n-type semiconductors. Based on its band gap, with the formula
$E_{\text{VB}} = E_{\text{CB}} + E_g$, valence band (VB) of CPNB is calculated to be 3.00 eV (vs SCE) (Fig. 7a). For GO, its Fermi energy level is higher than CB edge of CPNB, so after the coating of GO on CPNB, a new energy level is formed between the CPNB’s CB and Fermi energy level of GO, which can be considered as the CB of GO/CPNB.\(^{27}\) During this process, the VB energy level of CPNB is retained. This leads to the decreasing of band gap in the resulted composite material (Fig. 7b). So, under visible light, composite material can be excited and produce electron on VB of CPNB. Subsequently, electron injects to the CB of CPNB and then transferred to GO. Simultaneously, positive charged holes are formed on VB of CPNB. Thus the photogenerated electron-hole pair can be separated adequately and the recombination of electron and hole is reduced or inhabited. This enhances the efficiency of interfacial charge transfer to $\text{Cr}_2\text{O}_7^{2-}$ and accelerates its reduction reaction.

**Conclusions**

In summary, the wide responsive photocatalyst, GO/CPNB was successfully prepared with a facile colloidal blending process under mild conditions. The investigation of its photocatalytic activity exhibits GO/CPNB composite material possesses much better photocatalytic efficiency for the reduction of $\text{Cr}_2\text{O}_7^{2-}$ than CPNB, GO and their mechanical blended mixture. XPS illustrates CPNB is coated on GO through chemical bonds between Zn and functional groups on its surface. The formation of these bonds results in composite material with lower band gap and wide photoresponse region. Furthermore, this combination also leads to the generation of synergistic effect between CPNB and GO, which enhances the separation of photogenerated carrier and improve the photocatalytic efficiency. It has been demonstrated that GO/CPNB can be used in the treatment of Cr(VI) containing wastewater in industrial production. Moreover, the visible light driven photocatalytic
activity and excellent stability also render it to be a promising photoelectric conversion material with good potential applications in hydrogen production by sufficiently utilizing solar energy.

Acknowledgements

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Electronic supplementary information (ESI) available: Crystal data and structure refinement results, selected bond lengths and angles of CP; PXRD and FTIR patterns of CPNB and GO/CPNB; Reduction rate as the function of time by CPNB under UV light.
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Table 1 Values of reduction efficiency ($\eta$), rate constant ($k_0$) of Cr$_2$O$_7^{2-}$ with different photocatalysts and synergy factor (R) of GO/CPNB composite materials.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Condition</th>
<th>T (min)</th>
<th>$\eta$ (%)</th>
<th>$k_0$ (min$^{-1}$)</th>
<th>R$^2$ (%)</th>
<th>R</th>
</tr>
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<tbody>
<tr>
<td>CPNB</td>
<td>UV</td>
<td>360</td>
<td>67.05</td>
<td>0.0031</td>
<td>99.968</td>
<td>-</td>
</tr>
<tr>
<td>CPNB</td>
<td>Vis</td>
<td>360</td>
<td>3.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GO(A)/CPNB</td>
<td>Vis</td>
<td>360</td>
<td>67.51</td>
<td>0.0031</td>
<td>99.976</td>
<td>1.55</td>
</tr>
<tr>
<td>GO(B)/CPNB</td>
<td>Vis</td>
<td>360</td>
<td>77.32</td>
<td>0.0041</td>
<td>99.989</td>
<td>1.95</td>
</tr>
<tr>
<td>GO(C)/CPNB</td>
<td>Vis</td>
<td>180</td>
<td>85.42</td>
<td>0.0105</td>
<td>99.844</td>
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<td>GO(D)/CPNB</td>
<td>Vis</td>
<td>270</td>
<td>83.26</td>
<td>0.0063</td>
<td>99.246</td>
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<tr>
<td>GO(A)/CPNBM</td>
<td>Vis</td>
<td>360</td>
<td>51.48</td>
<td>0.0020</td>
<td>99.995</td>
<td>-</td>
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<tr>
<td>GO(B)/CPNBM</td>
<td>Vis</td>
<td>360</td>
<td>53.08</td>
<td>0.0021</td>
<td>99.788</td>
<td>-</td>
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<tr>
<td>GO(C)/CPNBM</td>
<td>Vis</td>
<td>360</td>
<td>54.36</td>
<td>0.0023</td>
<td>99.997</td>
<td>-</td>
</tr>
<tr>
<td>GO(D)/CPNBM</td>
<td>Vis</td>
<td>360</td>
<td>56.69</td>
<td>0.0024</td>
<td>99.991</td>
<td>-</td>
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Figure Captions

Figure 1 (a) 3D supramolecular network of CP; (b) SEM and EDX (inset) of CPNB.

Figure 2 SEM and the shape of a water droplet on the surface (inset): (a) GO(A); (b) GO(B); (c) GO(C); (d) GO(D).

Figure 3 SEM and EDX of CPNB in composite material (inset) (a) GO(A)/CPNB; (b) GO(B)/CPNB; (c) GO(C)/CPNB; (d) GO(D)/CPNB.

Figure 4 XPS of Zn and XPS survey (inset) (a) CPNB; (b) GO(A)/CPNB; (c) GO(B)/CPNB; (d) GO(C)/CPNB; (e) GO(D)/CPNB.

Figure 5 (a) DRS and Tauc plots (inset) of CPNB and GO/CPNB; (b) Photoluminescence spectra of CPNB and GO/CPNB; (c) Photocurrent spectra of CPNB and GO/CPNB; (d) Nyquist plots of CPNB and GO/CPNB.

Figure 6 (a) Reduction rate as the function of time by CPNB and GO/CPNB; (b) Conductivity of GO; (c) Cycling runs of the reduction of Cr$_2$O$_7^{2-}$ in the presence of GO(C)/CPNB; (d) PXRD of recycled GO(C)/CPNB; (e) FTIR of recycled GO(C)/CPNB; (f) Reduction rate as the function of time by GO/CPNB.

Figure 7 (a) Mott-Schotty plot of CPNB; (b) Diagram of the photocatalytic mechanism for GO/CPNB under visible light.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Graphical Abstract

Graphene Oxide Coated Coordination Polymer Nanobelt Composite Material: a New Kind of Visible Light Active and High Efficient Photocatalyst for Cr (VI) Reduction

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GO/CPNB was fabricated successfully, which displays very excellent photocatalytic activity in visible light. Furthermore, the influence of GO on photocatalytic activity was discussed.