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Article

Amorphous CoO_x coupled carbon dots as a spongy porous bifunctional catalyst for efficient photocatalytic water oxidation and CO_2 reduction

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ABSTRACT

Cobalt-based oxides, with high abundance, good stability and excellent catalytic performance, are regarded as promising photocatalysts for artificial photosynthetic systems to alleviate foreseeable energy shortages and global warming. Herein, for the first time, a series of novel spongy porous CDs@CoO_x materials were synthesized to act as an efficient and stable bifunctional photocatalyst for water oxidation and CO_2 reduction. Notably, the preparation temperatures visibly influence the morphologies and photocatalytic performances of the CDs@CoO_x . Under the optimal conditions, a maximum O_2 yield of 40.4% and pretty apparent quantum efficiency (AQE) of 58.6% at 460 nm were obtained over $\text{CDs@CoO}_x\text{-300}$ for water oxidation. Similarly, the optimized sample $\text{CDs@CoO}_x\text{-300}$ manifests significant enhancement on the CO_2 -to-CO conversion with a high selectivity of 89.3% and CO generation rate of 8.1 $\mu\text{mol/h}$, which is superior to most previous cobalt-based catalysts for CO_2 reduction. The composite $\text{CDs@CoO}_x\text{-300}$ not only exposes more active sites but also facilitates electron transport, which results in excellent photocatalytic activity. In addition, the boosted photocatalytic behavior is attributed to the synergistic effect between CoO_x and CDs, which was verified by the photocatalytic activity control experiments and electrochemical characterization. The work offers a novel strategy to fabricate a high performance bifunctional photocatalyst for water oxidation and CO_2 reduction.

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1. Introduction

Solar-driven photocatalytic water splitting and CO_2 reduction are deemed as the best green and promising strategy to alleviate energy shortages and global warming (Eq. (1)) [1–8].

The overall water splitting process comprises two half reactions, namely proton reduction and water oxidation reaction (Eqs. 2 and 3) [9–13]. Compared with proton reduction reaction, water oxidation involves a complicated four-electron transfer process, which is considered as the bottleneck of water

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splitting [14,15]. CO₂ reduction is an important half-reaction of photosynthesis (Eq. (4)), which is a typical thermodynamically uphill reaction with large overpotential [16–19]. Hence, the search for suitable catalysts to reduce the multielectron involved kinetic barriers for water oxidation and CO₂ reduction is considered as a critical step toward artificial photosynthesis [20–22]. It is highly desirable to seek robust, efficient and earth abundant catalysts with bifunctional performance for simultaneous photocatalytic water oxidation and CO₂ reduction in artificial photosynthetic systems [23,24].

Cobalt-based homogeneous and heterogeneous catalysts have been proved as attractive candidates for this purpose [25–29]. Particularly, cobalt-based heterogeneous catalysts, such as cobalt oxide, are usually robust, cheap, and easy to prepare [30–34]. However, their photocatalytic performance still need to be further improved for practical large-scale applications. Previous studies showed that amorphous phase catalysts as photocatalytically were inactive, which they focused on crystalline rather than amorphous phase [35,36]. But recent works have indicated that the amorphous morphology of cobalt-based oxides play a critical role in enhancing their photocatalytic performance [37–41]. As a new type of carbon nanomaterial containing abundant functional groups, carbon dots (CDs) were discovered in 2004 [42] and exploited for photocatalytic properties in 2010 [43]. Owing to its unique optical and electronic properties, CDs can serve as a versatile component in reported photocatalysts [44–48]. However, the CDs coupled CoO_x has never been studied as a bifunctional photocatalyst in dye-sensitizing water oxidation and CO₂ reduction systems.

Herein, a series of spongy porous bifunctional photocatalysts CDs@CoO_x were synthesized by controlling the crystallinity of the catalysts with changing the calcination temperature, which enhances the CoO_x photocatalytic activity assisted by CDs. Under the optimal conditions, a maximum O₂ yield of 40.4% and an apparent quantum efficiency (AQE) of 58.6% were obtained over CDs@CoO_x-300, when [Ru(bpy)₃](ClO₄)₂ was used as photosensitizer and Na₂S₂O₈ as sacrificial electron acceptor in borate buffer solution (pH 9.0). For the CO₂ reduction, a CO selectivity of 89.3% and a CO generation rate of 8.1 μmol/h were got when [Ru(bpy)₃]Cl₂ was used as photosensitizer and triethanolamine (TEOA) as electron donor. This work provides a promising route for developing stable cobalt-based carbon hybrids photocatalysts with high-performance for artificial photosynthesis.

2. Experimental

2.1. Synthesis of CDs@CoO_x

Firstly, the carbon dots (CDs) were synthesized by a “bottom-up” approach according to a previous literature with some modifications [49]. In a typical synthesis procedure, the mix-

tures of dicyandiamide (1.0 g) and glucose (0.2 g) (the mass ratio of two components is 5: 1) were dissolved in 10 mL de-ionized water, and transferred to a 25 mL Teflon autoclave, heating at 200 °C for 6 h. After the reaction, the mixture was cooled to room temperature naturally. The resulting product was filtered by a 0.22 μm filter to remove the large particles and get the uniform red-brown CDs solution. After removing solvent and freeze-drying further, the CDs powder was obtained and stored at 4 °C, which can be redispersed in ultrapure water for further characterization.

Subsequently, the 0.2 g Co(NO₃)₂·6H₂O was added in the above CDs solution under stirring for 30 min, then dried at 60 °C to collect the CDs-Co²⁺ powder. Finally, the black powder was annealed at 300 °C in a muffle furnace for 2 h (rate: 5 °C/min) under air atmosphere, recorded as CDs@CoO_x-300. The as-prepared catalyst of CDs@CoO_x-T with different calcination temperatures (T = 200, 300, 400 and 600 °C) were denoted as CDs@CoO_x-200, 300, 400 and 600, respectively. For comparison, the bare Co₃O₄ catalyst was prepared by the same way without adding the above acquired CDs.

2.2. Photocatalytic oxygen evolution and CO₂ reduction

The photocatalytic water oxidation experiments were investigated in a 25 mL flask (10 mL reaction solution) at room temperature and irradiated by a LED (Beijing Perfectlight, PLS-LED100, λ = 460 nm, light intensity = 33.8 mW/cm²). The desired concentration of catalyst was dispersed in borate buffer solution (80 mM) with different pH containing 5 mM Na₂S₂O₈ as electron acceptor and 1 mM [Ru(bpy)₃]Cl₂·6H₂O (bpy = 2,2'-bipyridine) as photosensitizer. Before photoreaction, the air inside photoreactor was deaerated by evacuation and purged with Ar gas several times and maintained the similar pressure in the reactor as atmospheric pressure. The amount of generated gas at the headspace of the reaction flask was withdrawn by an SGE gastight syringe and analyzed by gas chromatography (5 Å column with Ar carrier gas, Shimadzu GC-9A Gas) equipped with thermal conductivity detector (TCD).

The CO₂ reduction performance was tested by combining the catalysts (0.5 mg) and the 7.5 mg [Ru(bpy)₃]Cl₂·6H₂O in a gas-closed quartz reactor which contains MeCN/H₂O/TEOA (3 mL/2 mL/1 mL) mixture solution. Before illumination, the CO₂ gas was filled into the reactor for about 10 min to replacement the air. Afterwards, a 100 mW cm⁻² LED lamp (Beijing Perfectlight, PLS-LED100B, λ = 460 nm) was used as the light source. After a period of irradiation, a gas chromatography was used to detect the products (Shimadzu GC-9AMM Gas, CO was analyzed by thermal conductivity detectors).

3. Results and discussion

3.1. Characterization of CDs and CDs@CoO_x

The preparation diagram of the CDs@CoO_x photocatalyst is schematically depicted in Scheme 1. The CDs were synthesized by dehydration and polymerization via a facile one-pot hydro-

Scheme 1. Illustration of the preparation of CDs@CoO_x.

thermal route at 200 °C for 6 h. After adding 0.2 g of Co(NO₃)₂·6H₂O to the obtained CDs-Co²⁺ solution, the mixtures were dried at 60 °C and then treated with different calcination temperatures under air atmosphere to form CDs@CoO_x photocatalysts.

The successful preparation of the CDs was proved by the TEM and HR-TEM images. Fig. 1 shows the spherical and uniformly distributed carbon particles (2–6 nm in diameter) with a lattice spacing of 0.19 nm, corresponding to the [102] lattice plane spacing of graphitic carbon in the inserted (Fig. 1(b)) [50].

The functional groups of obtained CDs were measured by FT-IR spectra in Fig. S1, where the characteristic peaks at 3446, 1635, 1400 and 1255 cm⁻¹ can be assigned to the stretching vibration of O–H, C=C/C=O [51], C–N and C–C [52,53], respectively. In addition, the Raman spectrum of CDs@CoO_x-300 in Fig. S2 reveals the presence of the fabrication of graphitic carbon (typical D and G bands at 1200–1600 cm⁻¹).

As shown in Fig. 2, the bare Co₃O₄ is confirmed by XRD and matched well with its standard XRD pattern (JCPDS PDF No. 73-1701) [54]. When CDs are incorporated into CoO_x, the CDs@CoO_x samples at 200 and 300 °C show very poor crystallinity, indicating that they are nearly amorphous composite. Upon calcination at a higher temperature of 400 or 600 °C, the diffraction peaks of the CDs@CoO_x-400 and 600 are close to that of the bare Co₃O₄, indicating the better crystallinity of the sample prepared at a higher temperature.

The TEM images of bare Co₃O₄ and CDs@CoO_x sintered at different calcination temperature (200, 300, 400 and 600 °C) are presented in Figs. S3, S4 and 3. The bare Co₃O₄ shows an aggregated rodlike structure which was acquired by one-pot pyrolysis at 300 °C. When incorporated of CDs, the morphology of CDs@CoO_x changed, which indicate that the CDs@CoO_x-200 and CDs@CoO_x-300 are spongy porous morphology structures with pore sizes ranging from several tens to hundreds of na-

Fig. 1. TEM (inset: size distribution) (a) and HR-TEM (b) images (inset: lattice fringe image) of CDs.

Fig. 2. XRD patterns of bare Co₃O₄ and CDs@CoO_x catalysts.

nometers based on SEM and TEM results (Fig. 3(a) and 3(b)), respectively. The formation of porous property may be attributed to the release of gas molecules during the decomposition and recrystallization process [55]. As the calcination temperature increases, the morphologies of CDs@CoO_x show dispersive particles in Figs. S4(c) and S3(e), which the lattice fringe of 0.28 and 0.20 nm are clearly ascribed the [220] and [400] plane of Co₃O₄. These images reveal that the calcination temperature influences the morphology of CDs@CoO_x catalysts.

As shown in Fig. 3(e), the lattice fringes of 0.19 nm is ascribed to the [102] plane of graphitic carbon (dark-colored contrast). However, it is difficult to distinguish the lattice fringes (0.195 nm) of Co species (light-colored contrast), suggesting the formation of amorphous CDs@CoO_x-300, which the result is agreement with the results of XRD analysis. Moreover, the selected area electron diffraction (SAED) measurement of CDs@CoO_x-300 in the inserted Fig. 3(e) shows no diffraction spots or rings, indicating its amorphous feature. The elemental mapping images (Fig. 3(f)–(i)) show that the Co, C, N and O elements are distributed uniformly in the selected detection area of the hybrid material. The Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) indicates that the cobalt content in CDs@CoO_x-300 is 242.5 mg/g.

More importantly, the surface chemical compositions and valence states of CDs@CoO_x-300 was further investigated by

Fig. 3. SEM (a) and TEM (b, c) and HR-TEM (d, e) images and element mapping image (f–i) of CDs@CoO_x-300.

XPS. The survey XPS spectrum of CDs@CoO_x-300 (Fig. S5) depicts that the composite contains the elements C, O, Co and N. The five peaks at 284.2/284.8, 285.3, 286.1, and 288.3 eV in Fig. 4(a) are ascribed to C=C/C-C, C-N, C-OH, and COOH, respectively. The N 1s spectrum (Fig. 4(b)) fitted into three peaks at 399.1, 400.1 and 400.8 eV, which are corresponding to graphitized N, pyrrolic N and pyridinic N, respectively. The O 1s peaks at 532.0 and 533.2 eV display C=O/O-C-OH and C-OH (Fig. 4(c)), respectively. In addition, the O 1s peak XPS peak at 531.85 eV can be assigned to the lattice oxygen in the Co₃O₄ phase [56], which demonstrates the presence of Co₃O₄ in the CDs@CoO_x. In the high-resolution Co 2p spectrum (Fig. 4(d)), the four peaks for 2p_{1/2}/2p_{3/2} of Co²⁺ and Co³⁺ locate at 781.1/797.1 and 783.2/798.5 eV, where the corresponding satellite peaks are at 786.5 and 802.7 eV. Furthermore, the Co 2p_{3/2}-2p_{1/2} spin-orbit splitting (ΔE) is 15.3 eV for Co₃O₄ and 16.0 eV for CoO [57], respectively. Therefore, we conclude that the species of Co can be attributed to a mixture of Co²⁺ and Co³⁺, which is denoted as CoO_x for simplicity in the hybrid material. According to the XPS and ICP-AES results of CDs@CoO_x-300, the relative percentage of CDs in the CDs@CoO_x-300 is 66.97%–69.16%.

3.2. Photocatalytic water oxidation

The CDs@CoO_x for water oxidation were performed using the classical established [Ru(bpy)₃]Cl₂/catalyst/visible light/Na₂S₂O₈ system [58]. The kinetic curves of O₂ evolution with different catalysts are depicted in Fig. 5. Obviously, no or only a trace amount of O₂ was detected in the absence of any

ingredients, which reveals that light irradiation, photosensitizer ([Ru(bpy)₃]Cl₂) and electron sacrificial acceptor (Na₂S₂O₈) as well as the catalyst are indispensable for efficient visible-light-driven water oxidation reaction.

By tuning preparation temperatures of CDs@CoO_x catalyst (200, 300, 400 or 600 °C), it can be noted that the CDs@CoO_x with poor crystallinity material shows better photocatalytic water oxidation performance, while the CDs@CoO_x-400 and CDs@CoO_x-600 samples with high crystallinity exhibit the relatively poor water oxidation activity. Such phenomenon indicates that the incorporation of CDs is beneficial to form amorphous CDs@CoO_x-300, which is more favorable for water oxidation. This finding is in accordance with supplements previous reported results and establishes that amorphous cobalt-based carbon hybrids can be suitable as WOCs for light-driven water oxidation.

When a small amount of CDs@CoO_x-300 (0.01 g/L) was added, 4.6 μmol O₂ was released dramatically within initial light irradiation 30 s, indicating that CDs@CoO_x-300 truly serves as a catalyst for boosting the oxidation of water. Then the control experiments were optimized through varying different the pH value of the borate buffer solution (pH = 8.5, 9.0 or 9.5) and mass concentration of catalysts (0.01, 0.1, 0.2 or 0.5 g/L) (Figs. S8–S10). The highest oxygen evolution amount was obtained using 0.2 g/L of CDs@CoO_x-300 in the pH 9.0 of borate buffer solution (80 mM, 10 mL). In the initial reaction, the conditions were optimal. In general, a higher pH value was thermodynamically favorable for water oxidation and a fast rate in the initial reaction would be obtained. But as time goes on, on the one hand, the solution of pH value decreased gradu-

Fig. 4. High-resolution XPS spectra of C 1s (a), N 1s (b), O 1s (c) and Co 2p (d) for CDs@CoO_x-300.

Fig. 5. (a) Kinetics of oxygen evolution in the photocatalytic system using different 0.2 g/L catalyst; (b) amount of oxygen evolution using different photosensitizers. Conditions: 5 mM Na₂S₂O₈, 1 mM photosensitizers and 10 mL 80 mM borate buffer solution (pH 9.0) at λ_{LED} = 460 nm irradiation.

ally, which was thermodynamically unfavorable for water oxidation. On the other hand, the sacrificial electron acceptor of Na₂S₂O₈ was consumed up and photosensitizer of [Ru(bpy)₃]Cl₂ was decomposed during the photocatalytic process. Therefore, O₂ evolution rate began to decrease over time and reached a platform in 120 s.

As shown in Fig. 5(a), the CDs@CoO_x-300 shows the best catalytic activity among all photocatalysts evaluated under light driven water oxidation system. A maximum O₂ yield of 34.4% (8.6 μmol) is obtained in the presence of CDs@CoO_x-300, which is larger than those of CDs@CoO_x-200 (26.4%, 6.6 μmol), CDs@CoO_x-400 (28.4%, 7.1 μmol) and CDs@CoO_x-600 (19.2%, 4.8 μmol). In addition, a low O₂ yield of commercial Co₃O₄ (15.9%, 4 μmol) and bare Co₃O₄ (24.0%, 6 μmol) were measured. Moreover, there is no O₂ evolution was detected in the presence of CDs.

When [Ru(bpy)₃]Cl₂ was replaced by with the [Ru(bpy)₃](ClO₄)₂ as photosensitizer, CDs@CoO_x-300 exhibited better activity for water oxidation with an high O₂ yield and AQE. The possible reason for the improved water oxidation activity is as follow: Cl⁻ will consume the sacrificial reagent through transferring electrons to SO₄²⁻ thereby forming Cl₂, thus decreasing the catalytic activity in the photocatalytic water oxidation processes. In contrast, the Cl in Ru(bpy)₃(ClO₄)₂ has reached the highest valence and will not react with SO₄²⁻ to form other oxidative products [59]. Thus, the enhanced catalytic activity is obtained when [Ru(bpy)₃](ClO₄)₂ is used as a photosensitizer. As shown in Table S1, the O₂ yield 40.4% is in moderate level among all reported heterogeneous cobalt-based WOCs. AQE of CDs@CoO_x-300 is 58.6%, which is the third highest value among all reported heterogeneous cobalt-based WOCs. The outstanding results show that the synergistic effect between CoO_x and CDs leads to the significantly enhanced photocatalytic water oxidation performance.

In addition, the [Ru(bpy)₃]Cl₂ was selected as a photosensitizer, TEOA was used as sacrificial electron acceptor and CDs@CoO_x-300 was used as catalyst for photocatalytic hydrogen evolution (Fig. S11). A few amount of H₂ (0.53 μmol) when [Ru(bpy)₃]Cl₂ was solely added. The amount of hydrogen increased when the catalyst was added. The highest hydrogen evolution amount (1.43 μmol) was obtained using 3 mg of

CDs@CoO_x-300 in 10 mL 10% TEOA aqueous solution irradiated for 1 h.

3.3. Photocatalytic CO₂ reduction

The photocatalytic CO₂ reduction performances of all CDs@CoO_x catalysts were evaluated using [Ru(bpy)₃]Cl₂ as the photosensitizer and acetonitrile/H₂O/TEOA mixture as the reaction medium [60]. A series of comparative experiments were conducted to explore the fundamental impact factors determining the activity of the photoreduction catalysts. CO and H₂ were detected as the main products without the observation of any other potential products (such as CH₄), consistent with the reports in previous similar works [61]. Firstly, the influence of the calcinations temperatures on the photocatalytic performance of the CDs@CoO_x was investigated, in which the yields of CO and H₂ vary apparently in different samples (Fig. 6(a)). The CDs@CoO_x-300 with poor crystallinity exhibits the highest CO₂ reduction activity among the four samples. The influence of the amount of CDs@CoO_x-300 for the photocatalytic CO₂ reduction was investigated (Fig. 6(b)). When 0.5 mg of CDs@CoO_x-300 was added, the CO production rate and selectivity obviously increase. However, the amount of CO evolved decreases with the further increased amount of CDs@CoO_x-300. The depressed activity may be the following reasons [5]: (1) Excessive catalyst would cover the surface active sites on the photocatalyst and block its contact with reactants of CO₂, H₂O or TEOA. (2) Too much amount catalyst would prevent the incident light, thus decreasing the number of photogenerated electron-hole pairs.

The control experiments of CO₂ reduction were carefully conducted under various reaction conditions as shown in Fig. 6(c). No products were detected in the absence of light, [Ru(bpy)₃]Cl₂, or TEOA, which highlights the indispensability of photosensitizer, sacrificial agent and light illumination for CO₂ reduction, respectively (column 1–3). Furthermore, when [Ru(bpy)₃]Cl₂ was solely added, only a little amount of H₂ (0.45 μmol/h) and CO (0.37 μmol/h) were produced, which fully demonstrates the significance of presence CDs@CoO_x-300 catalyst (column 4). As shown in Fig. 6(c), there is only 0.42 μmol amount of CO produced in the presence of single CDs (column

Fig. 6. Generation of CO and H₂ from photoreduction of CO₂. (a) Under different calcination temperatures, (b) amount of catalyst of CDs@CoO_x-300; (c) under various conditions; (d) evolution of CO and H₂ as a function of reaction time over CDs@CoO_x-300.

5), which is almost the same as amount of CO without the catalyst (0.45 μmol/h, column 4).

To confirm the carbon origin of produced CO, a reference reaction replacing CO₂ with Ar under otherwise identical conditions was run (column 6). Only tiny amount of H₂ (0.24 μmol/h) was observed and no any CO was detected, implying that the CO evolved is derived from the CO₂ reduction rather than carbonaceous residuals of the photocatalyst itself. Under the optimal condition, CDs@CoO_x-300 exhibits a CO generation rate of 8.1 μmol/h with a high selectivity of 89.3% (column 9), which is obviously higher than those other analogical reported system (Table S2). The catalytic activity of CDs@CoO_x-300 is superior to that of commercial Co₃O₄ (column 7, 5.9 μmol/h, 67.8%) and bare Co₃O₄ (column 8, 7 μmol/h, 73.7%). In addition, the accumulated product of CDs@CoO_x-300 reaches 22.6 μmol of CO after 4 h reaction (Fig. 6(d)). The gradual decrease in the CO₂-to-CO conversion rate with a long time reaction is mainly attributed to the exhaustion of the photosensitizer [62,63].

3.4. Study on the photocatalytic mechanism and process

To further elucidate the synergistic effect between the CDs and CoO_x, the electrochemical, optical and photoelectrochemical experiments were conducted as following.

In general, the WOCs can be oxidized by photogenerated oxides to high-valence state active species during water oxidation process. This means that the half wave potential $E_{1/2}$ ($E_{1/2}$

= (E_{pa} + E_{pc})/2) of the photosensitizer ([Ru(bpy)₃]Cl₂) must be higher than the onset potential of the catalyst. The CV measurements of [Ru(bpy)₃]Cl₂ and CDs@CoO_x-300 were carried out in 80 mM borate buffer (pH 9.0) (Fig. S12). The $E_{1/2}$ of [Ru(bpy)₃]^{2+/3+} (1.31 V vs Ag/AgCl) is obviously larger than onset potential of CDs@CoO_x-300 (1.19 V vs Ag/AgCl), indicating Ru[(bpy)₃]³⁺ can oxidize CDs@CoO_x-300 to high-valence state active species and then catalyze oxidation of H₂O [8]. In addition, the anodic current of CDs@CoO_x-300 could reach approximately 220 μA at 1.50 V, which represents a strong catalytic current for water oxidation.

Then the transient photocurrent response of CDs, bare CoO_x and CDs@CoO_x-300 were recorded by chopping the light on and off at a constant potential of 1.00 V_{RHE}. As shown in Fig. 7(a), there is almost no photocurrent for the blank run and single CDs. Sample CDs@CoO_x-300 possesses a distinct enhancement in photocurrent value when compared with Co₃O₄ and CDs, suggesting an enhanced separation and transfer of photogenerated charge carriers of [Ru(bpy)₃]Cl₂ with the assist of CDs@CoO_x-300.

To validate the above analysis, photoluminescence (PL) spectra as a powerful instrument were conducted to analyze the carrier separation (electron-hole pairs) efficiency of the as-prepared samples under the excitation wavelength of 398 nm. As shown in Fig. 7(b), the bare [Ru(bpy)₃]Cl₂ aqueous solution exhibits a strong emission at about 600 nm owing to a recombination of photoexcited charge carriers. The addition of CDs@CoO_x-300 into the [Ru(bpy)₃]Cl₂ solution results in a

Fig. 7. Transient photocurrent responses curves in 1 mM [Ru(bpy)₃]Cl₂ solution (a), steady-state PL spectra (b), time-resolved PL spectra (c) and proposed mechanism (d) of CDs@CoO_x-300 for photocatalytic water oxidation.

more obvious PL quenching than that of blank [Ru(bpy)₃]Cl₂, suggesting reduced recombination of charge carriers in [Ru(bpy)₃]Cl₂/CDs@CoO_x-300 system. When Na₂S₂O₈ was further added, the photoluminescence intensity exhibits a dramatic decline, which signifies that the electrons are consumed by the Na₂S₂O₈ when the [Ru(bpy)₃]Cl₂ is excited.

Furthermore, time-resolved PL measurements were also studied. The lifetime of photosensitizer can be defined as the decay time from initial intensity to 1/e of the initial intensity. As shown in Figs. 7(c) and S11, the corresponding fluorescence lifetimes of [Ru(bpy)₃]Cl₂/Na₂S₂O₈/CDs@CoO_x-300 and [Ru(bpy)₃]²⁺ are 320.7 and 393.7 ns, respectively. Consequently, the shorter decay lifetime has the faster interfacial charge transfer, which corroborates the results of steady-state PL and analysis transient photocurrent response.

The overpotentials of the bare Co₃O₄ (1.35 V vs Ag/AgCl) and CDs@CoO_x-300 (1.08 V vs Ag/AgCl) at 1 mA/cm² in linear sweep voltammeter (LSVs) are shown in Fig. S13(a). Although CDs has no water oxidation activity, the electrocatalytic activity of CoO_x is greatly improved after the CDs incorporating. Meanwhile, to further acquire a deeper understanding of the charge transfer kinetics with/without CDs and the separation efficiency of photogenerated charge carriers during water oxidation, the electrochemical impedance spectroscopy (EIS) measurements were conducted in 80 mM borate buffer (pH 9.0). As shown in Fig. S9(b), compared with bare Co₃O₄, the CDs@CoO_x-300 shows much smaller arc radius, revealing that the introduction of CDs makes interfacial charge transfer faster,

and separation efficiency of photogenerated charge carriers higher. The EIS results were fitted with a model circuit (inset in Fig. S13(b)). The high frequency semicircle corresponds to the contact resistance (R_c), and the semicircle in medium-frequency region represents the charge transfer resistance of the electrode/electrolyte interface (R₁). The low frequency straight line corresponds to Warburg impedance (W₂) [64]. The fitted R₁ = 1057 value of CDs@CoO_x-300 significantly lower than those of bare Co₃O₄ (R₁ = 2415), indicating the superior charge transfer between the CDs@CoO_x electrolyte interfaces.

Based on the above discussions, a plausible mechanism for the CDs@CoO_x-300 in the typical photocatalytic water oxidation process is proposed. As shown in Fig. 7(d), the orange [Ru(bpy)₃]²⁺ is firstly excited to [Ru(bpy)₃]^{2+*} under the visible light irradiation. Subsequently, Na₂S₂O₈ reacts with the [Ru(bpy)₃]^{2+*} to generate oxidant of [Ru(bpy)₃]³⁺, SO₄²⁻ and SO₄^{•-}. Then the SO₄^{•-} with a potential of 2.4 V vs. NHE reacts with the two additional [Ru(bpy)₃]²⁺ in solution to form two [Ru(bpy)₃]³⁺. The produced [Ru(bpy)₃]³⁺ oxidizes CDs@CoO_x-300 to high valence state, which is responsible for the formation of O–O bonding. The restored [Ru(bpy)₃]²⁺ starts next cycle again.

As shown in Fig. 8(a), the addition of CDs@CoO_x-300 into the [Ru(bpy)₃]²⁺ solution in the presence of TEOA can obviously reduce the PL intensity than that of only [Ru(bpy)₃]²⁺ or with the catalyst. Meanwhile, transient absorption spectra (Fig. 8(b)) demonstrate that CDs@CoO_x-300 can accelerate the luminescence decay of [Ru(bpy)₃]Cl₂ from 387.9 to 271.0 ns. In

Fig. 8. Steady-state PL spectra (a), time-resolved PL spectra (b); LSV curves (c) and proposed mechanism (d) of CDs@CoO_x-300 for photocatalytic CO₂ reduction.

addition, the CO₂ reduction activities of bare Co₃O₄ and CDs@CoO_x-300 were evaluated by LSV in 0.5 M Na₂SO₄ solution (Fig. 8(c)). Although CDs shows no CO₂ reduction activity, the reduction current of the CDs@CoO_x-300 catalyst was greatly enhanced compared with that of bare Co₃O₄. The corresponding findings of PL spectra and LSV measurement indicate that the CDs@CoO_x-300 could efficiently expedite the separation and transfer of light-induced charges, and thus improving the CO₂ photoreduction activity.

According to the previously reported works [34,65], the possible process of the CO₂ photoreduction mechanism catalyzed by CDs@CoO_x-300 is presented in Fig. 8(d). Under visible light irradiation, the photosensitizer [Ru(bpy)₃]₂²⁺ is motivated to the excited state [Ru(bpy)₃]₂^{2+*}, which is reductively quenched by TEOA to form a reduced state [Ru(bpy)₃]₂^{•+}. Afterward, the excited electrons of [Ru(bpy)₃]₂^{•+} delocalizes and migrate to the CDs@CoO_x-300 catalyst to reduce the CO₂ molecules to the CO product, while the photosensitizer recover to the initial state. Alternatively, the electrons can react with the protons to form H₂.

Based on the above analysis and photocatalytic experiments, these results demonstrated that the incorporation of CDs into CoO_x plays a critical role in promoting the photocatalytic water oxidation and CO₂ reduction activities. Specifically, the CDs can serve as a nanosized template to regulate the crystallization process and then change the morphology according to the TEM results (Figs. 3(b) and S3). Thus, when coupled with carbon dots, the composite of CDs@CoO_x-300 not only exposes

more active sites but also facilitates electron transport. Ultimately, the synergistic effect between CoO_x and CDs boosted excellent photocatalytic behavior for water oxidation and CO₂ reduction.

3.5. Stability study

Besides the photocatalytic activity, the stability is another crucial factor parameter of a catalyst for further practical applications. Therefore, the cycling experiments of CDs@CoO_x-300 were conducted to visually evaluate the property of the catalyst. As shown in Fig. 9(a) and 9(b), after the five recycling runs, there is no significant change in the total amount of O₂ and CO evolution. In addition, the CDs@CoO_x-300 catalyst before and after photocatalytic reaction were examined by XPS. Fig. 9(c) and 9(d) show the similarity of Co 2p peak shapes and the satellite peaks of CDs@CoO_x-300 catalyst before and after reaction for water oxidation and CO₂ reduction, respectively, suggesting that there is no change in the valence state of Co 2p. In all, the cycling experiments and XPS analysis indicate that the CDs@CoO_x-300 is a highly robust catalyst during the photocatalytic reaction process.

4. Conclusions

In this work, we successfully synthesized a spongy porous CDs@CoO_x bifunctional photocatalyst by a facile hydrothermal and calcination method for enhancing the CoO_x water oxidation

Fig. 9. Amount of O₂ (a) and CO/H₂ (b) evolution in recycling tests and XPS spectra of fresh and used CDs@CoO_x-300 sample for water oxidation (c) and CO₂ reduction (d).

and CO₂ reduction activities for the first time. The morphological difference induced by the calcination temperature affects the photocatalytic performance of the CDs@CoO_x samples. Under the optimal conditions, it is notable that a maximum O₂ yield of 40.4% and an outstanding AQE of 58.6% are obtained over CDs@CoO_x-300. Furthermore, the optimized sample CDs@CoO_x-300 shows a CO selectivity of 89.3% and a CO generation rate of 8.1 μmol/h. Based on the photocatalytic control experiments, optical and electrochemical measurement, spongy porous amorphous composite CDs@CoO_x-300 can effectively enhance photocatalytic performances. The cycling experiments show that the CDs@CoO_x-300 is a highly robust catalyst during the photocatalytic reaction process. This work provides new insight for the design of feasible and stable cobalt-based carbon hybrids with high photocatalytic performance.

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Graphical Abstract

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Amorphous CoO_x coupled carbon dots as a spongy porous bifunctional catalyst for efficient photocatalytic water oxidation and CO₂ reduction

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A spongy porous catalyst CDs@CoO_x-300 was used as an efficient and stable bifunctional photocatalyst for water oxidation and CO₂-to-CO conversion, in which the boosted photocatalytic behavior is attributed to the synergistic effect between CoO_x and CDs.

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无定形 CoO_x 耦合碳点构筑海绵状多孔结构的双功能光催化剂用于提高水氧化和二氧化碳还原性能

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摘要: 随着化石燃料大量使用带来的温室效应、能源匮乏以及环境污染问题日趋严重, 寻找清洁高效的可再生能源用做传统化石燃料的替代品, 已经成为当今的研究重点. 太阳能驱动的水分解制备氢气和 CO_2 还原为CO, 不仅可以降低大气中 CO_2 的浓度, 而且提供了理想的能源气体 H_2 和有经济价值的化学物质, 实现了太阳能的转换/储存. 整个水分解反应包含两个半反应, 即质子还原和水的氧化. 其中水的氧化反应是一个涉及四个电子和四个质子转移的复杂过程, 需要很高的活化能, 被认为是全分解水反应的瓶颈步骤. 此外, CO_2 还原也是光合作用的重要半反应, 是将太阳能转化为化学燃料/原料的重要途径. 因此, 寻找一种同时具有高催化活性和稳定性的水氧化和 CO_2 还原双功能光催化剂至关重要.

本文以双氰胺和葡萄糖为原料, 通过简单的水热法脱水聚合得到碳点(CDs), 再与 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 形成均匀溶液烘干后, 通过改变不同煅烧温度(200, 300, 400和600 °C), 构筑了一系列 CoO_x 耦合碳点的海绵状多孔结构的双功能光催化剂 CDs@CoO_x , 并首次应用于光催化水氧化和 CO_2 还原. 我们发现, CDs可以作为模板来调节复合物的结晶度, 当在300 °C煅烧时得到的是无定形催化剂 CDs@CoO_x -300, 相比未掺杂的 Co_3O_4 , CDs的引入在促进光催化水氧化和 CO_2 还原活性方面起着关键作用. 因此, 当与碳点耦合时, CDs@CoO_x -300复合物不仅暴露了更多的活性位点, 而且促进了电荷分离. 最终, CoO_x 和CDs之间的协同作用促进了水氧化和 CO_2 还原.

当以 $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ 为光敏剂, $\text{Na}_2\text{S}_2\text{O}_8$ 为牺牲电子受体, 在pH为9.0的硼酸缓冲液中, CDs@CoO_x -300为光催化剂, 最大 O_2 收率为40.4%, 在460 nm处具有58.6%的表观量子效率. 同时将该催化剂 CDs@CoO_x -300用于以 $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ -TEOA的体系中进行光催化还原 CO_2 时, CO的生成速率为 $8.1 \mu\text{mol h}^{-1}$, 且CO选择性高达89.3%, 展现出了优异的催化性能. 此外, 在水氧化和 CO_2 还原循环测试中, 发现5次反应后, 催化活性无明显降低, 说明该双功能催化剂具有较高的稳定性. 本文为未来合理构建高效、稳定的碳掺杂的钴基双功能光催化剂提供了重要的启发和研究思路.

关键词: 碳点掺杂 CoO_x ; 双功能光催化剂; 水氧化; CO_2 还原; 协同效应

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