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Electrochemical Preparations and Photo-Electro Catalytic Properties of Flexible ZnNi/Al-LDHs/Carbon Fibers Composite

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Abstract: In this work, a promising flexible composite consisting of zinc (Zn), nickel (Ni) and aluminum (Al) layered double hydroxide coated carbon fibers (ZnNi/Al-LDHs/CFs) was prepared by electrochemical method with convenient recovery and separation. The structures, morphologies, and photo-electro catalytic properties of ZnNi/Al-LDHs/CFs were characterized by X-ray diffraction, infrared spectroscopy, field emission scanning electron microscopy, inductively coupled plasma atomic emission spectrometry and electrochemical impedance spectroscopy techniques. The excellent photo-electro bifunctional catalytic properties were obtained with the ZnNi/Al-LDHs/CFs composite as compared to that of Zn/Al-LDHs/CFs (photo catalyst) or Ni/Al-LDHs/CFs (electro catalyst) alone, which could be used in the electro-catalytic oxidations of methanol and ethanol, as well as the photo-electro synergistically catalytic degradation of 2,6-dichlorophenol.

Key words: electrochemical preparation; flexible carbon fibers composite; ZnNi/Al-LDHs; photo-electro double catalyst

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Among various layered double hydroxides (LDHs), Zn/Al-LDHs, Ni/Al-LDHs and ZnNi/Al-LDHs are interesting materials. Since they have typical common remarkable features of LDHs such as layered structure, adjustable textural properties and anion exchange capability^[1-3]. Zn/Al-LDHs were used as a photocatalyst for methyl-orange dye degradation^[4] except lubricant additives^[5], coolant in metal quenching^[6] and corrosion inhibitor^[7], because the layer structure can induce electron transfer, and prevent recombination of electrons and holes with increased photo-electronic transition efficiency compared to ZnO alone. Ni/Al-LDHs showed good electrocatalytic activity for methanol oxidation^[8] and enhanced electrochemical behaviors for supercapacitor^[9]. Recently, studies revealed that ZnNi/Al-LDHs could combine these capacities, and the addition of zinc in NiAl-LDHs could improve electrochemical performance in discharge potential, cycle stability and re-

versibility^[10]. ZnNi/Al-LDHs were also used in hydrogen production of ethanol and acetic acid steam reforming, low temperature hydrolysis of carbonyl sulfide^[10,13], and photocatalytic degradation of orange G^[14]. Electrochemical method is very attractive due to its simple and low cost at an atmospheric temperature and atmosphere. Surprisingly, only Zn/Al-LDHs and Ni/Al-LDHs were prepared using electrochemical method at inflexible sold electrodes up to now^[13,18,20], there was not any study for the electrochemical preparation of ZnNi/Al-LDHs except coprecipitation^[11,13] and dynamic urea hydrolysis^[12,14]. Moreover, the powder LDHs are inconvenient for practical photo or electro catalytic application with separation and recovery difficulties.

On the other hand, among many other conducting substrates, flexible carbon fibers have attracted much attention due to their unique properties such as high conductivity and knittability^[21-22], therefore, it

probably is a promising supporter material for LDHs with matching size. In this work, the Zn-Ni/Al-LDHs/CFs composite was firstly prepared by electrochemical method, which was characterized by various methods in detail. Ethanol, methanol and 2,6-dichlorophenol were used as probes to evaluate its photo and electro catalytic activities.

1 Experimental

1.1 Chemicals and Apparatus

Polyacrylonitrile-carbon fibers (CFs) were obtained from Dingfeng Carbon Fibers Fabrication Company of Yixing (China, Wuxi). One truss CFs have about 3000 branches with a diameter of $7 \pm 1 \mu\text{m}$, and it was snipped at 8 mm long in the following experiments. Chemical reagents of 2,6-dichlorophenol (2,6-2DCP), quercetin (Qu), aniline (An), $\text{Zn}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). $0.015 \text{ mol} \cdot \text{L}^{-1}$ Qu stock solution was prepared in ethanol. Phosphate buffer solution (PBS, $0.1 \text{ mol} \cdot \text{L}^{-1}$, pH 7.0) was prepared by mixing solutions of $0.1 \text{ mol} \cdot \text{L}^{-1}$ K_2HPO_4 and KH_2PO_4 . All other chemicals were of analytical grade and doubly-distilled water was used in all cases.

All electrochemical experiments were performed with a CHI 660B electrochemical workstation (Chenhua, Shanghai, China). Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 100 kHz to 0.10 Hz at an open circuit potential with an ac perturbation of 5 mV. Field emission scanning electron microscope (FE-SEM) images were obtained on a JSM-600 field emission scanning electron microanalyser (JEOL, Japan). X-ray diffraction (XRD) data of the samples were collected using a Rigaku D/MAX-rB diffractometer with $\text{Cu } K_\alpha$ radiation. Inductively coupled plasma atomic emission spectrometry (ICP-AES) data were collected on a Perkin-Elmer-Optima 7300 DV ICP-OES instrument (Perkin-Elmer Cooperation, USA). Infrared spectra (IR) were measured using KBr pellet at IR 200 spectrometer (Nicolet America). Photocatalysis experiments were carried out in 125 L

rectangular tin box equipped with a 300 W high pressure mercury (UV) lamp (Shanghai Yu Biotechnology Co. Ltd, China). Ultraviolet (UV) spectrum was measured at 2550 UV-visible spectrophotometer (Shimadzu, Japan). pH meter model was measured at HI 255 (Shanghai Leici Instruments). All experiments were conducted at room temperature.

1.2 Preparation of AQ/CFs

CFs were soaked in a mixed acid solution of nitric acid and perchloric acid (7:3) with ultrasonic agitation for 7 h^[22], then washed with doubly distilled water, and dried in vacuum. Since An and Qu have good electrochemical activities, and Qu with five -OH radicals has good chelate ability to metal ions^[23], the CFs were modified by polyaniline doped Qu using cyclic voltammetry (CV) to adhere the NiZn/Al-LDHs firstly. Here, polyaniline plays a role for embedding quercetin. After the CFs were undergone 8 cycles (reached a balance) in $0.1 \text{ mol} \cdot \text{L}^{-1}$, pH 7.0 PBS + $0.5 \text{ mmol} \cdot \text{L}^{-1}$ Qu + $0.5 \text{ mmol} \cdot \text{L}^{-1}$ An, the polymer modified CFs were rinsed with water to remove any physically adsorbed substances, and stored in $0.1 \text{ mol} \cdot \text{L}^{-1}$, pH 7.0 PBS at 4 °C for next use (signed as AQ/CFs).

1.3 Preparation of ZnNi/Al-LDHs/CFs

In 100 mL mixing solution containing $0.5 \text{ mol} \cdot \text{L}^{-1}$ KNO_3 , $0.03 \text{ mol} \cdot \text{L}^{-1}$ $\text{Zn}(\text{NO}_3)_2$, $0.03 \text{ mol} \cdot \text{L}^{-1}$ $\text{Ni}(\text{NO}_3)_2$ and $0.02 \text{ mol} \cdot \text{L}^{-1}$ $\text{Al}(\text{NO}_3)_3$, $1.0 \text{ mol} \cdot \text{L}^{-1}$ KOH was used to adjust pH to 4. 0.5 g AQ/CFs (8 trusses) was immersed into the mixing solution, cathodic deposition was carried out at a potential range of -0.2 to -1.6 V and a scan rate of $30 \text{ mV} \cdot \text{s}^{-1}$ for 8 cycles. The resulting carbon fibers were thoroughly rinsed by deionized water, and dried at 60 °C for 10 h in an oven, then stored in a refrigerator at 4 °C for next use (signed as ZnNi/Al-LDHs/CFs).

1.4 Photo and Electro Catalysis Tests

The photo and electro catalytic activities of Zn-Ni/Al-LDHs/CFs were evaluated by using methanol, ethanol and 2,6-2DCP as probes. The homemade Zn-Ni/Al-LDHs/CFs composite was the working electrode. The twisted platinum wire and Ag/AgCl were the counter electrode and reference electrode, respec-

tively.

During the photo and electro catalytic degradation tests of 2,6-2DCP, the source of irradiation was a 300 W high pressure mercury (UV) lamp. The experiments were carried out according to the following procedure: 100 mL 0.1 mol · L⁻¹ Na₂SO₄ containing 0.123 mmol · L⁻¹ 2,6-2DCP was put into a 200 mL reactor. Firstly, 2,6-2DCP was electro-oxidized at ZnNi/Al-LDHs/CFs, the source of irradiation was shut. Secondly, 2,6-2DCP was photo-catalytically degraded, the electrochemical system was kept at an open circuit. Thirdly, 2,6-2DCP underwent a simultaneously photo and electro catalytic degradation. In order to determine the effect, the lamp was turned on, and aliquots were sampled every 30 min during 3 h. The content in the sample was analyzed by measuring the maximum adsorption band (λ = 283 nm).

2 Results and Discussion

2.1 Characterizations

To adhere NiZn/Al-LDHs, the polyaniline (An) doped quercetin (Qu) film was firstly electro-polymerized at the surface of CFs^[23], constant (*K_{sp}*) values of Al(OH)₃, Zn(OH)₂ and Ni(OH)₂ are 3 × 10⁻³⁴, 1.2 ×

10⁻¹⁷ and 2.0 × 10⁻¹⁵, respectively, Al(OH)₃ and Zn(OH)₂ are amphoteric hydroxides. Al(OH)₃ is first essential precipitate due to its very low solubility, which completely covers the surface of AQ/CFs. As long as the NO₃⁻ reduction goes on, the concentration of OH⁻ rapidly increases, causing Al(OH)₃ dissolution, following the formation of Zn(OH)₂. With the continuous increase of OH⁻, Al(OH)₃ and Zn(OH)₂ dissolutions take place, and then ZnNi/Al-LDHs structure precipitates at the surface of AQ/CFs (Eq. 2) (signed as ZnNi/Al-LDHs/CFs)^[19]. The reaction takes place effectively, probably because the local pH around the AQ/CFs is much alkaline. In Fig. 2A, the inset, a little H₂ air bubble (-1.2 V) could be observed in the continuous scan probably due to the catalytic reduction of ZnNi/Al-LDHs/CFs toward H₂O (the inset, solid lines). But there was not any response at AQ/CFs (the inset, dashed line). Fig. 2B shows the CVs of CFs (a), AQ/CFs (b) and ZnNi/Al-LDHs/CFs (c) in 0.1 mol · L⁻¹ NaOH. A pair of peaks (0.45/0.22 V) could be observed corresponding to transition of Ni(III) and Ni(II) in Eq. 3, suggesting the formation of ZnNi/Al-LDHs/CFs.

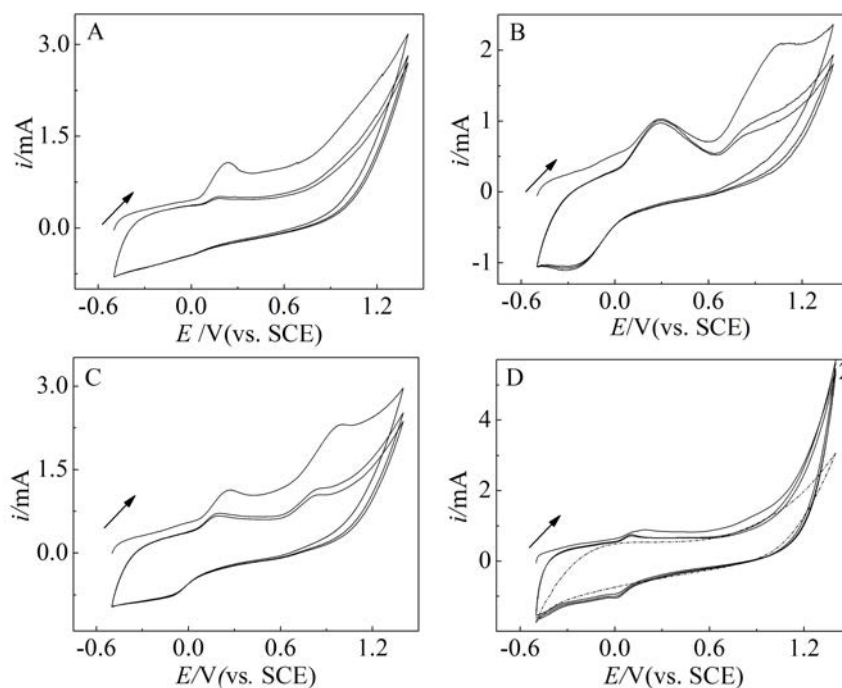
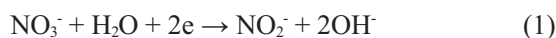


Fig. 1 CVs of CFs in 0.5 mmol · L⁻¹ Qu (A), 0.5 mmol · L⁻¹ An (B) and 0.5 mmol · L⁻¹ Qu + 0.5 mmol · L⁻¹ An (C). CVs of AQ/CFs (D, 2) and CFs (D, 1) in 0.1 mol · L⁻¹ PBS. Buffer: 0.1 mol · L⁻¹ pH 7.0 PBS. Scan rate: 50 mV · s⁻¹.

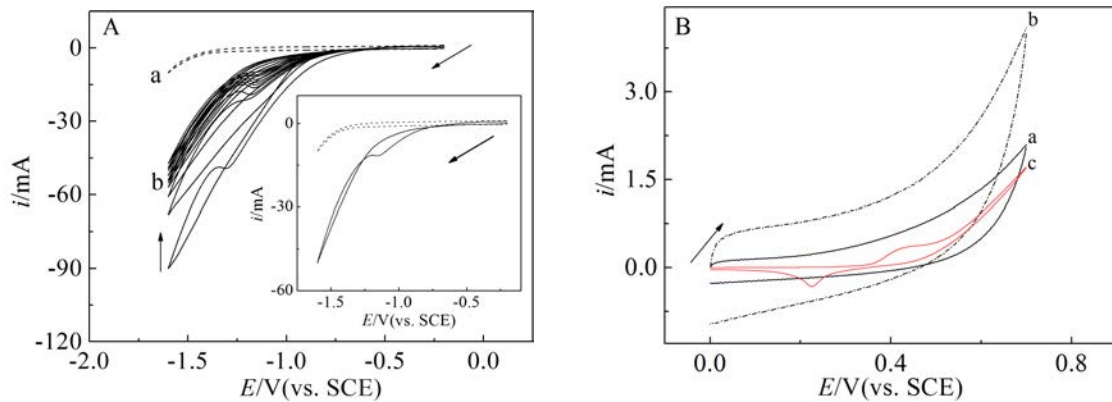
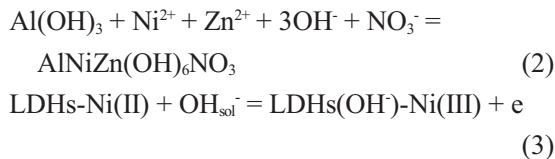


Fig. 2 A. CVs of AQ/CFs in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{KNO}_3$ (dashed line), and mixture solution including $0.5 \text{ mol} \cdot \text{L}^{-1} \text{KNO}_3$, $0.03 \text{ mol} \cdot \text{L}^{-1} \text{Zn}(\text{NO}_3)_2$, $0.03 \text{ mol} \cdot \text{L}^{-1} \text{Ni}(\text{NO}_3)_2$, $0.02 \text{ mol} \cdot \text{L}^{-1} \text{Al}(\text{NO}_3)_3$ (solid lines); Inset: CVs of ZnNi/Al-LDHs/CFs (solid lines) and AQ/CFs (dashed line) in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{KNO}_3$. Scan rate: $30 \text{ mV} \cdot \text{s}^{-1}$. B. CVs of CFs (a), AQ/CFs (b) and ZnNi/Al-LDHs/CFs (c) in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{NaOH}$. Scan rate: $50 \text{ mV} \cdot \text{s}^{-1}$.



In order to further investigate the interface properties of ZnNi/Al-LDHs/CFs, the EIS measurements were carried out. Fig. 3 shows the Nyquist plots and corresponding fitting equivalent circuits (the insets), and Table 1 summarizes the fitting data. Where R_s is the electrolyte resistance, R_i is the electric resistance of the LDHs coating, C_c is the capacitance of the LDHs coating, R_{ct} is the charge transfer resistance, C_{dl} is the double layer capacitance, and Z_w is the Warburg finite diffusion impedance. In Fig. 3A, after poly aniline doped quercetin was modified at CFs (AQ/CFs), the R_{ct} is obviously decreased from 15.97 to 8.814 Ω , suggesting an improved electroconductivity. In Fig. 3B, after the ZnNi/Al-LDHs composite was formed at AQ/CFs with continuous 5(c), 10(d), 20(e), 30(f) and 50 (g) cycles, both R_{ct} and R_i values are significantly increased, implying increasing charge transfer resistance.

Fig. 4(A-B) show the FE-SEM images of AQ/CFs, CFs and ZnNi/Al-LDHs/CFs materials. The surface AQ/CFs composite was coarse compared to that of original CFs (the inset) in Fig. 4A. However, a great deal of flowers-like morphology could be observed in Fig. 4B, and all the compositions consisted

of different sizes of layers, which were orderly stacked to form unit arrangement with a porous microstructure, suggesting the formation of ZnNi/Al-LDHs/CFs.

Fig. 5 shows the XRD pattern of ZnNi/Al-LDHs/CFs. The diffraction peaks appeared in the 2θ range of $5^\circ \sim 80^\circ$. The characteristic peaks at 10.0° , 19.73° and 41.5° corresponded to the reflections of (003), (006) and (015), respectively^[11,13]. Two “saw tooth” broad reflections at 33.54° and 60.76° should be labeled as 10 and 11 to indicate their 2-D origin, suggesting a turbostratically disordered structure. Moreover, the characteristic peak of carbon was near 24.1° ^[22].

FT-IR spectra of several materials including CFs (a), poly aniline (PA/CFs, b), poly quercetin (PQ/CFs, c), poly aniline doped AQ (AQ/CFs, d) and ZnNi/Al-LDHs/CFs (e) are given in Fig. 6. In Curve a, the IR bands at 3442 and 1631 cm^{-1} corresponded to -OH stretching and -COOH asymmetric stretching vibrations at CFs. In Curve b, the spectrum of PA/CFs showed a series of IR bands at 3442 cm^{-1} due to N-H stretching vibration, 1594 and 1436 cm^{-1} due to C=C of quinoid and benzenoid unit stretching modes, 1340 and 1211 cm^{-1} due to C-N stretching vibration, 1140 and 813 cm^{-1} due to C-H in-plane bending vibration and out of plane bending vibration of para disubstituted benzene ring^[26-27]. Moreover, the band at 1730 cm^{-1} probably matched to benzanilide (PhNHCO-) formed by aniline oxidation^[28-29]. In Curve c, the peaks

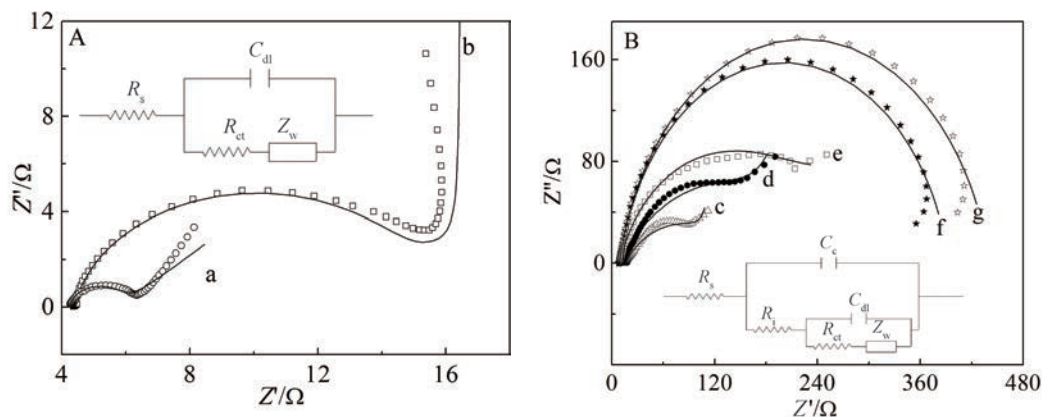


Fig. 3 A. EIS data and an equivalent circuit model (the inset) of CFs (a) and AQ/CFs (b). Bias potential: 0.31 V vs. SCE; B. EIS data and an equivalent circuit model (the inset) of ZnNi/Al-LDHs/CFs formed with continuous 5 (c), 10 (d), 20 (e), 30 (f) and 50 (g) cycles. Bias potential: 0.56 V vs. SCE. Solution: 0.1 mol·L⁻¹ NaOH. Frequency range: 0.01 ~ 0.10 Hz; Amplitude: 5 mV; The solid curves are the simulated plots obtained using the equivalent circuits shown in the corresponding insets.

Tab. 1 Model parameters simulated from the experimental EIS data in Fig. 3

Material	R_s/Ω	t/F	R_t/Ω	C_{dl}/F	R_{ct}/Ω	Z_w/Ω	
CFs	4.416	—	—	0.002374	15.97	0.1814	
AQ/CFs	4.279	—	—	0.001425	8.814	0.2285	
ZnNi/Al-LDHs/CFs	5 cycles	15.69	0.0008905	11.74	0.005611	125.5	0.05593
	10 cycles	11.45	0.002114	17.72	0.008257	188.0	0.03955
	20 cycles	9.582	0.0009803	18.29	0.001292	222.2	0.01695
	30 cycles	8.716	0.00151	60.41	0.001233	384.6	0.06051
	50 cycles	8.131	0.001418	69.27	0.001259	431.9	0.05065

at 1651 cm⁻¹ belonged to C=O absorption band, while 1376 and 1170 cm⁻¹ to -C-OH bending vibration of Qu inner surface^[30-31]. The band at 1313 cm⁻¹ matched to =C-O-C antisymmetrical or symmetrical stretching vibration. In Curve d, it is notable that all the peaks in Curves b and c could be observed, suggesting the formation of polyaniline doped Qu film at CFs (AQ/CFs). In Curve e, after ZnNi/Al-LDHs was electrodeposited at the surface AQ/CFs, all the peaks were hardly seen except the bands at 1630 ~ 1650 cm⁻¹. Two new peaks at 1386 and 823 cm⁻¹ related to the presence of nitrate ions in ZnNi/Al-LDHs^[20], and a broad peak centered at 3442 cm⁻¹ was generated by the -OH stretching of the LDH layer as well as the interlayer water molecules. These illustrate that the resulting ZnNi/Al-LDHs almost covered at the surface

of AQ/CFs.

Moreover, the ICP analysis results showed that the ratio of Zn²⁺:Ni²⁺:Al³⁺ was 0.34:1:0.66 in the ZnNi/Al-LDHs at CFs, and M(II):M(III) was 2:1. Combining the results from FTIR and ICP analyses, the compositions of the ZnNi/Al-LDHs at AQ/CFs would be best described as Zn_{0.34}Ni₁Al_{0.66}(OH)₃(NO₃)_{1.66}·xH₂O.

2.2 Photo and Electro Catalytic Applications

In order to evaluate the electro catalytic capabilities of ZnNi/Al-LDHs/CFs. Methanol, ethanol and 2,6-2DCP were used as electro-catalytic probs. Fig. 7 (A and B) show that the oxidation currents of methanol and ethanol were remarkably increased at ZnNi/Al-LDHs/CFs (c), compared to those at CFs (a), Zn/Al-LDHs/CFs (b) and Ni/Al-LDHs/CFs (c) in 0.1 mol·L⁻¹

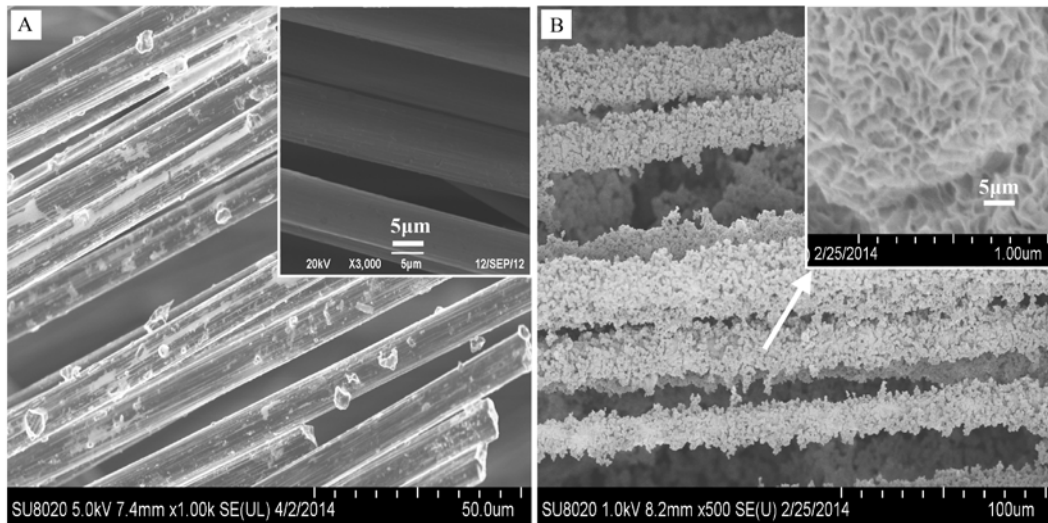


Fig. 4 FE-SEM images of AQ/CFs (A) , CFs (A, the inset), ZnNi/Al-LDHs/CFs (B and the inset)

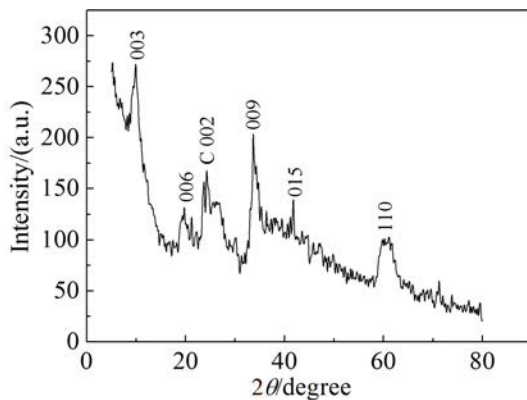


Fig. 5. XRD pattern of ZnNi/Al-LDHs/CFs

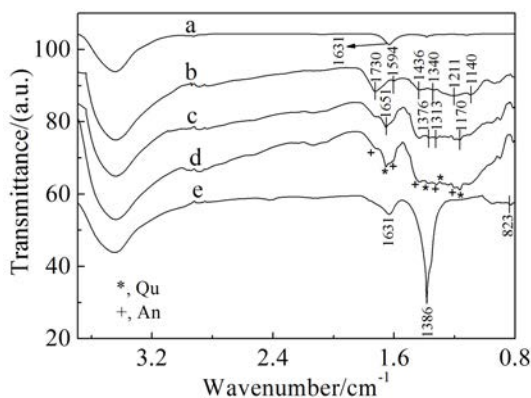


Fig. 6 IR spectra of CFs (a), PA/CFs (b), PQ/CFs (c), AQ/CFs (d) and ZnNi/Al-LDHs/CFs (e)

NaOH. It illustrates that ZnNi/Al-LDHs/CFs composite is a good catalyst for potential applications in fuel cell.

The photo and electro catalytic activities of ZnNi/Al-LDHs/CFs were evaluated by the degradation of 2,6-2DCP. Fig. 8 presents the UV spectra of 0.123 mmol · L⁻¹ 2,6-2DCP at ZnNi/Al-LDHs/CFs with 1.2 V in 3 h (c), in the absence (b) and presence (d) of ZnNi/Al-LDHs/CFs with irradiation of 300 W in 3 h, and simultaneous treatment at 1.2 V and irradiation of 300 W in 1 h (e) and 2 h (f). Curve a shows the maximum adsorption band of original 0.123 mmol · L⁻¹ 2,6-2DCP at 283 nm. For the photocatalytic activity, the degradation efficiency was obviously increased in the presence (d, 47.2%) compared to that in absence (b, 3.3%) of ZnNi/Al-LDHs/CFs with irradiation of 300 W in 3 h, suggesting a good photocatalysis. For the photo-electro synergistic catalytic activity, after 2,6-2DCP was oxidized at 1.2 V in 3 h (Curve c), a new sharp peak at 300 nm could be seen and matched to quinone^[32]. When 2,6-2DCP was simultaneously treated in the presences of ZnNi/Al-LDHs/CFs at 1.2 V and irradiation of 300 W with 1 h (e) and 2 h (f), the degradation efficiencies were significantly increased to 81.7% and 95.3%, respectively. Therefore, the ZnNi/Al-LDHs/CFs revealed an excellent photo-electro synergistic catalysis toward the degradation of 2,6-2DCP with the enhancing degradation efficiency compared to that of only photo or electro catalysis. The 2,6-2DCP could be quickly electro-catalyzed to quinone firstly, which was beneficial to the photo-

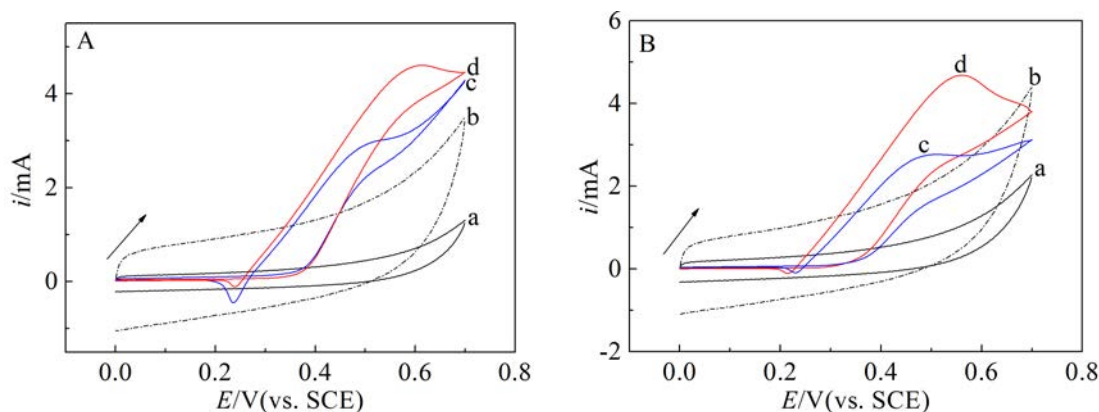


Fig. 7 CVs of CFs (a), Zn/Al-LDHs/CFs (b) and Ni/Al-LDHs/CFs (c) and ZnNi/Al-LDHs/CFs (d) in 0.1 mol·L⁻¹ methanol (A) and ethanol (B) containing 0.1 mol·L⁻¹ NaOH. Scan rate: 50 mV·s⁻¹.

catalytic degradation. As a result, the quinine could be further photo-catalyzed to organic smaller molecule, CO₂ and H₂O^[32]. Meanwhile, the degradation efficiencies of 2,6-2DCP were 69.1%, 81.7%, 89.2% and 95.3% with the degradation time at 0.5, 1, 1.5 and 2 h, respectively, suggesting an increased effect (not shown).

Moreover, after use, the ZnNi/Al-LDHs/CFs composite was cleaned by CV scans from 0 to 1.0 V for 30 cycles in 0.1 mol·L⁻¹ NaOH. The ZnNi/Al-LDHs/CFs composite was reused for 7 times at the same conditions to investigate the reusability. It was found that the sequential degradation efficiencies were 95.3%, 95.3%, 95.2%, 94.7%, 94.4%, 94.1% and 94.0% upon 7 times, suggesting a good reusability.

3 Conclusions

The ZnNi/Al-LDHs/CFs composite was obtained by an electrochemical method with a facile one-step procedure. Experiment results proved that the ZnNi/Al-LDHs/CFs composite was an excellent electrode and catalyst material with convenient recovery and separation. It could be successfully used as an electro catalyst for the oxidations of methanol and ethanol, as well as a photo-electro bifunctional catalyst for the degradation of 2,6-2DCP. This study explored a new opportunity to prepare the promising flexible ZnNi/Al-LDHs/CFs composite and demonstrated possible applications in fuel cell and organic wastewater treatment.

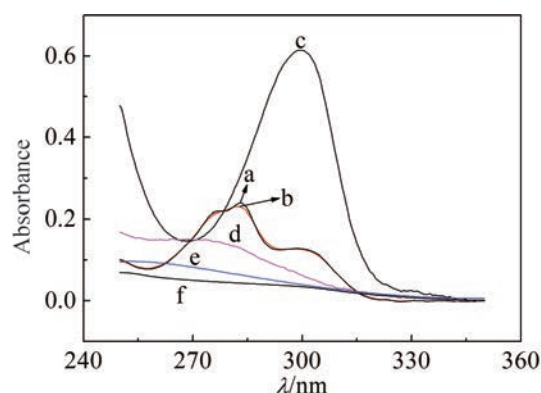


Fig. 8 UV spectra of 2,6-2DCP at ZnNi/Al-LDHs/CFs without treatment at 1.2 V (a) and with 1.2 V in 3 h (c). UV spectra of 2,6-2DCP in the absence (b) and presence (d) of ZnNi/Al-LDHs/CFs with irradiation of 300 W in 3 h, and simultaneous treatment at 1.2 V and irradiation of 300 W in 1 h (e) and 2 h (f). System: 0.1 mol·L⁻¹ NaSO₄. 2,6-2DCP concentration: 0.123 mmol·L⁻¹.

Acknowledgments

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柔性锌镍/铝层状双羟基/碳纤维复合材料的 电化学制备及光电催化性能

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摘要: 本文采用电化学方法, 制备了一种便于回收和分离的柔性锌镍/铝层状双羟基/碳纤维(ZnNi/Al-LDHs/CFs)复合材料. 采用 X 射线衍射、红外光谱、场发射扫描电镜、电感耦合等离子体原子发射光谱和电化学阻抗光谱技术表征了 ZnNi/Al-LDHs/CFs 复合材料的结构、形貌和光电催化性能. 与单独使用 Zn/Al-LDHs/CFs 作为光催化剂或 Ni/Al-LDHs/CFs 作为电催化剂相比较, ZnNi/Al-LDHs/CFs 复合材料显示了良好的光-电双功能催化特性, 既可被用作乙醇和甲醇氧化的电催化剂, 也可光电协同催化 2,6-二氯苯酚降解.

关键词: 电化学制备; 柔性碳纤维复合材料; 锌镍/铝层状双羟基/碳纤维; 光电双功能催化剂