Improvement of Trisodium Citrate-Modified NiFe-Layered Double Hydroxide Nanosheets with Carbon Black for Oxygen Evolution Reaction

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Abstract: The pursuit of highly active and cost-effective catalysts toward oxygen evolution reaction (OER) is a crucial strategy to resolve the imminent energy crisis. NiFe layered double hydroxide (NiFe LDH) is acknowledged as one of the most promising OER electrocatalysts in alkaline electrolytes. Herein, we report a novel stepwise approach to synthesize NiFe LDHs materials merging with carbon black (CB) via trisodium citrate (TC), modifying toward OER. Benefiting from the inimitable wrapped structure, the decreased size of porous nanosheets and the superconductivity of CB substrate, NiFe LDHs/CB-TC presents excellent catalytic features with a comparative overpotential (236 mV at 10 mA cm⁻²) and an ultralow Tafel slope (31 mV dec⁻¹), which are almost lower than those of advanced catalysts associated with expensive carbonaceous materials. Therefore, it is expected that such a high-activity and low-cost material can be a promising catalyst employed for the electrochemical energy storage and conversion systems.

Keywords: oxygen evolution reaction; layered double hydroxide; carbon black; trisodium citrate; electrocatalysts

1. Introduction

With the rapid depletion and quick decrease of fossil fuels, renewable and environmentally friendly energy sources have been intensely researched as substituents [1,2]. In particular, hydrogen is recognized as one of the most promising next-generation energies [3,4]. As a valid approach to generate high-purity hydrogen, electrochemical water splitting has been largely hampered by its anodic oxygen evolution reaction (OER), due to the sluggish reaction kinetics [5–8]. The early used OER catalysts are some noble metal materials such as RuO₂ and IrO₂ for their high electrochemical performance. However, high cost and low reserve limit their wide-ranging application [9,10]. Thus, cost-effective electrocatalysts based on abundant free noble metals have stimulated extensive research interests currently [11–15].

Among various promising catalysts, layered double hydroxides (LDHs) consisting of first-row transition metals (Ni, Fe, Co, Mn etc.) have triggered considerable focus on OER owing to their specific two-dimensional anionic clays and adjustable components characteristics [16–21]. Especially, NiFe LDHs has been considered to be a promising class of catalytic materials toward OER [22–26]. Its highly effect on catalytic properties can be ascribed to the synergistic interactions between Ni and Fe atoms...
compared with the single Ni and Fe components [27–29]. Nevertheless, the OER performances of NiFe LDHs are still obstructed by their low exposure of active sites and poor electrical conductivity. To overcome these difficulties, LDHs combining with diversified carbon materials with higher electrical conductivity have been further investigated. The carbon materials are as follow: graphene [30–32], carbon nanotubes (CNTs) [33], and carbon quantum dots (CQDs) [34]. It is widely acknowledged that the smaller size of materials could lead to more exposed areas [35]. All sorts of approaches to synthesizing LDHs have been carried out with designated functionalities. However, the specific carbonaceous materials are difficult to form an efficient synergistic effect between Ni and Fe, resulting in relatively fewer active sites for NiFe LDHs. Moreover, the common approaches to synthesizing NiFe LDHs have the disadvantage of higher cost and complexity to realize large-scale production for industrial application. Therefore, fabricating a cost-effective nanostructure of NiFe LDHs with large catalytic surface areas is critically needed in the pursuit of superior OER electrocatalysts.

Herein, encouraged by these findings, we propose a novel approach to synthesize trisodium citrate (TC)-modified NiFe LDHs catalysts merging with low-cost carbon black (CB) toward OER for the first time. The CB provides both high electrical conductivity and large specific surface areas, while NH4F could make the surface of LDH layers form abundant pores due to the etching effect [36,37]. Alternatively, as a chelating agent, TC enhances the synergism between Ni and Fe, as well as the coupling between LDHs and CB substrate. Moreover, decreasing and adjusting the size of nanoparticles is also one of the prominent abilities of TC [38]. Consequently, the as-fabricated NiFe LDHs/CB-TC, which contains fast electron transfer and a large number of active sites, exhibits a relatively low overpotential of 236 mV at a current density of 10 mA/cm² and an ultralow Tafel slope of 31 mV-dec⁻¹.

2. Results and Discussion

In recent years, NiFe LDHs associated with various carbon materials in 1D to 3D have been synthesized and employed as oxygen evolution reaction (OER) electrocatalysts. Nonetheless, a strong combination of NiFe LDHs and amorphous carbon black (CB) so far was rarely reported. As depicted in Figure 1, a novel stepwise fabrication process of NiFe LDHs/CB-TC is schematically presented. We first synthesized a flower-like NiFe LDHs through a modified hydrothermal method. After the doping of oxidized CB via nitrate method (black), NiFe LDHs layers (yellow) generally showed a porous surface. However, the simple bonding of both was too poor to exhibit an excellent OER performance. To solve this problem, we introduced trisodium citrate (TC) to the reaction system to obtain a strongly bonded NiFe LDHs/CB-TC material, where LDHs nanosheets were integrally wrapped by CB.

Figure 1. A schematic of the synthesis process of NiFe layered double hydroxides (NiFe LDHs)/carbon black (CB)-trisodium citrate (TC).

Morphological features and the distinct microstructure of as-prepared samples were analyzed by scanning electron microscope (SEM), field-emission scanning electron microscopy (FESEM), and transmission electron microscope (TEM), respectively. FESEM (Figure 2a) and TEM (Figure 3a,b) images of BP2000 (the kind of CB used in this work) indicate its rough surface and amorphous structure owing to the nonuniform spiral lattice fringes. The NiFe LDHs material consisting of numerous radially
arranged and slightly wrinkled nanosheets presents a self-assembled flower-like morphology with a size of about 6 \( \mu \)m in diameter (Figure 2b, Figure S1a,b). Furthermore, TEM images (Figure 3c,d) of NiFe LDHs appear smooth, unbroken surface without any pores. Figure 2c and Figure S1c,d display the morphology of NiFe LDHs/CB, suggesting that CB is randomly adsorbed on the outer surface of the LDHs, which can be further proved by a control group (focal length) of TEM images (Figure S2a,b). According to Figure 3e, NiFe LDHs/CB has an averaged lateral size of 200 nm. To further investigate its microstructure, TEM images of NiFe LDHs/CB under higher magnification are picked up (Figure 3f, Figure S2c,e). The abundant pores (4–7 nm, caused by the etching effect of NH₄F) on the surface of nanosheets are clearly displayed by the sharp contrast between NiFe LDHs and NiFe LDHs/CB. Revealed by HRTEM image (Figure S2f), NiFe LDHs/CB show lattice fringes (015) with a d-spacing of 0.238 nm. To further confirm the key role of NH₄F, another control group study of NiFe LDHs/CB with and without NH₄F was conducted. The XRD patterns of the two compared samples (Figure S3) indicate that the adding of NH₄F can promote the crystallization. It is observed that (see Figure S4) the surface of NiFe LDHs/CB without NH₄F is relatively smooth, while NiFe LDHs/CB with NH₄F (twice the molar quantities of the standard sample used in this work) presents plenty of uniform pores, showing a better catalytic performance (see Figure S5). This sort of porous structure is expected to provide a great number of active sites, which is beneficial for the diffusion of ions and the generated gas. From Figure 4a,b, one can see that NiFe LDHs/CB-TC is distinctively oriented from the other three samples. The randomly arranged nanosheets are fully wrapped by amorphous CB via a TC modified method so that a strong interface connection between LDHs and CB can be ensured, which facilitates the electron transfer during the OER procedure. An enlarged TEM image (Figure 4c) confirmed that the lateral size of NiFe LDHs/CB-TC is about 100 nm on average compared to a size of 200 nm for NiFe LDHs/CB. A high-resolution TEM image (Figure 4d) shows that the dominant lattice for NiFe LDHs/CB-TC is determined to be the (015) crystal plane with a d spacing of 0.238 nm.

![Figure 2. FESEM images of (a) BP2000, (b) NiFe LDHs, (c) NiFe LDHs/CB, and (d) NiFe LDHs/CB-TC.](image-url)
Figure 3. Original and the enlarged TEM images of (a,b) BP2000, (c,d) NiFe LDHs, and (e,f) NiFe LDHs/CB.

The crystalline structural information of the as-prepared materials was examined by X-ray diffraction (XRD), as illustrated in Figure 5a. It is observed that BP2000 has no characteristic peaks, indicating its amorphous structure. The XRD profiles of NiFe LDHs (Figure S6) and NiFe LDHs/CB well match the standard pattern (black curve, JCPDS card No. 38-0715), exhibiting a series of (003), (006), (101), (012), (015), (018), (110), and (113) reflections at 2-theta of 11.3°, 22.7°, 33.4°, 34.4°, 38.7°,
45.9°, 59.9°, and 61.2°. Specifically, the intensity of NiFe LDHs/CB is integrally weaker than that of NiFe LDHs because of the doping of amorphous BP2000. According to the formula of Scherrer: 

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

the diffusion broadening of the diffraction line means a smaller grain size. As depicted by the NiFe LDHs/CB-TC XRD pattern, the two significantly broadened diffraction peaks at 33.7° and 60.1° might be ascribed to the stacking defects and decreasing crystallite sizes, corresponding to the (101) and (110) reflection of NiFe LDHs. Besides, the broad peak at about 23° is assigned to the (002) lattice plane of carbon [40].

To further study the surface chemical compositions and oxidation states of NiFe LDHs/CB-TC, X-ray photoelectron spectroscopy (XPS) is determined. The XPS spectrum is illustrated in Figure 5b, where a series of peaks related to C, O, Ni, and Fe elements can be observed. As shown in Figure S7, the binding energies at 284.6 eV and 531.9 eV are attributed to C 1s and O 1s, respectively. The high-resolution XPS spectrum (Figure 5c) of Ni 2p can be split into six peaks. The peaks positioned at 856.6 eV and 862.4 eV are assigned to Ni²⁺ 2p1/2 and Ni²⁺ 2p3/2, and the peaks located at 874.2 eV and 880.3 eV are related to Ni³⁺ 2p1/2 and Ni³⁺ 2p3/2. Meanwhile, the satellite peak of Ni 2p3/2 and Ni 2p1/2 occur at 864.6 eV and 882.5 eV, respectively [41]. Moreover, the ratio of Ni²⁺ and Ni³⁺ is determined to be 2.1 by XPS spectrum, suggesting the dominant valence state of Ni. Figure 5d exhibits the high-resolution XPS spectrum of Fe 2p, which are deconvoluted into eight peaks. The signals at 709.8 eV, 713.4 eV, 724.0 eV, and 726.8 eV correspond to Fe²⁺ 2p3/2, Fe³⁺ 2p3/2, Fe²⁺ 2p1/2, and Fe³⁺ 2p1/2, while their respective satellites occur at 717.4 eV, 720.2 eV, 730.5 eV, and 734.0 eV [42]. The ratio of Fe³⁺ and Fe²⁺ is calculated to be 4.1, indicating the main valence state of NiFe LDHs/CB-TC is Fe³⁺. The above-mentioned results confirm the formation of Ni(II)Fe(III) LDHs-TC as we designed. Typically, the LDH presents laminated structure in which divalent (M²⁺, e.g., Mg, Ni, Co) and trivalent (M³⁺, e.g., Al, FeCr) cations coordinated with a hydroxyl group constitute a brucite-like major layer; besides, anion and water

Figure 4. (a–c) TEM and (d) HRTEM images of NiFe LDHs/CB-TC, inset in (d) is the FFT (Fast Fourier Transform) pattern.
molecules occupy the interlamellar space [43]. However, in the actual synthesis, there will be different valence states of the same metal in LDHs. It is worth noting that the results of XPS in this job reveal the existence of a small amount of Ni$^{3+}$ and Fe$^{2+}$. The existence of Ni$^{2+}$ is considered as unusual, which plays an important role in improving OER performance [44]. In contrast, Ni$^{3+}$ deriving from oxidation on the surface of CB may be an inactive species for OER owing to the high valence states and difficulties for further oxidation. Thus, the ratio (2.1) of Ni$^{2+}$ to Ni$^{3+}$ implies the high electrocatalytic activity of NiFe LDHs-TC for OER. It is known to us that the H$_2$O molecule can be dissociated into hydrogen (H%) and hydroxyl (OH%) radicals by sonolysis [45]. The increased Fe$^{2+}$ might be from Fe$^{3+}$ having reacted with H% radicals during ultrasonication.

Additionally, the composition of Ni and Fe atoms estimated by EDS (Energy Dispersive Spectrometer, Figure S8) is listed in Table S1. We conclude that the ratio of nickel and iron for NiFe LDHs, NiFe LDHs/CB, and NiFe LDHs/CB-TC, is about 2.07, 2.24, and 1.88, respectively, which is in accordance with the initial ratio of raw materials. Specifically, it can be observed that the atomic percentage of C has a sharp increase for NiFe LDHs/CB in contrast to NiFe LDHs, suggesting the successful introduction of CB. Furthermore, the C composition of NiFe LDHs/CB-TC is higher than that of NiFe LDHs/CB, owing to the decreased C loss as the reaction proceeds, confirming the more effective bonding between LDHs and CB caused by the introduction of TC.

The ratio of the Ni to Fe calculated by XPS for NiFe LDHs/CB-TC is also taken into account. The result (1.81) is approximately to the EDS result (1.88) but with a slight difference. This subtle difference may stem from the limitations of both tests. XPS can detect surface elements to a depth of a few nanometers, while EDS can detect with a depth of micrometers. In this work, combining the structure diagram and the TEM results, it can be seen that the surface of NiFe LDHs/CB-TC has a certain thickness of the carbon layer. Thus, the unevenness of the internal and external components will cause the result of XPS to be slightly different from that of EDS. A rational molar ratio of M$^{2+}$/M$^{3+}$ cation for stable structural NiFe LDHs is normally in the range of 2.0–4.0. According to Geng et al.’s work, the Ni/Fe ratio could be varied from 0.1–9.0 in the LDHs, and Ni$_3$Fe$_4$ LDHs possesses the best OER performance [39]. In this work, we have altered the Ni/Fe ratio of NiFe LDHs from 2.0 to 5.0 in

Figure 5. (a) XRD patterns of all samples; (b) XPS survey, (c) Ni 2p, (d) Fe 2p spectrum of NiFe LDHs/CB-TC.
the starting solution. The corresponding result of LSV confirms that Ni$_2$Fe$_{1}$ LDHs is the optimum catalyst (Figure S9).

N$_2$ adsorption/desorption was employed to determine the mesoporous nature of materials. Figure S10 shows the adsorption/desorption isotherms of NiFe LDHs as control, NiFe LDHs/CB and NiFe LDHs/CB-TC, respectively. We discovered that the Brunauer Emmett Teller (BET) surface area of NiFe LDHs/CB-TC reached 627.4 m$^2$ g$^{-1}$, which is approximately 17 times that of NiFe LDHs (37.4 m$^2$ g$^{-1}$) and 2 times that of NiFe LDHs/CB (375.0 m$^2$ g$^{-1}$). The adsorption–desorption isotherms of NiFe LDHs/CB-TC is classified as type-IV with a distinct hysteresis loop located in the relative pressure (P/P$_0$) range of 0.6–1.0, indicating a typical feature of mesoporous material [46]. As shown in Figures S11–S13, the pore sizes of as-prepared samples are estimated by the Nonlocal Density Functional Theory (NLDFT) method from 0 nm to 40 nm. NiFe LDHs presents a non-porous structure, while NiFe LDHs/CB exhibits a mesoporous structure. The above results are consistent with TEM. Notably, for NiFe LDHs/CB-TC, its pore size distribution mainly centers at 1.5–2.0 nm, 2.0–7.5 nm, 7.5–12.5 nm, and 12.5–35.0 nm, which further proves that the sample owns the pore form of the mesopores. The mesoporous structure was caused by the addition of NH$_4$F, and it is obvious that the higher BET surface area was due to the introduction of TC. According to Wang’s work, trisodium citrate can function as a chelating agent. Besides, the citrate ion, a layer intercalated agent, can control the morphology and size of the $\alpha$-Ni(OH)$_2$ precursor growth of hierarchically porous NiO [47]. In this work, we not only make full use of the properties, but also prove the enhancing bonding between LDHs and CB by means of TC modifying to further improve the specific areas. The large specific surface area and proper pore size facilitate the diffusion of electrons and OH$^-$ and lead to the fast release of O$_2$ during oxygen evolution reaction. Furthermore, the large specific surface area can also provide a great deal of active sites and more defects, resulting in excellent OER activities [48].

The electrocatalytic oxygen evolution reaction (OER) activities of as-obtained samples were evaluated in O$_2$$^-$ saturated 1.0 M KOH solution under a typical three-electrode system at room temperature (25 °C). All the materials associated, of which the catalyst loading is 0.25 mg/cm$^2$, were subjected to repeated cyclic voltammogram scans (CV) for 50 cycles firstly. IR-corrected polarization curves were detected at a scan rate of 5 mV/s to minimize the capacitive current. According to the previous report, the overpotential ($\eta$) calculated from IR-corrected polarization curves at 10 mA cm$^{-2}$ was an important criterion to evaluate the OER activity [49]. As shown in Figure 6a,b, NiFe LDHs/CB-TC requires a much smaller overpotential of 236 mV to afford a current density of 10 mA cm$^{-2}$, compared to 362 mV for BP2000, 315 mV for NiFe LDHs, and 283 mV for NiFe LDHs/CB, respectively. To avoid influencing the evaluation of the catalyst due to the overlapped with the Ni$^{2+}$ to Ni$^{3+}$ oxidation peak, we give the standard at 20 mA/cm$^2$ as follows: 264 mV, 308 mV, 346 mV, and 400 mV for NiFe LDHs/CB-TC, NiFe LDHs/CB, NiFe LDHs, and BP2000, respectively. The linear portions of polarization curves were fitted in the light of Tafel equation: $\eta = b \log j + a$, where $\eta$ is the overpotential, j is the current density, and b is the Tafel slope [33]. As depicted in Figure 6c, NiFe LDHs/CB-TC exhibits an impressive Tafel slope of 31 mV·dec$^{-1}$, indicating much better performance than that of NiFe LDHs/CB (73 mV·dec$^{-1}$), NiFe LDHs (77 mV·dec$^{-1}$), and BP2000 (97 mV·dec$^{-1}$). The high electrocatalytic activity of the NiFe LDHs/CB-TC compares favourably with those of many high-performance Ni–Fe LDH-based and commercial OER electrocatalysts in 1.0 M KOH (Table S2). The outstanding OER performance of NiFe LDHs/CB-TC can be ascribed to the unique wrapped structure, the decreased size of nanosheets, as well as the abundant pores on the surface of LDHs and the superconductivity of the CB substrate. In detail, aside from the prime synergistic effect between Ni and Fe, this surrounded porous conformation provides not only sufficient active sites for the OER reaction but also adequate channels for the diffusion of the ions and the generated gas. In addition, the ability of electron transfer can also be strengthened by the superconductive CB substrate.
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Figure 6. (a) Polarization curves of various samples and corresponding (b) comparison of overpotential at 10 mA/cm², (c) Tafel slopes; (d) Linear plots of cathodic charging currents versus the scan rate and (e) electrochemical impedance spectra of NiFe LDHs, NiFe LDHs/CB, NiFe LDHs/CB-TC; (f) Chronopotentiometry test of NiFe LDHs/CB-TC at 10 mA/cm² in 1M KOH.

To underlie the mechanism for the superior activity and the size-dependent synergy catalytic effect, the electrochemical active surface area (ECSA) measurement was conducted after cyclic voltammograms (CVs) at 100 mV/s for 50 cycles (Figure S14a). Figure S11b–d display the CVs obtained with different scan rates in a non-Faradaic region (0.0 V–0.1 V versus SCE). The double layer capacitance (Cdl), which is estimated by the slope of the scan rate versus the current density plot, can be adopted as a reasonable parameter to represent the improved active surface areas [50]. As depicted in Figure 6d, NiFe LDHs/CB-TC exhibits the larger Cdl (205.66 μF cm⁻²) than that of NiFe LDHs/CB (179.08 μF cm⁻²) and NiFe LDHs (74.54 μF cm⁻²), demonstrating the intrinsic extraordinary catalytic activity of the active sites in NiFe LDHs/CB-TC. Electrochemical impedance spectroscopy (EIS) was performed to examine the charge-transfer kinetics for OER. According to Figure 6e, NiFe LDHs and NiFe LDHs/CB possess an Rct value (the charge transfer resistance, calculated approximately from the diameter of the semicircle [51]) of 1.20 Ω cm⁻² and 1.06 Ω cm⁻², respectively, both of which are larger than that of NiFe LDHs/CB-TC (0.90 Ω cm⁻²). This indicates that the hybrid of CB via the TC-modified method can facilitate the accelerated electron/proton transfer for OER. The corresponding equivalent circuit of all samples for EIS can refer to Figure S15. Besides, the long-term durability of NiFe LDHs/CB-TC was determined by chronopotentiometry at a constant anodic current density of 10 mA cm⁻² for at least 6 h. The NiFe LDHs/CB-TC catalyst presents good stability with a slight shift from 1.47 V to 1.59 V (versus RHE, Reversible Hydrogen Electrode) after a 21,600-s continuous test. During the
chronopotentiometry test, we observe that the mechanical binding between the NiFe LDH/CB-TC powder and GC electrode is weak: even if we add Nafion as a binder, many pieces of catalyst were lost to the electrolyte. Moreover, the oxygen that is continuously precipitated in the working electrode during the electrochemical process may cause slight damage to the structure, and both situations can be ascribed to the slight decay of durability.

According to the above discussion and analysis, the superior electrocatalytic activities of the as-prepared NiFe LDHs/CB-TC sample toward OER can be ascribed to the introduction of TC for the following four possible reasons. (a) Before adding the precipitant, TC as a dispersant can effectively prevent the agglomeration of LDHs precursors and CB, which can create a uniform and stable environment for the nucleation reaction. During the following step, TC is employed to decrease the nucleation and growth rate of crystals but increase self-attachment interaction, resulting in uniform hierarchical structures [52]. (b) As a chelating agent, a TC molecule possesses one hydroxyl group (OH) and three carboxyl groups (COO). Both the COO and OH can serve as binding sites to coordinate with metal ions [53]. In this work, TC interacts with Fe$^{3+}$ and Ni$^{2+}$ to form complexes, which enhances the ligand effect and stabilizes the configuration of LDHs. (c) More importantly, TC possesses a superior capping capability, which can be proved by the LDHs structure covered by CB (NiFe LDHs/CB-TC) compared to the random and scattered distribution of CB on the surface of LDHs (NiFe LDHs/CB). This high coverage of CB can offer a high conductivity and prevent the LDHs from corrosion under the harsh reaction medium to achieve a high and stable activity. (d) Finally, combined with NH$_4$F, we take full advantage of these properties of TC to design a carbon-encapsulated porous LDHs structure. In contrast to NiFe LDHs/CB, the synergistic effect of CB and the NiFe LDHs nanosheet is enhanced to effectively promote OER activity due to the unique construction. Moreover, porous LDHs with a high exposure of active sites could greatly accelerate electron/mass transfer and promote electrolyte diffusion. Therefore, the result indicates that as-prepared NiFe LDHs/CB-TC is a cost-effective catalyst toward OER in alkaline electrolyte.

3. Materials and Methods

3.1. Chemicals and Materials

Nickel(II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O), iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O), urea (CO(NH$_2$)$_2$), ammonium fluoride (NH$_4$F), nitric acid (HNO$_3$), absolute ethanol (C$_2$H$_5$OH), trisodium citrate (Na$_3$C$_6$H$_5$O$_7$, TC) were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the above chemicals were of analytical reagent grade and obtained without any further purification. Carbon black (CB, BLACK PEARLS® 2000) was from Cabot Corporation (Boston, MA, USA), while ionomer solution was Nafion (5 wt %) from DuPont (Wilmington, DE, USA). Ultrapure water was utilized throughout the experiments by a EPED-10TS Purification System (EPED-10TS, Chinese EPED Corporation, Shanghai, China).

3.2. Preparation of Carbon Black (CB)

Prior to the synthesis, the concentrated nitric acid was essentially used as a treatment solution for carbon black (CB). Firstly, a mixed solution consists of concentrated nitric acid (68 wt %, 9.265 g) and ultrapure water (27 g) was placed in a 100 mL beaker. With the addition of CB (2 g), the mixture was then gradually poured into the flask under a magnetically stirring at 90 °C for 4 h. After cooling down to room temperature, the mixture was transferred into a measuring beaker of exact 500 mL. Following this, 16 g NaOH was dispersed in 200 mL of ultrapure water to form a 2 mol/L solution, which was then added dropwise to the beaker until the pH was up to 7. Finally, the precipitate was thoroughly washed with ultrapure water 8 times and dried in vacuum at 60 °C overnight.
3.3. Preparation of NiFe LDHs, NiFe LDHs/CB

In a standard hydrothermal method of NiFe LDHs preparation, 0.8 mM Ni(NO$_3$)$_2$·6H$_2$O, 0.4 mM Fe(NO$_3$)$_3$·9H$_2$O, and 3.6 mM NH$_4$F were utterly dissolved in 20 mL of ultrapure water firstly. The total molar amount of metal cations was kept as a constant. Afterwards, 360 mg of urea was added to the solution, which was then set in an ultrasound bath for 30 min. Subsequently, the resulting suspension was subjected to a hydrothermal method at 120 °C for 12 h. After cooling down to room temperature, the as-synthesized sediment was gathered, followed by rinsing with ultrapure water and absolute ethanol three times, respectively. At last, the production was aged in a vacuum oven at 60 °C throughout the night. For the NiFe LDHs/CB composites, the processes are the same as that of NiFe LDHs except for the addition of CB (2.0 g/L).

3.4. Preparation of NiFe LDHs/CB-TC

In brief, synthesized CB (2.0 g/L) and Na$_3$C$_6$H$_5$O$_7$ (1.2 mM, TC) was dispersed in 20 mL of ultrapure water, firstly. After 30 min of ultrasound, Ni(NO$_3$)$_2$·6H$_2$O (0.8 mM), Fe(NO$_3$)$_3$·9H$_2$O (0.4 mM), and NH$_4$F (3.6 mM) were dissolved in the suspension. For the sufficient adsorption of Fe$^{3+}$ and Ni$^{2+}$ ions onto the CB surface, the mixture was sonicated for another 30 min. Then, the solution was stirred vigorously at 60 °C for 10 min with the addition of urea (6.0 mM). The subsequent procedure was the same as the synthesis of NiFe LDHs.

3.5. Characterizations

The crystalline phases were identified by an X-ray diffractometer (XRD, D8 Advance, Cu Kα, Bruker, Billerica, MA, USA) at a scan speed of 0.2, ranging from 10° to 80°. To acquire the potential information of the materials’ microstructure, the scanning electron microscope (SEM, Hitachi, Tokyo, Japan) measurement was conducted on S-3400N II at 30 kV, while the field emission scanning electron microscope (FESEM, FEI, Hillsboro, OR, USA) determination was performed on an FEI NOVA NanoSEM230. The high-resolution transmission electron microscope (HRTEM, FEI, Hillsboro, OR, USA) images were taken by a TECNAI F20. The X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, Chigasaki, Japan) data were recorded by PHI 5000 VersaProbe with an Al Kα radiator at 5 kV. Nitrogen sorption isotherms of the LDHs composites were collected at 77K by ASAP 2020. Brunauer Emmett Teller (BET, Micromeritics, Norcross, GA, USA) and Nonlocal Density Functional Theory (NLDFT) were used for the specific surface area and porosity evaluations, respectively.

3.6. Electrochemical Measurements

All electrochemical measurements were conducted on an electrochemical workstation (Gamry Reference 3000, Warminster, PA, USA) in a configured three-electrode system, of which a glassy carbon disk electrode (GC, 5 mm in diameter) acted as a working electrode, a saturated calomel electrode (SCE) served as a reference electrode, and a platinum wire worked as a counter electrode. The catalyst ink was fabricated as follows: 5 mg of catalyst was first dispersed in 1 mL of solution, which consists of 0.95 mL of ethanol and 0.05 mL of Nafion (5% wt), followed by ultrasonication for 30 min to generate a homogeneous ink (for pure NiFe LDHs, adding extra 2 mg XC-72). Then, 9.8 µL of the ink was dripped onto the polished GC electrode with a loading amount of 0.25 mg/cm$^2$. Prior to the test, the electrolyte using 1.0 M KOH was purged by O$_2$ for at least 30 min. If without extra statement, all the potentials presented were converted to the RHE reference scale based on the formula ($E_{RHE} = E_{SCE} + 0.059 \times pH + 0.241$ V). Meanwhile, all the data appeared was IR-corrected.

The cyclic voltammetry measurement (CV) was carried out to activate the samples ranging from 1.0 V to 1.5 V versus RHE for 50 cycles. Linear sweep voltammetry (LSV) curves were recorded at a scan rate of 5 mV/s. The electrochemically active surface area (ECSA), which was determined by the double layer capacitance ($C_{dl}$), was obtained by CVs within the range of 0.0–0.1 V versus SCE at various scan rates (20, 40, 60, 80, and 100 mV/s). Electrochemical impedance spectroscopy (EIS) was
conducted on the same system with AC impedance over a frequency from 0.01 to 10⁶ Hz. With the current density set at 10 mA/cm², chronopotentiometry (CP) measurements were examined for 6 h.

4. Conclusions

In summary, after a systematic study, we contributed a novel stepwise strategy to synthesize trisodium citrate (TC)-modified NiFe LDHs catalysts merging with low-cost carbon black (CB) toward OER for the first time. The optimized NiFe LDHs/CB-TC catalyst is more active than NiFe LDHs/CB and NiFe LDHs. This excellent OER performance can be ascribed to its unique structural advantages. The superconductive CB substrate ensures fast charge transfer, and the porous surface of NiFe LDHs can provide an efficient channel to active sites for ion access and oxygen escape. Furthermore, the integrally wrapped structure and the decreased average size of NiFe LDHs from 200 to 100 nm result in a larger surface area to afford more active sites, indicating a strong interface connection with the bonding of LDHs and CB as well as the enhancement of the synergistic effect between Ni and Fe. Consequently, NiFe LDHs/CB-TC exhibits superior electrochemical features toward OER with a low overpotential (236 mV at 10 mA cm⁻²) and Tafel slope (31 mV dec⁻¹), which are almost lower than that of those NiFe-based catalysts coupling with expensive carbon materials. This work aims to provide a facile strategy to synthesize a cost-effective OER catalyst as substituents to realize large-scale production for industrial application. Moreover, we also offer a valid approach to solving the problem in the formation of an efficient synergistic effect between Ni and Fe with the specific carbonaceous materials. It is expected that such a high-activity and low-cost catalyst can be promising for employment in electrochemical energy storage and conversion systems.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/4/431/s1, Figure S1: SEM images of as-prepared (a,b) NiFe LDHs, (c,d) NiFe LDHs/CB, (e,f) NiFe LDHs/CB-TC, Figure S2: (a–e) additional TEM and (f) HRTEM images of NiFe LDHs/CB, inset in (f) is the FFT pattern, Figure S3: XRD patterns of NiFe LDHs/CB with no NH₄F and with NH₄F (twice the molar quantities of the standard sample used in this work), respectively, Figure S4: TEM images of NiFe LDHs/CB (a,b) without NH₄F, (c,d) with NH₄F (twice the molar quantities of the standard sample used in this work), respectively, Figure S5: LSV patterns of NiFe LDHs/CB with no NH₄F and with NH₄F (twice the molar quantities of the standard sample used in this work), respectively, Figure S6: XRD pattern of NiFe LDHs, Figure S7: XPS spectra of NiFe LDHs/CB-TC for (a) C 1s, (b) O 1s, Figure S8: EDS spectra of (a) NiFe LDHs, (b) NiFe LDHs/CB, (c) NiFe LDHs/CB-TC, Figure S9: XRD pattern of NiFe LDHs with Ni/Fe ratio from 2–5, Figure S10: N₂ adsorption-desorption isotherm curve of as-prepared samples, Figure S11: Pore size distribution curve of NiFe LDHs/CB-TC in high resolution, Figure S12: Pore size distribution histogram of NiFe LDHs/CB-TC, Figure S14: (a) Cyclic voltammograms of all samples ranging from 1.0 – 1.6 V vs. RHE at 100 mV/s; Cyclic voltammograms of NiFe LDHs/CB-TC, (b) NiFe LDHs, (c) NiFe LDHs/CB, (d) NiFe LDHs/CB-TC within the range 0.0–0.1 V vs. SCE at various scan rates (20, 40, 60, 80, 100 mV/s), Figure S15: Equivalent circuit of all samples for EIS, Table S1: Comparison of atomic percentages determined by EDS, Table S2: Comparison of electrocatalytic OER activities of this work with other NiFe-based and commercial OER catalysts in 1M KOH, References.

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References

1. Montoya, J.H.; Seitz, L.C.; Chakthranont, P.; Vojvodic, A.; Jaramillo, T.F.; Norskov, J.K. Materials for solar fuels and chemicals. Nat. Mater. 2016, 16, 70–81. [CrossRef] [PubMed]
2. Zhang, H.; Nai, J.; Yu, L.; Lou, X.W. Metal-Organic-Framework-Based Materials as Platforms for Renewable Energy and Environmental Applications. Joule 2017, 1, 77–107. [CrossRef]
3. Pendashteh, A.; Palma, J.; Anderson, M.; Marcilla, R. NiCoMnO$_4$ nanoparticles on N-doped graphene: Highly efficient bifunctional electrocatalyst for oxygen reduction/evolution reactions. Appl. Catal. B 2017, 201, 241–252. [CrossRef]
4. Gu, Y.; Chen, S.; Ren, J.; Jia, Y.A.; Chen, C.; Komarneni, S.; Yang, D.; Yao, X. Electronic Structure Tuning in Ni$_3$FeN/r-GO Aerogel toward Bifunctional Electro catalyst for Overall Water Splitting. ACS Nano 2018, 12, 245–253. [CrossRef] [PubMed]
5. Lu, Q.; Yu, Y.; Ma, Q.; Chen, B.; Zhang, H. 2D Transition-Metal-Dichalcogenide-Nanosheet-Based Composites for Photocatalytic and Electrocatalytic Hydrogen Evolution Reactions. Adv. Mater. 2016, 28, 1917–1933. [CrossRef] [PubMed]
6. Zhao, S.; Wang, Y.; Dong, J.; He, C.-T.; Yin, H.; An, P.; Zhao, K.; Zhang, X.; Gao, C.; Zhang, L.; et al. Ultrathin metal–organic framework nanosheets for electrocatalytic oxygen evolution. Nat. Energy 2016, 1, 1–10. [CrossRef]
7. Seh, Z.W.; Kibsgaard, J.; Dickens, C.F.; Chorkendorff, I.; Norskov, J.K.; Jaramillo, T.F. Combining theory and experiment in electrocatalysis: Insights into materials design. Science 2017, 355. [CrossRef]
8. Zhang, B.-T.; Liu, J.; Yue, S.; Teng, Y.; Wang, Z.; Li, X.; Qu, S.; Wang, Z. Hot electron injection: An efficacious approach to charge LaCoO$_3$ for improving the water splitting efficiency. Appl. Catal. B 2017, 219, 432–438. [CrossRef]
9. Siracusano, S.; Van Dijk, N.; Payne-Johnson, E.; Baglio, V.; Aricò, A.S. Nanosized IrOx and IrRuOx electrocatalysts for the O$_2$ evolution reaction in PEM water electrolyzers. Appl. Catal. B 2015, 164, 488–495. [CrossRef]
10. Sun, W.; Song, Y.; Gong, X.Q.; Cao, L.M.; Yang, J. Hollandite Structure K(x approximately 0.25)IrO$_2$ Catalyst with Highly Efficient Oxygen Evolution Reaction. ACS Appl. Mater. Interfaces 2016, 8, 820–826. [CrossRef]
11. Han, L.; Dong, S.; Wang, E. Transition-Metal (Co, Ni, and Fe)-Based Electro catalysts for the Water Oxidation Reaction. Adv. Mater. 2016, 28, 9266–9291. [CrossRef] [PubMed]
12. Xu, X.; Song, F.; Hu, X. A nickel iron diselenide-derived efficient oxygen-evolution catalyst. Nat. Commun. 2016, 7, 12324. [CrossRef] [PubMed]
13. Guan, B.Y.; Yu, X.Y.; Wu, H.B.; Lou, X.W.D. Complex Nanostructures from Materials based on Metal-Organic Frameworks for Electrochemical Energy Storage and Conversion. Adv. Mater. 2017, 29. [CrossRef]
14. Zhu, Y.P.; Guo, C.; Zheng, Y.; Qiao, S.Z. Surface and Interface Engineering of Noble-Metal-Free Electro catalysts for Efficient Energy Conversion Processes. Acc. Chem. Res. 2017, 50, 915–923. [CrossRef] [PubMed]
15. Shi, Y.; Yu, Y.; Liang, Y.; Du, Y.; Zhang, B. In Situ Electrochemical Conversion of an Ultrathin Tannin Nickel Iron Complex Film as an Efficient Oxygen Evolution Reaction Electro catalyst. Angew. Chem. Int. Ed. Engl. 2019, 58, 3769–3773. [CrossRef] [PubMed]
16. Han, N.; Zhao, F.; Li, Y. Ultrathin nickel–iron layered double hydroxide nanosheets intercalated with molybdate anions for electrocatalytic water oxidation. J. Mater. Chem. A 2015, 3, 16348–16353. [CrossRef]
17. Li, Z.; Shao, M.; An, H.; Wang, Z.; Xu, S.; Wei, M.; Evans, D.G.; Duan, X. Fast electro synthesis of Fe-containing layered double hydroxide arrays toward highly efficient electrocatalytic oxidation reactions. Chem. Sci. 2015, 6, 6624–6631. [CrossRef]
18. Liang, H.; Meng, F.; Caban-Acevedo, M.; Li, L; Forticaux, A.; Xiu, L.; Wang, Z.; Jin, S. Hydrothermal continuous flow synthesis and exfoliation of NiCo layered double hydroxide nanosheets for enhanced oxygen evolution catalysis. Nano Lett. 2015, 15, 1421–1427. [CrossRef]
19. Qiao, Z.; Zhang, Y.; Zhu, Y.; Cao, C.; Bao, X.; Xu, J. One-step synthesis of zinc–cobalt layered double hydroxide (Zn–Co-LDH) nanosheets for high-efficiency oxygen evolution reaction. J. Mater. Chem. A 2015, 3, 6878–6883. [CrossRef]
20. Shao, M.; Zhang, R.; Li, Z.; Wei, M.; Evans, D.G.; Duan, X. Layered double hydroxides toward electrochemical energy storage and conversion: Design, synthesis and applications. Chem. Commun. 2015, 51, 15880–15893. [CrossRef]
21. Xu, Y.; Hao, Y.; Zhang, G.; Lu, Z.; Han, S.; Li, Y.; Sun, X. Room-temperature synthetic NiFe layered double hydroxide with different anions intercalation as an excellent oxygen evolution catalyst. RSC Adv. 2015, 5, 55131–55135. [CrossRef]
22. Tang, C.; Wang, H.S.; Wang, H.F.; Zhang, Q.; Tian, G.L.; Nie, J.Q.; Wei, F. Spatially Confined Hybridization of Nanometer-Sized NiFe Hydroxides into Nitrogen-Doped Graphene Frameworks Leading to Superior Oxygen Evolution Reactivity. Adv. Mater. 2015, 27, 4516–4522. [CrossRef] [PubMed]
23. Yu, X.; Zhang, M.; Yuan, W.; Shi, G. A high-performance three-dimensional Ni–Fe layered double hydroxide/graphene electrode for water oxidation. *J. Mater. Chem. A* **2015**, *3*, 6921–6928. [CrossRef]

24. Dionigi, F.; Strasser, P. NiFe-Based (Oxy)hydroxide Catalysts for Oxygen Evolution Reaction in Non-Acidic Electrolytes. *Adv. Energy Mater.* **2016**, *6*, 1600621. [CrossRef]

25. Hunter, B.M.; Hieringer, W.; Winkler, J.R.; Gray, H.B.; Müller, A.M. Effect of interlayer anions on [NiFe]-LDH nanosheet water oxidation activity. *Energy Environ. Sci.* **2016**, *9*, 1734–1743. [CrossRef]

26. Luo, M.; Cai, Z.; Wang, C.; Bi, Y.; Qian, L.; Hao, Y.; Li, L.; Kuang, Y.; Li, Y.; Lei, X.; et al. Phosphorus oxoanion-intercalated layered double hydroxides for high-performance oxygen evolution. *Nano Res.* **2017**, *10*, 1732–1739. [CrossRef]

27. Dong, Y.; Zhang, P.; Kou, Y.; Yang, Z.; Li, Y.; Sun, X. A First-Principles Study of Oxygen Formation Over NiFe-Layered Double Hydroxide Surface. *Catal. Lett.* **2015**, *145*, 1541–1548. [CrossRef]

28. Friebel, D.; Louie, M.W.; Bajdich, M.; Sanwald, K.E.; Cai, Y.; Wise, A.M.; Cheng, M.J.; Sokaras, D.; Weng, T.C.; et al. Phosphorus citrate reduced gold nanoparticles. *Mater. Char. Phys.* **2019**, *253*, 303–309. [CrossRef]

29. Morales-Guio, C.G.; Liardet, L.; Hu, X. Oxidatively Electrodeposited Thin-Film Transition Metal (Oxy)hydroxides as Oxygen Evolution Catalysts. *J. Am. Chem. Soc.* **2016**, *138*, 8946–8957. [CrossRef]

30. Ma, W.; Ma, R.; Wang, C.; Liang, J.; Liu, X.; Zhou, K.; Sasaki, T. A superlattice of alternately stacked Ni–Fe hydroxide nanosheets and graphene for efficient splitting of water. *ACS Nano* **2015**, *9*, 1977–1984. [CrossRef]

31. Youn, D.H.; Park, Y.B.; Kim, J.Y.; Magesh, G.; Jang, Y.J.; Lee, J.S. One-pot synthesis of NiFe layered double hydroxide/reduced graphene oxide composite as an efficient electrocatalyst for electrochemical and photoelectrochemical water oxidation. *J. Power Sources* **2015**, *294*, 437–443. [CrossRef]

32. Zhan, T.; Liu, X.; Lu, S.; Hou, W. Nitrogen doped NiFe layered double hydroxide/reduced graphene oxide mesoporous nanosaurus as an effective bifunctional electrocatalyst for oxygen evolution and evolution reactions. *Appl. Catal. B* **2017**, *205*, 551–558. [CrossRef]

33. Gong, M.; Li, Y.; Wang, H.; Liang, Y.; Wu, J.Z.; Zhou, J.; Wang, J.; Regier, T.; Wei, F.; Dai, H. An advanced NiFe layered double hydroxide electrocatalyst for water oxidation. *J. Am. Chem. Soc.* **2013**, *135*, 8452–8455. [CrossRef] [PubMed]

34. Tang, D.; Liu, J.; Wu, X.; Liu, R.; Han, X.; Han, Y.; Huang, H.; Liu, Y.; Kang, Z. Carbon quantum dot/NiFe layered double-hydroxide composite as a highly efficient electrocatalyst for water oxidation. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7918–7925. [CrossRef]

35. Basahel, S.N.; Al-Thabaiti, S.A.; Narasimharao, K.; Ahmed, N.S.; Mokhtar, M. Nanostructured Mg-Al hydrotalcite as catalyst for fine chemical synthesis. *J. Nanosci. Nanotechnol.* **2014**, *14*, 1931–1946. [CrossRef]

36. Qu, B.; Yu, X.; Chen, Y.; Zhu, C.; Li, C.; Yin, Z.; Zhang, X. Ultrathin MoSe2 Nanosheets Decorated on Carbon Fiber Cloth as Binder-Free and High-Performance Electrocatalyst for Hydrogen Evolution. *ACS Appl. Mater. Interfaces* **2015**, *7*, 14170–14175. [CrossRef]

37. Qin, Z.; Melinte, G.; Gilson, J.P.; Jaber, M.; Bozhilov, K.; Boullay, P.; Mintova, S.; Ersen, O.; Valchek, V. The mosaic structure of zeolite crystals. *Angew. Chem. Int. Ed.* **2016**, *55*, 15049–15052. [CrossRef]

38. Ngumbi, P.K.; Mugo, S.W.; Ngaruiya, J.M.; King’ondu, C.K. Multiple plasmon resonances in small-sized citrate reduced gold nanoparticles. *Mater. Chem. Phys.* **2019**, *233*, 263–266. [CrossRef]

39. Zhang, K.; Wang, W.; Kuai, L.; Geng, B. A facile and efficient strategy to gram-scale preparation of composition-controllable Ni-Fe LDHs nanosheets for superior OER catalysis. *Electrochim. Acta* **2017**, *225*, 303–309. [CrossRef]

40. Yang, D.; Gu, J.; Liu, X.; He, H.; Wang, M.; Wang, P.; Zhu, Y.; Fan, Q.; Huang, R. Monodispersed Pt3Ni Nanoparticles as a Highly Efficient Electro catalyst for PEMFCs. *Catalysts* **2019**, *9*, 588. [CrossRef]

41. Guo, J.; Li, X.; Sun, Y.; Liu, Q.; Quan, Z.; Zhang, X. In-situ confined formation of NiFe layered double hydroxide quantum dots in expanded graphite for active electrocatalytic oxygen evolution. *J. Solid State Chem.* **2018**, *262*, 181–185. [CrossRef]

42. Bhargava, G.; Gouzman, I.; Chun, C.M.; Ramanarayanan, T.A.; Bernasek, S.L. Characterization of the “native” surface thin film on pure polycrystalline iron: A high resolution XPS and TEM study. *Appl. Surf. Sci.* **2007**, *253*, 4322–4329. [CrossRef]

43. Meng, X.; Han, J.; Lu, L.; Qiu, G.; Wang, Z.L.; Sun, C. Fe(2+) -Doped Layered Double (Ni, Fe) Hydroxides as Efficient Electrocatalysts for Water Splitting and Self-Powered Electrochemical Systems. *Small* **2019**, *15*, e1902551. [CrossRef] [PubMed]
44. Chi, J.-Q.; Yan, K.-L.; Xiao, Z.; Dong, B.; Shang, X.; Gao, W.-K.; Li, X.; Chai, Y.-M.; Liu, C.-G. Trimetallic Ni Fe Co selenides nanoparticles supported on carbon fiber cloth as efficient electrocatalyst for oxygen evolution reaction. Int. J. Hydrogen Energy 2017, 42, 20599–20607. [CrossRef]

45. Munonde, T.S.; Zheng, H.; Nomngongo, P.N. Ultrasonic exfoliation of NiFe LDH/CB nanosheets for enhanced oxygen evolution catalysis. Ultrason. Sonochem. 2019, 59, 104716. [CrossRef]

46. Wang, N.; Sun, B.; Zhao, P.; Yao, M.; Hu, W.; Komarneni, S. Electrodeposition preparation of NiCo2O4 mesoporous film on ultrafine nickel wire for flexible asymmetric supercapacitors. Chem. Eng. J. 2018, 345, 31–38. [CrossRef]

47. Han, D.; Xu, P.; Jing, X.; Wang, J.; Yang, P.; Shen, Q.; Liu, J.; Song, D.; Gao, Z.; Zhang, M. Trisodium citrate assisted synthesis of hierarchical NiO nanospheres with improved supercapacitor performance. J. Power Sources 2013, 235, 45–53. [CrossRef]

48. Cai, S.; Meng, Z.; Tang, H.; Wang, Y.; Tsiakaras, P. 3D Co-N-doped hollow carbon spheres as excellent bifunctional electrocatalysts for oxygen reduction reaction and oxygen evolution reaction. Appl. Catal. B 2017, 217, 477–484. [CrossRef]

49. Suen, N.T.; Hung, S.F.; Quan, Q.; Zhang, N.; Xu, Y.J.; Chen, H.M. Electrocatalysis for the oxygen evolution reaction: Recent development and future perspectives. Chem. Soc. Rev. 2017, 46, 337–365. [CrossRef]

50. McCrory, C.C.; Jung, S.; Peters, J.C.; Jaramillo, T.F. Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction. J. Am. Chem. Soc. 2013, 135, 16977-16987. [CrossRef]

51. Li, X.; Hao, X.; Wang, Z.; Abudula, A.; Guan, G. In-situ intercalation of NiFe LDH materials: An efficient approach to improve electrocatalytic activity and stability for water splitting. J. Power Sources 2017, 347, 193–200. [CrossRef]

52. Liang, Q.; Ma, W.; Shi, Y.; Li, Z.; Yang, X. Hierarchical Ag3PO4 porous microcubes with enhanced photocatalytic properties synthetized with the assistance of trisodium citrate. CrystEngComm 2012, 14, 2966. [CrossRef]

53. Huang, Z.; Zhao, Y.; Song, Y.; Zhao, Y.; Zhao, J. Trisodium citrate assisted synthesis of flowerlike hierarchical Co3O4 nanostructures with enhanced catalytic properties. Colloids Surf. A 2017, 516, 106–114. [CrossRef]