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Synergistic Effect between Ni and Ce Dual Active Centers Initiated by Activated Fullerene Soot for Electro-Fenton Degradation of Tetracycline

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Abstract: The degradation of a high concentration of organic pollutants has long been a challenge to water restoration, and the development of electro-Fenton catalysis offers a practical approach to solving this problem. In this study, a novel electro-Fenton catalyst, activated fullerene soot-loaded NiO-doped CeO₂ (0.4(0.4NiO-CeO₂)-AFS) nanoparticles, was prepared through the impregnation of 0.4NiO-CeO₂ particles and activated fullerene soot (AFS). When applied for the degradation of 200 mg/L of tetracycline, this catalyst demonstrated a degradation rate as high as 99%. Even after 20 cycles, the degradation rate was more than 80%. Moreover, it was concluded that AFS could initiate the synergistic effect between Ni and Ce dual active centers in the degradation of tetracycline; this can be ascribed to the extremely large specific surface area of AFS.

Keywords: fullerene soot; NiO-doped CeO₂; tetracycline; degrading efficiency; electro-Fenton



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1. Introduction

Recently, CeO₂ has been intensively investigated as an electro-Fenton catalyst for the degradation of organic pollutants, mainly owing to their abundant crystal defects, unique crystal structure, and reversible +3/+4 valence changing ability [1–3]. However, pure CeO₂ does not demonstrate adequate electro-Fenton efficiency because of its easy aggregation and low conductivity [2,3]. To overcome these disadvantages, scientists have paid much attention to composites of CeO₂ nanoparticles and other materials, including carbon materials, transition metal oxide, and others [4,5]. Kuang et al. synthesized a composite of CeO₂ and carbon nanotubes for the electro-Fenton degradation of acid complexes in livestock wastewater [6]. Transmission electron microscopy (TEM) images confirmed that the carbon nanotubes can effectively prevent the aggregation of CeO₂ particles, and therefore, the composite demonstrates good catalytic activity. Chen et al. prepared biocarbon-supported CeO₂ hollow spheres for the electro-Fenton degradation of phenol and demonstrated that the carbon material could effectively improve electrochemical activity [7]. Li et al. reported a three-dimensional CeO₂/RGO electrocatalyst [8], which exhibited a much higher efficiency of H₂O₂ and ·OH generation than CeO₂ particles toward the degradation of ciprofloxacin. As for the compositions of CeO₂ and transition metal oxides, they are found to have many novel properties favoring the decomposition of organic pollutants. Zhang et al. applied Prussian-blue-modified CeO₂ to degrade norfloxacin and ascribed its much-enhanced catalytic activity to the synergistic effect between Fe³⁺/Fe²⁺ and Ce³⁺/Ce⁴⁺ [9]. It is worth mentioning that the doping of non-metallic heteroatoms on CeO₂ can often lead to a change in the local electronic environment and the enhancement of the defect degree, which result in the excellent catalytic activity of CeO₂ [10]. Han et al. prepared N, P co-doped carbon-encapsulated CeO₂, which showed the properties of enhanced electron transfer and activity of H₂O₂ [11].

Moreover, it was recently reported that NiO and its composite have great performance in many electrocatalytic reactions, e.g., oxygen reduction reaction (ORR) [12], oxygen evolution reaction (OER) [13], and hydrogen evolution reaction (HER) [14]. When applied in advanced oxidation technology, it can effectively activate persulfate and H_2O_2 , thus effectively accelerating the decomposition of phenol [15]. The author found that the degree of oxygen defects in nickel oxide is proportional to the catalytic activity and that the nickel ion at the defect plays a crucial role. Jian et al. determined the active crystal plane of NiO through experimental methods, which guided subsequent research [16]. Jo et al. reported a composite of NiO nanoparticles and porous carbon for the degradation of aqueous microcystins and discovered that the crystal structure of NiO hardly changed after multiple degradation reactions, indicating that NiO naturally possesses good structural stability [17]. Yu et al. designed a carbon-coated trimetallic metal-organic framework (MOF) (with Fe, Ni, and Al) for aqueous pesticides [18]. The results indicate that this composite achieved over 90% napropamide degradation within 60 min and found that embedded NiO shows a synergistic effect for promoting the catalytic activity of Fe sites.

Fullerene soot (FS) is the insoluble residual solid obtained after the extraction of soluble fullerene and polyaromatic hydrocarbon from the soot. With the increasing use of fullerenes in biological, medical, and energy fields, the scale of fullerene production is also increasing year by year; however, how to reuse the residual FS remains a problem [19]. Chen et al. studied the use of FS as a carbonaceous adsorbent and found that FS shows good adsorption capacity for volatile organic compounds [20]. Gao et al. used FS as the precursor to prepare active carbon particles [21]. When it was applied as the anode material in the supercapacitor, it showed good electrical double-layer capacitor activity. This implies that FS has the potential to be used as an electrocatalyst. Silva et al. found that heat-treated FS has a larger specific capacitance and higher charge transfer efficiency than traditional activated carbon [22]. Compared with other porous carbon forms, FS has a very high degree of graphitization; therefore, it is considered to be an ideal activated carbon electrode material.

In this study, we prepared FS by the arc-discharge method and then used KOH activation to fabricate activated fullerene soot (AFS). Then, we used the co-precipitation method to prepare NiO-doped CeO_2 ($\gamma\text{NiO-CeO}_2$) nanoparticles and loaded them on AFS by the impregnation method. According to the definition of dual active centers, two similar catalysts participate in catalyzing the same type of reaction in a system [23], and the prepared composite of 0.4NiO-CeO_2 fully meets this standard. As a result, $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$ thus formed shows remarkable performance for the electro-Fenton degradation of tetracycline (TC). $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$ is expected to be a promising and widely applicable electro-Fenton catalyst for the effective degradation of organic pollutants in water environments.

2. Results

2.1. Material Characterization

Figure 1a shows the XRD patterns of FS, AFS, $0.4\text{CeO}_2\text{-AFS}$, 0.4NiO-AFS , and $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$ composites. A characteristic peak in FS can be ascribed to the (002) plane of the graphite phase by referring to JCPDS 41-1487. In comparison, two broad peaks in AFS are well indexed to the (002) and (101) planes of the quasi-graphite phase, respectively. In line with the Debye-Scherrer equation, the average crystallite sizes of AFS are considerably smaller than those of FS, and smaller grain sizes inevitably expose more surface area and increase the number of active sites, consistent with the Brunauer-Emmett-Teller (BET) surface area analysis in Figure 2a. In addition, the diffraction patterns of $0.4\text{CeO}_2\text{-AFS}$ correspond to fluorite structural CeO_2 , according to JCPDS 43-1002, and the diffraction peaks of 0.4NiO-AFS are assigned to bunsenite structural NiO, according to JCPDS 47-1049. Two phases' diffraction signals appear in $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$, indicating that Ni was dispersed on CeO_2 in the form of NiO instead of entering into the lattice of CeO_2 . This implies that there is more than one active center in the system. Figure 1b displays the

diffraction patterns of $0.4(y\text{NiO}-\text{CeO}_2)\text{-AFS}$ ($y = 0.1\text{--}0.6$). With the proportion of NiO in $0.4(y\text{NiO}-\text{CeO}_2)\text{-AFS}$ gradually increasing, the intensity of peaks corresponding to NiO increases, proving that the chemical composition in $0.4(y\text{NiO}-\text{CeO}_2)\text{-AFS}$ ($x = 0.1\text{--}0.6$) changes regularly.

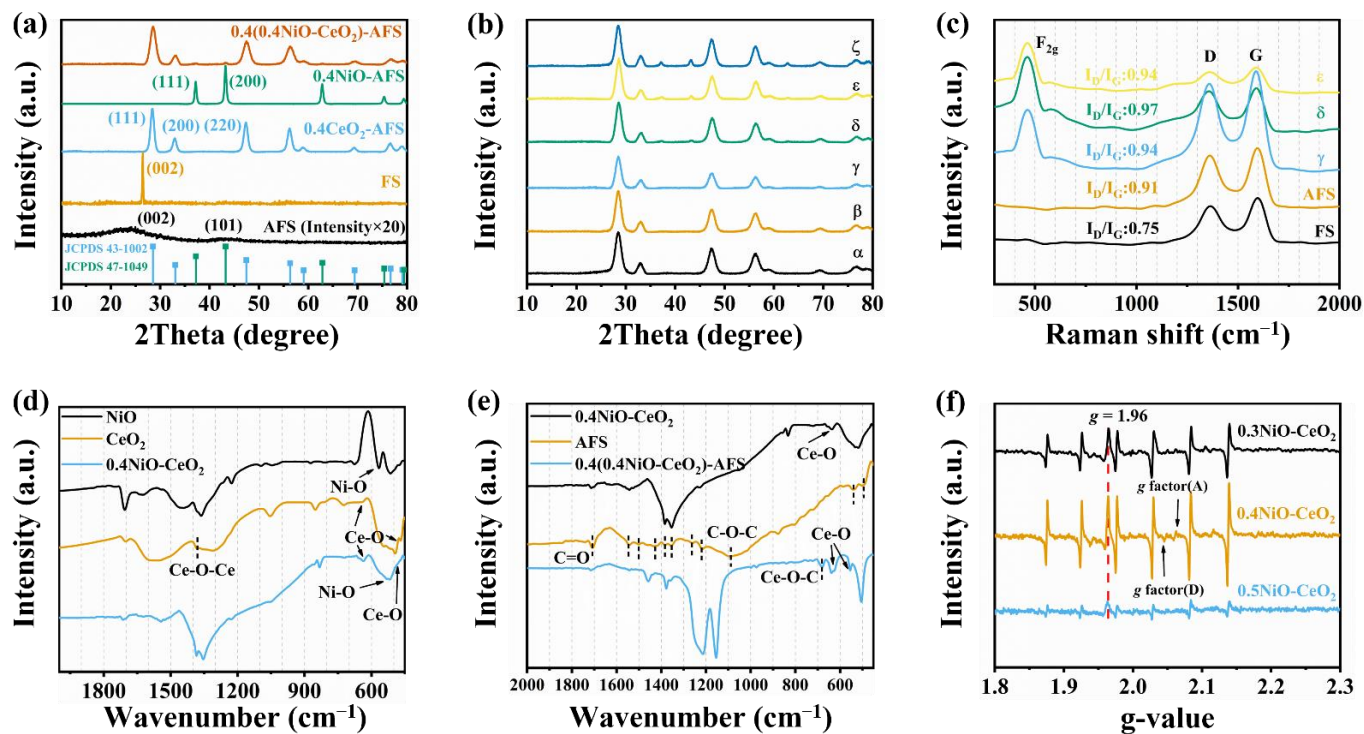


Figure 1. XRD patterns (a,b), Raman spectra (c), FT-IR spectra (d,e), and EPR spectra (f) of different samples. $\alpha - \zeta$ are y values from 0.1 to 0.6 in $0.4(y\text{NiO}-\text{CeO}_2)\text{-AFS}$, respectively.

Figure 1c shows the Raman spectra of FS , AFS , and $0.4(y\text{NiO}-\text{CeO}_2)\text{-AFS}$ ($y = 0.3\text{--}0.5$). The characteristic D and G peaks of graphite are clearly observed for these samples. Note that the calculated I_D/I_G values increase from 0.75 to 0.91 for FS and AFS , while those for AFS and $0.4(y\text{NiO}-\text{CeO}_2)\text{-AFS}$ ($y = 0.3\text{--}0.5$) are approximately equal. It is known that much gas is released during the pyrolysis of KOH and carbonaceous material, forcing the sp^2 hybrid long-ordered structure to adjust correspondingly, thereby causing more point, line, and cavity defects to rebuild a new electronic environment. Despite the loading of $y\text{NiO}-\text{CeO}_2$ nanoparticles having little effect on the crystal structure of AFS , the D and G peaks of $0.4(0.4\text{NiO}-\text{CeO}_2)\text{-AFS}$ at 1359 and 1589 cm^{-1} are lower than those of AFS at 1365 and 1601 cm^{-1} . This red-shifting phenomenon is caused by an interaction between AFS and $y\text{NiO}-\text{CeO}_2$. In addition, the characteristic signal of the F_{2g} model of the Ce-O bond is observed at around 466 cm^{-1} [24], further indirectly confirming the successful preparation of $0.4(y\text{NiO}-\text{CeO}_2)\text{-AFS}$ ($y = 0.3\text{--}0.5$).

Figure 1d shows the FT-IR spectra of as-synthesized NiO , CeO_2 , and $0.4\text{NiO}-\text{CeO}_2$. A characteristic peak observed around 560 cm^{-1} in synthetic NiO is assigned to the stretching of the Ni-O bond [25,26]. Characteristic vibration peaks at 640 , 495 , and 469 cm^{-1} in CeO_2 are ascribed to the different stretching vibration modes of the Ce-O bond, and that at 1380 cm^{-1} is attributed to the stretching vibration of the Ce-O-Ce bond [27,28]. These characteristic peaks of the Ce-O and Ni-O bonds appear again in $0.4\text{NiO}-\text{CeO}_2$ and show some shifting, indicative of the interaction between NiO and CeO_2 . Figure 1e clearly indicates two peaks around 1090 and 1213 cm^{-1} in AFS , which are assigned to the alkoxy and epoxy groups, and three peaks around 1385 and 1706 cm^{-1} , belonging to the stretching vibrations of the O-C=O and C=O bonds [29]. Obviously, the distribution of unreduced oxygen-containing groups on AFS favors the loading of $y\text{NiO}-\text{CeO}_2$. The broadband

around 1107 cm^{-1} in AFS is ascribed to the C-O-C bond from ether groups. The ortho-carbon atom in ether groups has recently been identified as a valid site for the 2e-ORR [30]; this implies that AFS should have the activity to produce H_2O_2 in the electro-Fenton system. In addition, a new broadband below 700 cm^{-1} in $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$ is assigned to the Ce-O-C bond [31,32], directly proving that 0.4NiO-CeO_2 is anchored on AFS, which will contribute to prolonging the catalytic sustainability of the composite for degrading TC. A peak at 624 cm^{-1} in $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$ is ascribed to the Ce-O bond [28], which red-shifted from 633 cm^{-1} in 0.4NiO-CeO_2 , suggesting that AFS possibly transfers its electrons near the defective structure to 0.4NiO-CeO_2 to further facilitate the electron transfer from sites to the O_2 or H_2O_2 molecule. These results again offer additional evidence for the successful anchoring of 0.4NiO-CeO_2 on AFS.

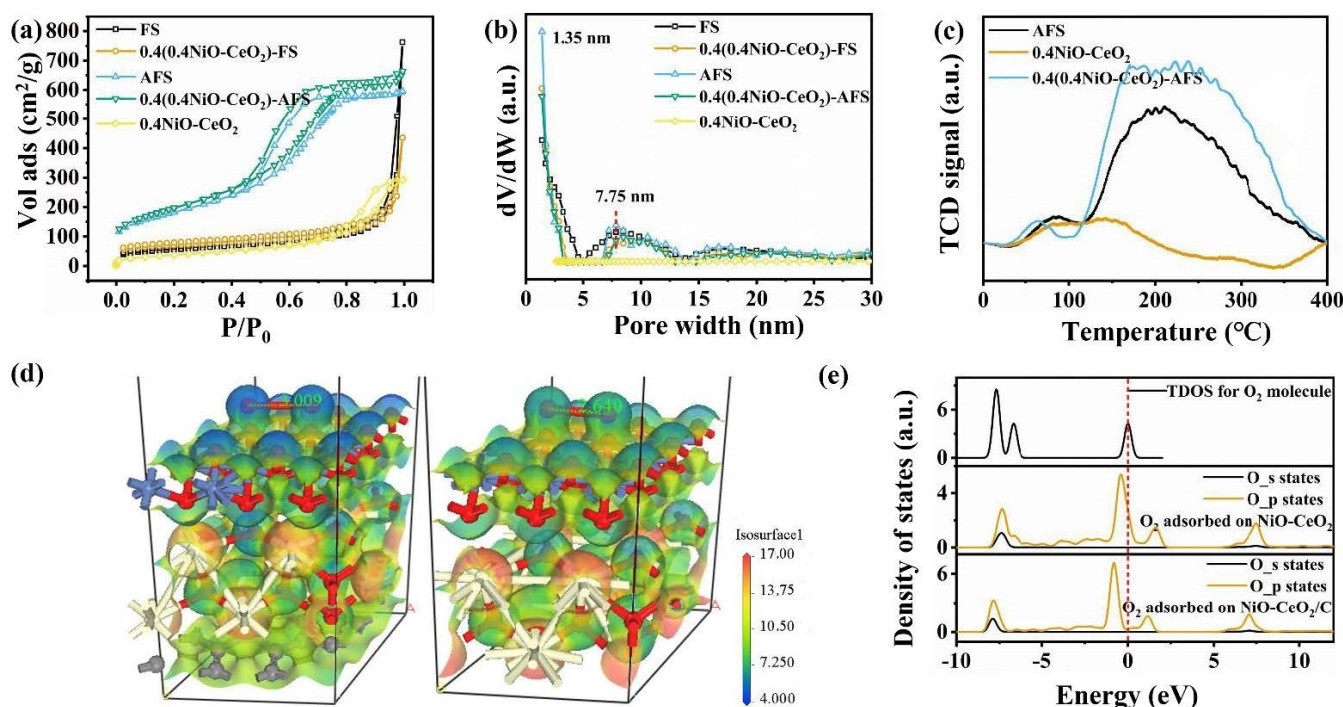


Figure 2. N_2 adsorption-desorption isotherms (a), pore size distribution (b), and O_2 -TPD patterns (c) of different samples. Electrostatic potential map based on optimized adsorption model (d). Density of states (DOS) for the O_2 molecule on 0.4NiO-CeO_2 (NiO/CeO_2 model) and $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$ ($\text{NiO/CeO}_2/\text{C}$ model) (e). The atoms in yellow, red, blue, and gray are cerium, oxygen, nickel, and carbon atoms, respectively; the left is the $\text{NiO-CeO}_2\text{-AFS}$ model, and the right is the NiO-CeO_2 model.

The higher concentration of oxygen vacancies in CeO_2 reflects the generation of more catalytic sites. Several free-electron signals are detected in electron paramagnetic resonance (EPR) spectra, as shown in Figure 1f. Signal A is ascribed to the stable Ce^{3+} in the fluorite structural lattice defect, while signal D corresponds to Ce^{3+} with easily shifted ligands [33]. Moreover, a signal at $g = 1.96$ is considered to be typical non-stoichiometric CeO_2 with Ce^{3+} [34]. With the gradual increase in the proportion of NiO in $y\text{NiO-CeO}_2$ from 0.3NiO-CeO_2 to 0.5NiO-CeO_2 , the intensities of signals A and D first increase and then weaken. This implies that the proportion of NiO in $y\text{NiO-CeO}_2$ can affect the concentration of oxygen vacancies in CeO_2 . As the dominant defect type on CeO_2 , oxygen vacancies could create abundant micro-regions rich in electrons, with a strong electron donor capacity for reducing O_2 or H_2O_2 . The above-mentioned fact that 0.4NiO-CeO_2 has a higher concentration of oxygen vacancies compared with 0.3NiO-CeO_2 or 0.5NiO-CeO_2 suggests that it has higher catalytic activity for degrading TC, in theory.

Figure 2a demonstrates the N_2 adsorption-desorption isotherms of FS, 0.4NiO-CeO_2 , $0.4(0.4\text{NiO-CeO}_2)\text{-FS}$, AFS, and $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$. 0.4NiO-CeO_2 displayed a type-II

isotherm and an H2-type hysteresis loop in the high P/P_0 range of 0.7–1.0. This suggests that it was composed of fractured pore materials with crack- or wedge-shaped porous structures [35]. For FS and 0.4(0.4NiO-CeO₂)-FS, two similar isotherms in the P/P_0 range of 0–1.0 exhibit a type-II isotherm and inconspicuous H4-type hysteresis loops, evidencing the coexistence of micropores and wedge-shaped meso-/micropores [21]. By contrast, for AFS, the significantly increased adsorption amount at a low range of P/P_0 confirms the extremely large specific surface area increased by KOH activation treatment. AFS and 0.4(0.4NiO-CeO₂)-AFS display type-IV isotherms and H2-type hysteresis loops in a low P/P_0 range of 0.4–0.8, indicating that they comprise abundant narrow slit-like pore structures [36]. Moreover, the Brunauer-Emmett-Teller (BET) surface areas were calculated to be 80.2, 170.0, 260.1, 1008.3, and 1475.5 m²/g for 0.4NiO-CeO₂, FS, 0.4(0.4NiO-CeO₂)-FS, AFS, and 0.4(0.4NiO-CeO₂)-AFS, respectively (see Table S1). It is obvious that the specific area of fullerene soot substantially increases after alkali activation. More importantly, the specific surface area reaches a value as high as 1475.5 m²/g when NiO-CeO₂ is composited with AFS. Thus, 0.4(0.4NiO-CeO₂)-AFS is expected to be an excellent electro-Fenton catalyst for the degradation of organic pollutants.

It can be seen in Figure 2b that the pore width of the composited 0.4(0.4NiO-CeO₂)-AFS catalyst mainly centers around 1.35 nm, accompanied by a modest peak around 7.75 nm, evidencing the coexistence of large micropores (>1 nm) and mesopores. In line with Gao et al. [21], micropores with a smaller curvature radius possess stronger interaction forces with electrolyte ions, whereas the mesopores allow the diffusion of ions with low steric hindrance. Therefore, the abundant porous structure and the extremely large specific area of the composited 0.4(0.4NiO-CeO₂)-AFS catalyst are beneficial to the transport of electrolyte ions as well as to the adsorption of TC molecules [21].

We further tested the O₂-temperature-programmed desorption (TPD) of AFS, 0.4NiO-CeO₂, and 0.4(0.4NiO-CeO₂)-AFS, as shown in Figure 2c. The broad peaks between 150 and 400 °C are assigned to chemisorbed oxygen species [37]. AFS presents a high oxygen storage capacity, closely related to its concentration of oxygen-containing groups. After 0.4NiO-CeO₂ was loaded on AFS, all of the peaks for 0.4(0.4NiO-CeO₂)-AFS were higher than the corresponding ones for AFS or 0.4NiO-CeO₂. The electrogeneration of H₂O₂ first requires oxygen molecules to be chemisorbed to the catalytic site and to exist stably in the form of chemisorbed oxygen species. Perhaps this means that the content of chemisorbed oxygen is positively correlated with the number of catalytic sites. These results indicate that 0.4(0.4NiO-CeO₂)-AFS might have an advantage for reactions involving oxygen species.

Density Functional Theory (DFT) was further used to compare the difference in the adsorption energy of oxygen molecules on 0.4NiO-CeO₂ and 0.4(0.4NiO-CeO₂)-AFS, as shown in Figure 2d. The corresponding adsorption energies (E_{ads}) toward oxygen molecules were −1.205 and −2.111 eV, suggesting that the oxygen molecules adsorbed on the two models spontaneously and preferentially adsorbed on the latter. In addition, the electrostatic potential map is an intuitive means to qualitatively analyze the interaction strength between oxygen molecules and catalytic sites. The red regions represent high electron density, whereas the blue areas are low electron density. The larger potential difference between oxygen molecules and the catalyst in the latter proves that the interaction strength is stronger than in the former. Correspondingly, the length of the O-O bond in the latter is significantly longer than that in the former. This once again confirms that oxygen is more easily activated on the latter. Figure 2f shows the density of states (DOSs) of oxygen molecules on the two models. After adsorption, the O 2p states were clearly delocalized and highly distributed around 7.5 eV. Relatively speaking, the O 2p states in the former shifted to a higher energy position than in the latter, thereby showing that electron transfer from catalytic sites to oxygen molecules was weaker than in the latter [38].

The morphology of 0.4(0.4NiO-CeO₂)-AFS was observed by SEM and TEM. Figure 3a shows that FS is composed of quasi-spherical carbon particles with an average size of approximately 50 nm. After KOH activation, the AFS showed a rough outer wall, as observed in Figure 3b. These rough outer walls on AFS can provide a large specific

surface area and increase the anchoring and absorption sites. Moreover, as observed in the TEM image of AFS shown in Figure 3c, different electron beam transmittance appears in different regions, and the micro-regions between alternative light and dark regions further emphasize micropore enrichment in AFS. Figure 3d shows that a large number of 0.4NiO-CeO₂ nanoparticles are evenly anchored on AFS. The high-resolution transmission electron microscopy (HRTEM) images of 0.4(0.4NiO-CeO₂)-AFS are displayed in Figure 3e,f; they further demonstrate a carbonaceous structure feature and discontinuous serpentine lattice fringes, indicating plentiful structural and periodic defects in AFS. Furthermore, the fringe spacing of 0.380 nm in AFS is significantly wider than that of standard graphite (0.336 nm), again proving that AFS has abundant crystal structural defects. The (111), (200), (220), and (400) planes of CeO₂ and the (111) plane of NiO are observed, consistent with the XRD results. HRTEM mapping confirms the dispersion of O, Ni, and Ce elements on AFS, as shown in Figure 3g–j. These results undoubtedly prove that the composite was successfully prepared. Furthermore, energy dispersive spectroscopy (EDS) quantitative analysis of pure 0.4NiO-CeO₂ reveals the presence of expected Ni, Ce, and O elements, as shown in Figure S1. The actual molar ratio of Ni versus Ce was calculated to be 0.178:1, illustrating that the actual proportion of NiO in 0.4NiO-CeO₂ is less than the input ratio.

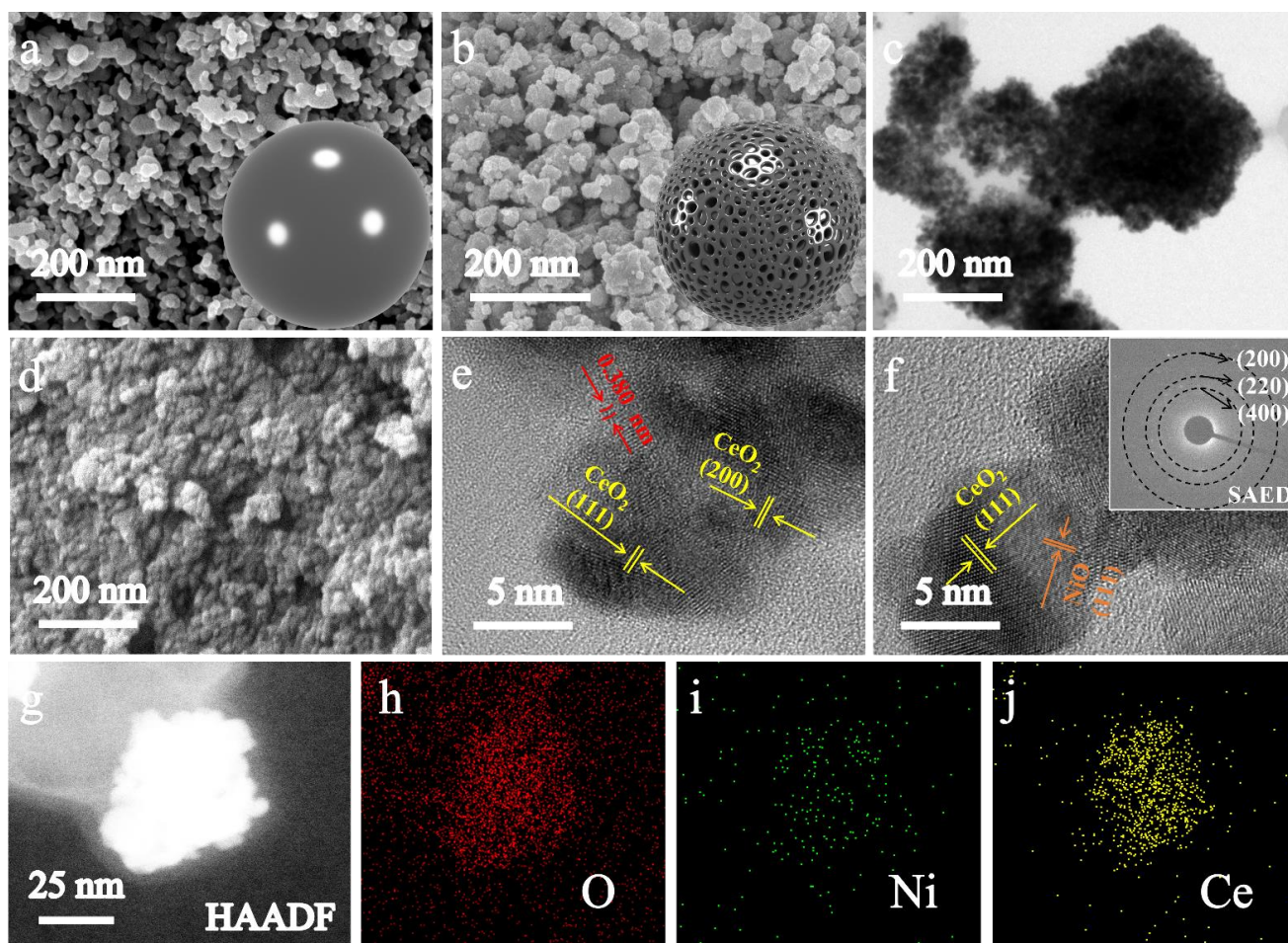


Figure 3. SEM images of FS (a), AFS (b), and 0.4(0.4NiO-CeO₂)-AFS (d). TEM images of AFS (c). HRTEM images of 0.4(0.4NiO-CeO₂)-AFS (e,f). Elemental color mapping (g–j) of 0.4(0.4NiO-CeO₂)-AFS.

X-ray photoelectron spectroscopy (XPS) analysis was employed to characterize the surface chemical bonding states of the 0.4(0.4NiO-CeO₂)-AFS composite before and after the reaction. As shown in Figure S2, the survey spectrum confirms the coexistence of C 1s, O 1s, Ni 2p, and Ce 3d regions. Based on the XPS quantification analysis, the actual molar ratio of Ni versus Ce was determined to be approximately 0.16:1, nearly consistent with the result of the EDS analysis. Figure 4a shows the deconvoluted C 1s spectra, wherein peaks at 281.8, 283.1, and 285.9 eV correspond to C=C (sp²), C-OH (sp³), and C=O bonds, respectively [7]. Figure 4b exhibits the deconvoluted O 1s spectra, wherein three peaks at 526.8, 529.2, and 530.2 eV are attributed to lattice oxygen, hydroxyl oxygen, and carbonyl oxygen, respectively [7]. After the reactions, the changed relative peak area indicates that the chemical environment in 0.4(0.4NiO-CeO₂)-AFS changed. Figure 4c shows the deconvoluted Ni 2p spectra, with three peaks at 851.2, 855.8, and 860.0 eV attributed to Ni²⁺, and peaks at 863.7, 872.0, and 879.6 eV attributed to Ni³⁺ [39,40]. Figure 4d shows the deconvoluted Ce 3d spectra, with peaks at 890.2 and 914.0 eV attributed to Ce³⁺, and six peaks at 879.9, 884.6, 895.9, 898.0, 903.9, and 922.3 eV attributed to Ce⁴⁺ [7,41]. After the reactions, the relative peak areas of Ni 2p and Ce 3d were changed to different degrees, suggesting NiO and CeO₂ as the two members taking part in the degradation reaction. This result is completely consistent with the definition of dual active centers [23], thus proving that the hypothesis about Ni-Ce dual active centers is tenable.

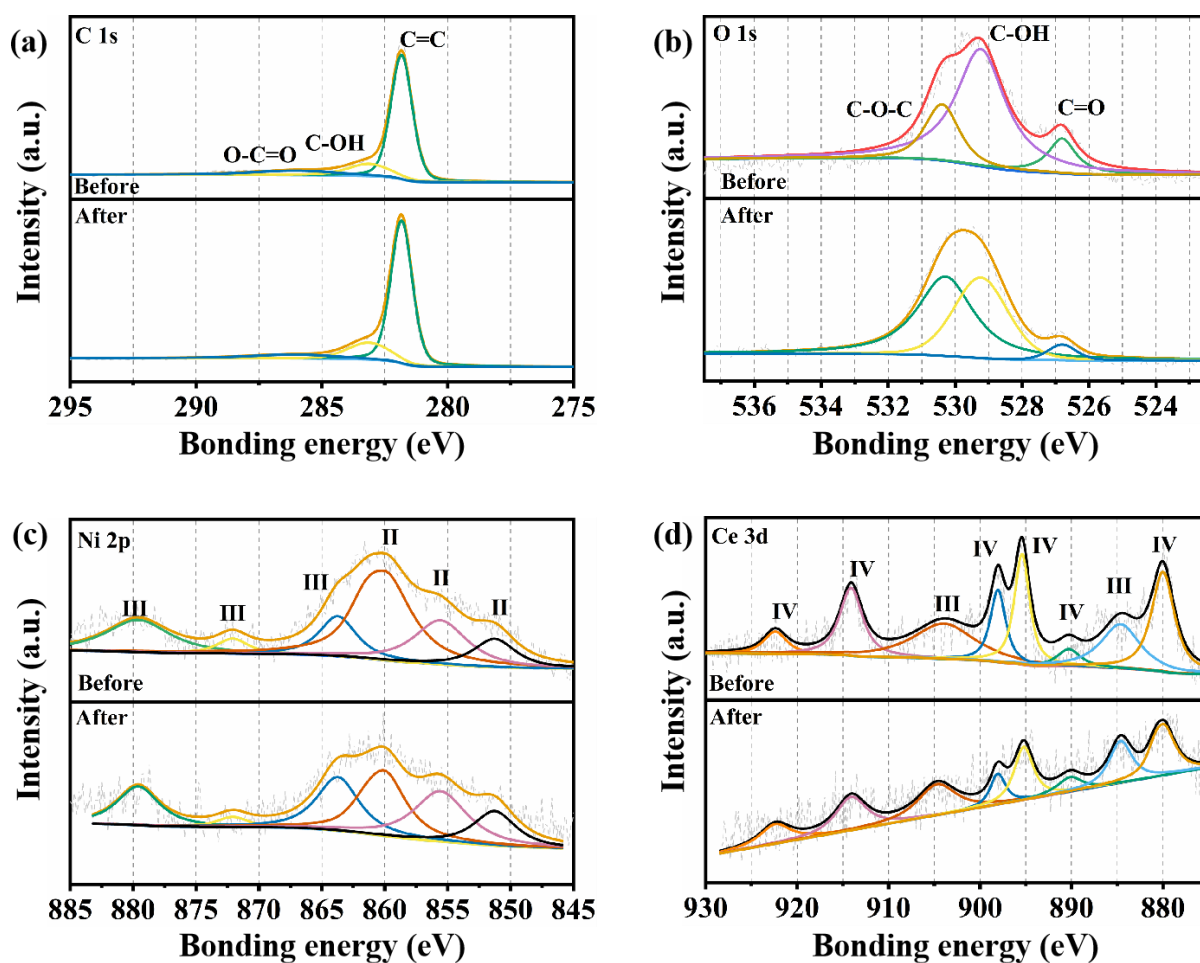


Figure 4. Deconvoluted C 1s (a), O 1s (b), Ni 2p (c), and Ce 3d (d) spectra of 0.4(0.4NiO-CeO₂)-AFS before and after reaction.

2.2. Degradation of Tetracycline on the 0.4(0.4NiO-CeO₂)-AFS Composite Electrode

2.2.1. Degradation of Tetracycline on Relevant Electro-Fenton Catalysts

The electro-Fenton degradation of TC by NiO, CeO₂, and 0.4NiO-CeO₂ composites was investigated. Figure 5a shows that 0.4NiO-CeO₂ has an obvious advantage for the degradation of TC over NiO and CeO₂. Because the degradation rate of TC by 0.4NiO-CeO₂ is higher than that by individual compounds under identical experimental conditions, interaction between Ni and Ce dual active centers is established. On the one hand, this is due to the increase in reaction paths after the combination of both NiO and CeO₂, and on the other hand, doped NiO causes more oxygen defects on CeO₂, thereby increasing the catalytic sites on CeO₂. Figure 5b shows the corresponding pseudo-first-order kinetic curves. The calculated rate constants for NiO, CeO₂, and 0.4NiO-CeO₂ are 2.43×10^{-3} , 3.54×10^{-3} , and $5.05 \times 10^{-3} \text{ min}^{-1}$, respectively. In line with its definition, the synergistic index (SI) was calculated to be 0.84, implying that the interaction strength between NiO and CeO₂ is not up to the standard of a synergistic effect. The degradation curves after the introduction of AFS are shown in Figure 5c. Clearly, the catalytic activity of composites containing AFS is significantly higher than that of composites without AFS, and 0.4(0.4NiO-CeO₂)-AFS has a greater advantage for degrading TC than 0.4CeO₂-AFS and 0.4NiO-AFS. Figure 5d further shows that the reaction rate constants are 4.95×10^{-3} , 6.07×10^{-3} , and $2.56 \times 10^{-2} \text{ min}^{-1}$ for 0.4NiO-AFS, 0.4CeO₂-AFS, and 0.4(0.4NiO-CeO₂)-AFS, respectively. Their reactivity values are 2.03, 1.71, and 5.06 times those of NiO, CeO₂, and 0.4NiO-CeO₂, respectively. Moreover, the SI was calculated to be 2.32, suggesting that AFS could significantly enhance the synergistic effect between Ni and Ce dual active centers for degrading TC. To further confirm that the introduction of AFS enhances the interaction strength between Ni and Ce dual active centers, we adjusted the proportion of NiO in 0.4(yNiO-CeO₂)-AFS ($x = 0.1\text{--}0.6$) and observed the change in degradation percentage, as shown in Figure 5e. As the proportion of NiO continuously increased from 0.4(0.1NiO-CeO₂)-AFS to 0.4(0.4NiO-CeO₂)-AFS, the degradation rate of TC improved from 84% to 99%. When the proportion of NiO further increased from 0.4(0.4NiO-CeO₂)-AFS to 0.4(0.6NiO-CeO₂)-AFS, the degradation rate of TC decreased to 87%; however, this value is still much higher than the degradation rate of TC by 0.4NiO-AFS and 0.4CeO₂-AFS. To confirm that the catalytic activity of 0.4(0.4NiO-CeO₂)-AFS was not contributed to by AFS itself, the degradation of TC by AFS was also investigated, as shown in Figure 5f. The degradation rate of TC by AFS is negligible and is much lower than those of all samples. The reaction rate constant of AFS was calculated to be 3.01×10^{-3} from Figure 5g. The SI among AFS, 0.4NiO-CeO₂, and 0.4(0.4NiO-CeO₂)-AFS was calculated to be 3.17, suggesting that a stronger synergistic effect was established between AFS and 0.4NiO-CeO₂. To confirm the existence of such an interaction, we further adjusted the proportion of 0.4NiO-CeO₂ in x(0.4NiO-CeO₂)-AFS ($x = 0.2\text{--}0.5$) to determine the difference in the degradation percentage, as shown in Figure 5h. As the proportion of 0.4NiO-CeO₂ increased from 0.2(0.4NiO-CeO₂)-AFS to 0.4(0.4NiO-CeO₂)-AFS, the degradation rate of TC increased from 76% to 99%. When the proportion of 0.4NiO-CeO₂ further increased from 0.4(0.4NiO-CeO₂)-AFS to 0.5(0.4NiO-CeO₂)-AFS, the degradation rate of TC decreased to 84%; however, it is still considerably higher than that of pure 0.4NiO-CeO₂. The above results undoubtedly prove that AFS can initiate the synergistic effect between Ni and Ce dual active centers for degrading TC. As a matter of fact, when the 0.4NiO-CeO₂ nanoparticles were loaded on AFS, the area of active components and the numbers of catalytic sites greatly increased, and the adsorbed capacity and types for TC molecules improved. Meanwhile, AFS also increased the content of chemisorption oxygen species in the composite, which facilitates the generation of H₂O₂ and free radicals. As we know, NiO and CeO₂ are semiconductors with poor conductivity; therefore, the introduction of AFS can also improve the conductivity of the composite, greatly enhancing the electrochemical activity, facilitating the reduction of Ce⁴⁺ and Ni³⁺ for rebuilding reaction sites, and ultimately accelerating the generation of free radicals. In addition, the interconnected channels within AFS also reduce mass transfer resistance, accelerating the transportation of dissolved oxygen molecules from electrolytic cells to catalytic sites.

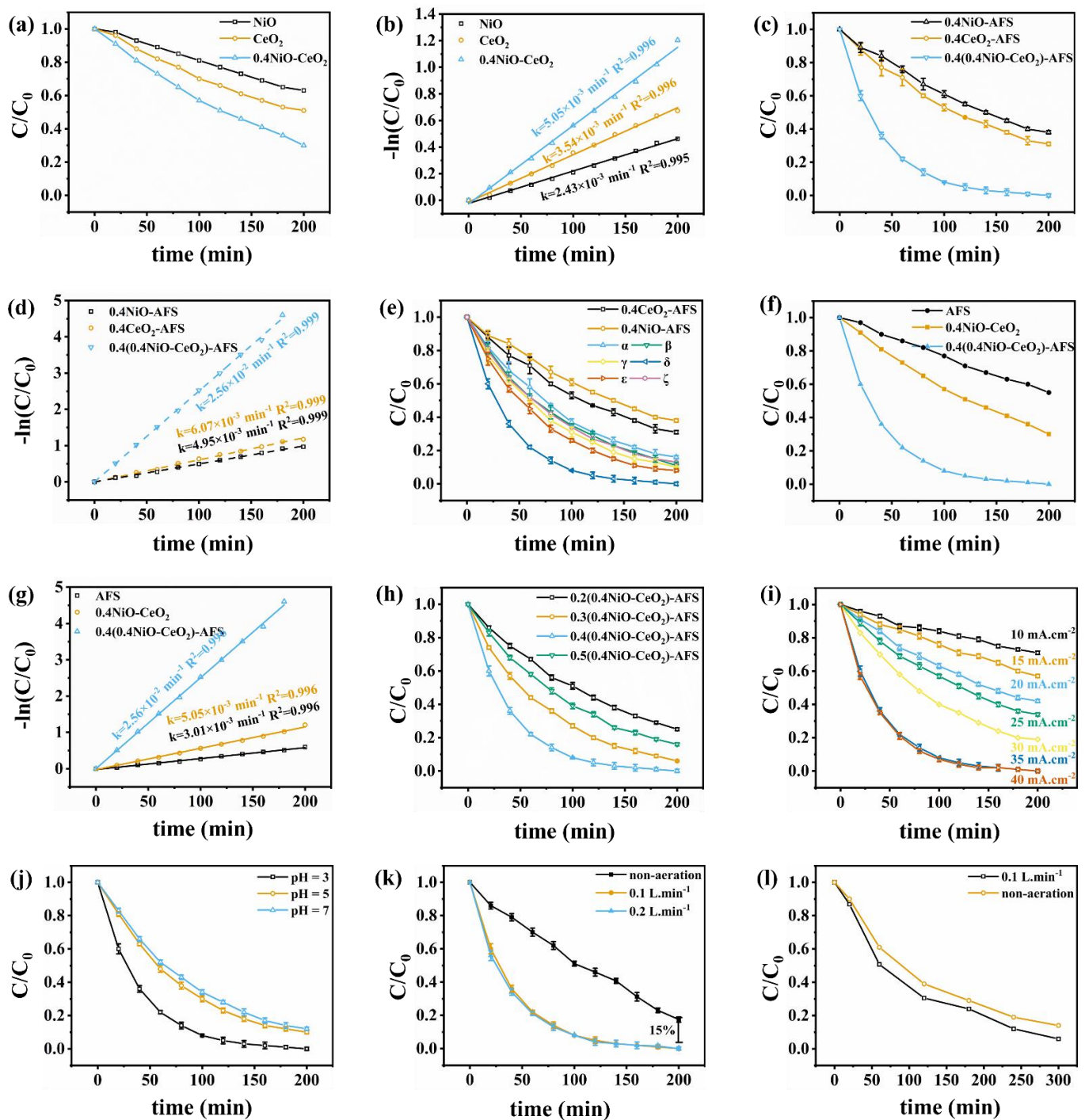


Figure 5. Degradation curves (a) of TC and corresponding pseudo-first-order kinetic curves (b) for NiO, CeO_2 , and 0.4NiO-CeO_2 . The degradation curves (c) of TC and kinetic curves (d) for 0.4NiO-CeO_2 , $0.4\text{CeO}_2\text{-AFS}$, and $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$. The degradation curves (e) of TC by a series of samples ($\alpha - \zeta$ are y values from 0.1 to 0.6 in $0.4(y\text{NiO-CeO}_2)\text{-AFS}$). The degradation curves (f) of TC and kinetic curves (g) for AFS, 0.4NiO-CeO_2 , and $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$. The degradation curves (h) of TC for $x(0.4\text{NiO-CeO}_2)\text{-AFS}$ ($x = 0.2$ – 0.5). The degradation curves of TC by $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$ under different current densities (i), pH (j), and aeration velocity (k). The TOC removal curves (l) of TC by $0.4(0.4\text{NiO-CeO}_2)\text{-AFS}$ in 300 min under different aeration velocities. (Standard experimental conditions: $[\text{TC}] = 200 \text{ ppm}$; $\text{pH} = 3$; $35 \text{ mA}/\text{cm}^2$; and $0.1 \text{ L}/\text{min}$).

2.2.2. Optimized Experimental Conditions of Catalytic Degradation

Subsequently, we optimized the experimental parameters for the degradation of TC. Figure 5i shows the degradation curves of TC by 0.4(0.4NiO-CeO₂)-AFS at different current densities. When the current density increased from 10 to 35 mA/cm², the degradation rate of TC increased from 29% to 99% in 200 min. More energy input can result in a higher generation of H₂O₂, naturally facilitating the formation of free radicals. However, with the further increase in the current density from 35 to 40 mA/cm², the degradation rate of TC hardly changed; this is because an excessive current density is usually accompanied by a high overpotential, causing a series of side reactions, e.g., HER and 4e-ORR, on the 0.4(0.4NiO-CeO₂)-AFS electrode, which compete for H⁺, O₂, and H₂O₂, thus preventing the degradation of TC [42]. In short, 35 mA/cm² is defined as the optimum current density value.

In acidic environments, it is generally believed that a high concentration of H⁺ favors the electrochemical generation of H₂O₂. We used 1 mol/L H₂SO₄ to adjust the initial pH value of the TC solution to 3, 5, and 7. As shown in Figure 5j, the degradation rate of TC was the highest in an acidic environment with an initial pH = 3. When the initial pH value of the TC solution was gradually increased from 3 to 7, the degradation rate of TC decreased from 99% to 84%, which is still acceptable and far higher than that of the referenced catalysts (Table S2).

Aeration operation (where air is continuously pumped into the TC solution) can largely increase the dissolved oxygen concentration in the TC solution and then promote H₂O₂ generation. As shown in Figure 5k, when the aeration velocity increased from 0.1 to 0.2 L/min, the degradation rate of TC did not improve. On the contrary, when aeration was not performed, the degradation rate of TC decreased from 99% to 84%. The results indicate that the 0.1 L/min aeration velocity satisfies the need for dissolved oxygen for the degradation experiment. Because excessive aeration means higher operating costs, 0.1 L/min is determined as an appropriate value.

Figure 5l demonstrates the mineralization curves of TC by 0.4(0.4NiO-CeO₂)-AFS at different aeration conditions, and the mineralization rates were calculated to be 86% (non-aeration) and 94% (aeration). This implies that the majority of TC is oxidized to organic micromolecules and then decomposed to CO₂, H₂O, and NH₄⁺ [29], undoubtedly proving that the prepared 0.4(0.4NiO-CeO₂)-AFS electrode has excellent electro-Fenton activity.

2.2.3. Possible Degradation Mechanism

In cyclic voltammetry (CV) tests, the peak current density and integral area are the crucial criteria for evaluating electrochemical activity. As shown in Figure 6a, AFS exhibits a quasi-rectangular-shaped curve in acid, whereas 0.4NiO-CeO₂ and 0.4(0.4NiO-CeO₂)-AFS have fusiform curves, and 0.4(0.4NiO-CeO₂)-AFS has faster electrochemical activity and higher electron transfer efficiency. In an alkaline environment, 0.4(0.4NiO-CeO₂)-AFS also has the highest responding current compared to other materials. The above results indicate that 0.4(0.4NiO-CeO₂)-AFS should have faster rates for the electrochemical generation of H₂O₂. To further compare the electrochemical activity difference among the series of 0.4(yNiO-CeO₂)-AFS ($y = 0.1$ – 0.6) materials, we tested a series of CV curves in acid and alkali, as shown in Figure S3a,b. With the gradual increase in the proportion of NiO in 0.4(yNiO-CeO₂)-AFS from 0.4(0.1NiO-CeO₂)-AFS to 0.4(0.4NiO-CeO₂)-AFS, the polarization current density and curve area monotonously increased, and when the proportion further increased from 0.4(0.4NiO-CeO₂)-AFS to 0.4(0.6NiO-CeO₂)-AFS, the electrochemical activity monotonously decreased. These results are consistent with the trend observed in the degradation experiment. Then, we investigated the electrochemical activity difference among the series of x(0.4NiO-CeO₂)-AFS ($x = 0.3$ – 0.5) materials, as shown in Figure S4a,b. With the increasing proportion of 0.4NiO-CeO₂ in x(0.4NiO-CeO₂)-AFS from 0.3(0.4NiO-CeO₂)-AFS to 0.5(0.4NiO-CeO₂)-AFS, the electrochemical activity first increased and then decreased irrespective of whether in it was the acid or alkali electrolyte. These results are also consistent with the trend in the degradation experiment

of TC. In conclusion, 0.4(0.4NiO-CeO₂)-AFS has higher electrochemical activity than the other measured materials.

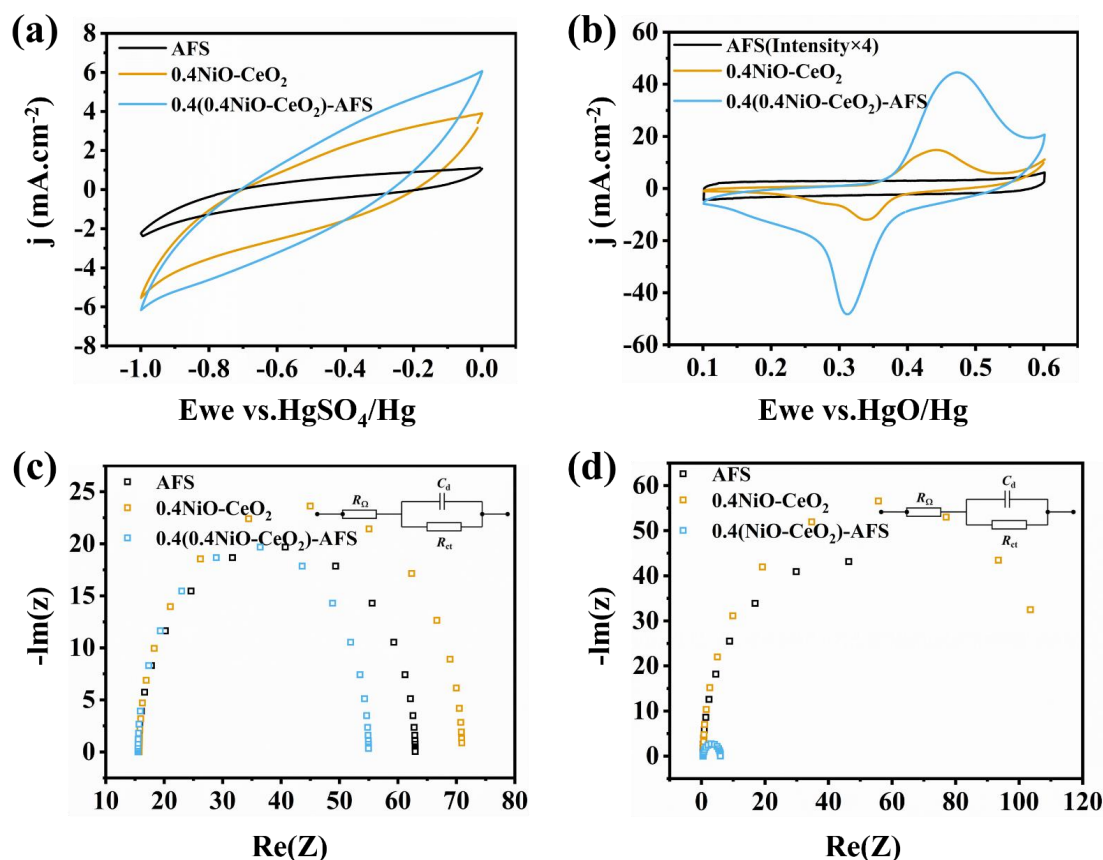


Figure 6. CV curves in acid (a) and alkali (b) and EIS Nyquist curves in acid (c) and alkali (d) for AFS, 0.4NiO-CeO₂, and 0.4(0.4NiO-CeO₂)-AFS.

In electrochemical impedance spectroscopy (EIS) tests, the size of a semicircle is an important criterion for evaluating the effect of ion diffusion. Figure 6c,d show the EIS curves of AFS, 0.4NiO-CeO₂, and 0.4(0.4NiO-CeO₂)-AFS in acid and alkali, respectively. It is observed that 0.4(0.4NiO-CeO₂)-AFS has a smaller semicircle than AFS and 0.4NiO-CeO₂, indicating that it has the smallest charge transfer resistance and optimal ion diffusion on the solid-liquid interface. As shown in Figure S3c,d, we further obtained the EIS curves of 0.4(yNiO-CeO₂)-AFS ($y = 0.1-0.6$) in acid and alkali. With the gradual increase in the proportion of NiO in 0.4(yNiO-CeO₂)-AFS from 0.4(0.1NiO-CeO₂)-AFS to 0.4(0.6NiO-CeO₂)-AFS, the size of the semicircle first decreased and then increased, suggesting that the proportion of NiO affects the electron driving force on the composite. The EIS curves of $x(0.4\text{NiO-CeO}_2)\text{-AFS}$ ($x = 0.3-0.5$) in acidic and alkaline environments were obtained, as shown in Figure S4c,d. The results confirm that 0.4(0.4NiO-CeO₂)-AFS still has a better ion diffusion performance than other samples.

It is well accepted that $\cdot\text{OH}$ is the specific active species in Fenton or Fenton-like systems. To investigate the major reactive species formed in this system, free radical scavenging experiments were performed with tertiary butanol (t-BuOH) and benzoquinone (BQ) as scavengers to quench $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, respectively. As shown in Figure 7a, the degradation rates of TC decreased by 77% and 49% after the addition of t-BuOH and BQ, respectively. Therefore, the electrocatalytic degradation of TC is mainly achieved with the participation of $\cdot\text{OH}$, while $\cdot\text{O}_2^-$ is a sub-main active species. As it is well known, highly saturated dissolved oxygen is conducive to the production of $\cdot\text{OH}$ by facilitating the 2e-ORR; however, the degradation rate of TC is not significantly enhanced in an oxygen

saturation environment. This again proves that the 0.1 L/min aeration velocity is an appropriate setting.

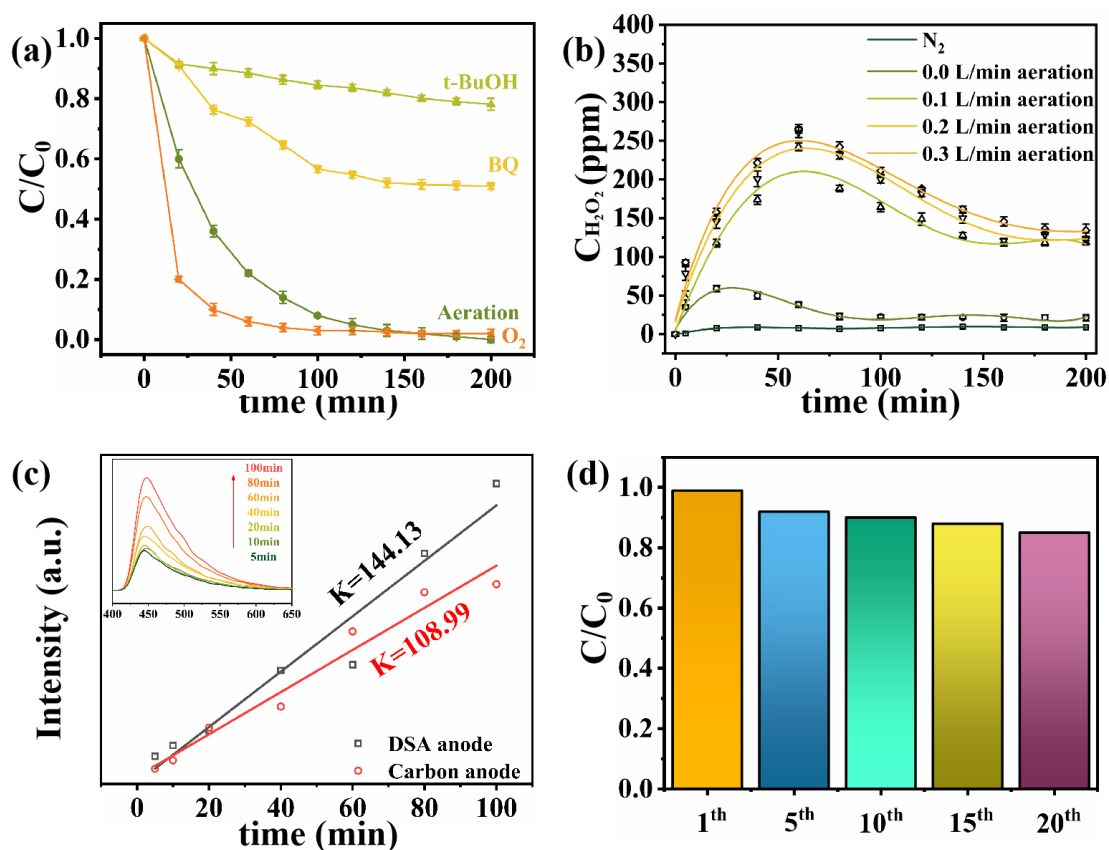


Figure 7. Free radical scavenging experiments (a). Hydrogen peroxide concentration detection experiments (b). Hydroxyl radical detection experiments (c). Stability test (d) by degradation of TC.

A higher concentration of H_2O_2 can enhance its conversion effectiveness to $\cdot OH$. Figure 7b shows that the fitting curves of H_2O_2 concentration at various aeration velocities have an analogical trend. The H_2O_2 concentration gradually decreased with time after (non-aeration) and 60 min (aeration) until a dynamic equilibrium state was achieved. When the aeration velocity increased from 0.1 to 0.3 L/min, this trend was still maintained but hardly influenced the increase in H_2O_2 concentration. By contrast, when nitrogen was pumped continuously into the system, the concentration of H_2O_2 was small and barely increased over time, suggesting that the 2e-ORR is restrained. This proves that the supplement of oxygen is important for H_2O_2 generation. Briefly, it can be inferred that a high concentration of H_2O_2 must be able to transform into a high concentration of $\cdot OH$.

We then used the fluorescence trap method with terephthalic acid as the trapping active species for $\cdot OH$ to observe the change in the concentration of $\cdot OH$ in the degradation of TC. As shown in Figure 7c (inset), the characteristic fluorescence intensity increased sharply in 100 min, indicating that the $\cdot OH$ concentration increases with time, thus confirming the in situ conversion from electrogenerated H_2O_2 to $\cdot OH$. When the Ti/IrO₂/RuO₂ anode was replaced with carbon cloth (2 × 7 cm) under aeration conditions, the increased rate constant of fluorescence intensity was slightly decreased, indicating that the Ti/IrO₂/RuO₂ anode also produces a small number of $\cdot OH$ through the water electrolysis reaction; however, it is negligible.

Undoubtedly, the catalytic stability of 0.4(0.4NiO-CeO₂)-AFS is extremely crucial for practical applications. Batch experiments were performed to evaluate the electrocatalytic stability of the 0.4(0.4NiO-CeO₂)-AFS electrode for TC degradation. The typical experimental operation of the whole stability testing process did not require repair

of the electrode from the first to the last experiment. A fresh TC solution was replaced every 200 min, the precipitate impurities on the electrode surface were rinsed with water, and the next degradation experiment was directly executed. As shown in Figure 7d, the degradation rate decreased only slightly after 20 cycles, suggesting that the composite electrode possesses acceptable catalytic stability. This confirms that the redox reaction on the electrode is continuous and reversible, and this result agrees with the CV analysis result.

A reasonable electro-Fenton degradation mechanism based on this system is shown in Figure 8. In fact, the electro-Fenton degradation of TC involves its adsorption on the 0.4(0.4NiO-CeO₂)-AFS electrode and subsequent oxidation by free radicals in real time. The porous structure of quasi-spherical AFS provides numerous channels for the strong absorption and quick migration of TC molecules, mainly owing to the strong π - π interactions between the sp² hybrid AFS framework and TC molecules, which naturally facilitates the enrichment of TC molecules on 0.4(0.4NiO-CeO₂)-AFS. Thus, the collision probability between TC and free radicals is also naturally enhanced, which favors the following decomposition of TC. In contrast to individual CeO₂, NiO, and 0.4NiO-CeO₂, the 0.4(0.4NiO-CeO₂)-AFS composite has the optimal diffusion drive force for electrolyte ions, decreasing the resistance of the TC flowing on it, thereby accelerating the above process. At the same time, AFS allows dissolved oxygen and electrogenerated H₂O₂ in the TC solution to be efficiently fed to the related reaction sites to ultimately form $\cdot\text{OH}$. In addition, the concentration of $\cdot\text{OH}$ increases rapidly in the local area, which will lead to a high-quality Haber-Weiss cycle to form $\cdot\text{O}_2^-$, further promoting the decomposition of TC to some extent. Based on the above discussions, the synergistic effect between Ni-Ce dual active centers in the electro-Fenton degradation of tetracycline can be initiated by AFS because of its appropriate porous structure, large specific surface area, and strong adsorption to the tetracycline molecule.

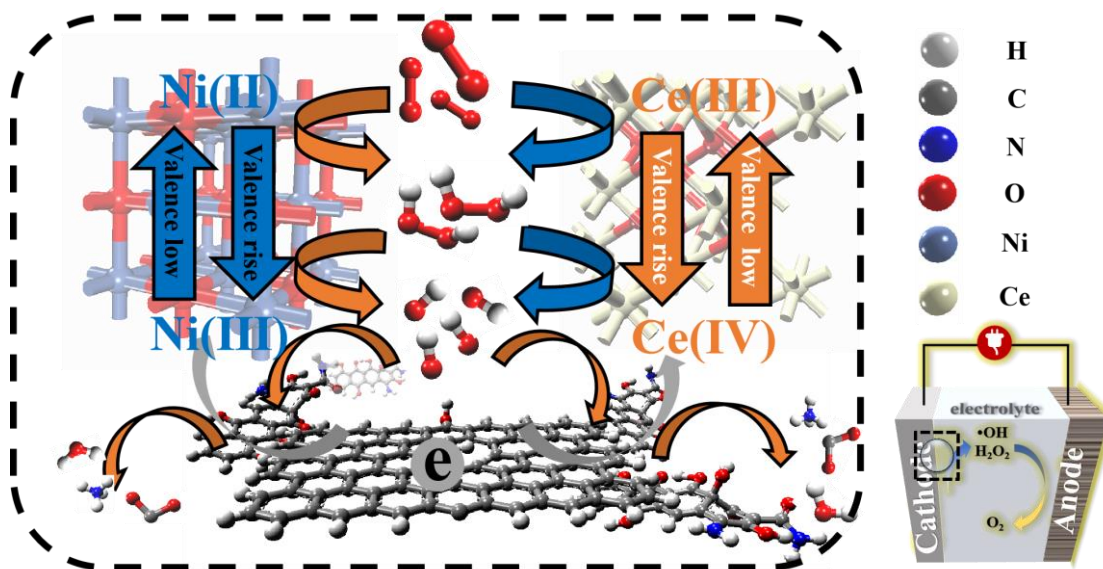
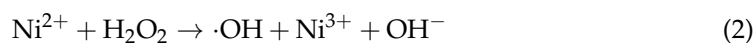
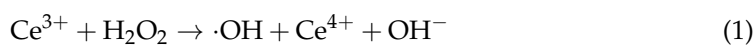


Figure 8. Schematic diagram of the electrocatalytic mechanism.

Note that the support of AFS also enhances the trend of electron transfers from catalytic sites on 0.4NiO-CeO₂ to O₂, which contributes to the generation of H₂O₂. Moreover, doped NiO forces CeO₂ to adjust the local structure and rearrange the electron environment in return for the formation of more Ce³⁺, which directly facilitates the Fenton reaction rate (Equation (1)). Surely, Ni²⁺ in NiO as an independent reaction also takes part in the Fenton reaction (Equation (2)). Therefore, the above processes clearly indicate that the Fenton reaction rate is limited by the concentration of H₂O₂. Interconnected channels in AFS with high conductivity can quickly transfer more electrons for adsorbed O₂ molecules to

perform 2e-ORR (Equation (3)), generating more H_2O_2 . A higher concentration of H_2O_2 is bound to activate more $\cdot\text{OH}$ in situ, promoting the contact of $\cdot\text{OH}$ and TC. This is probably why AFS can enhance the interaction strength between Ni and Ce dual activity centers.



From the degradation experiments of TC, we can intuitively observe that the synergistic effect between Ni and Ce dual activity centers enhanced by AFS is actually due to a stronger synergistic effect established between AFS and 0.4NiO-CeO₂ because with the intervention of AFS, the chemisorbed oxygen species content of the 0.4(0.4NiO-CeO₂)-AFS composite becomes higher than that of individual AFS or 0.4NiO-CeO₂. Thus, the composite undoubtedly becomes more sensitive to reactions involving oxygen. Most importantly, electrons from an external electric field are able to rebuild Fenton reaction sites (rate-limiting step: the reduction of Ni^{3+} and Ce^{4+}) on 0.4NiO-CeO₂ with AFS as a bridge; thus, the sustainability of redox reactions on the composite electrode (Equations (4) and (5)) is ensured. From this viewpoint, AFS can amplify the above process, thereby improving the interaction strength between Ni and Ce dual activity centers.

In the proposed reasonable electrocatalytic degradation mechanism of the 0.4(0.4NiO-CeO₂)-AFS composite, AFS plays the role of cocatalyst to enhance the synergistic effect between Ni and Ce dual activity centers. The reduction of O_2 and H_2O_2 molecules is accelerated by the rapid electron transfer on AFS, and AFS also enlarges the surface area of active regions for adsorption and reactions. As a result, not only is O_2 rapidly reduced to H_2O_2 , but H_2O_2 is also activated as $\cdot\text{OH}$ in real time, thereby improving the degradation rate of TC.

3. Materials and Methods

3.1. Materials

The following materials were used throughout the experiments: analytical grade ethanol absolute (Tianjin Zhiyuan Chemical Reagent Co., Ltd. Tianjin, China), KOH (Tianjin Zhiyuan Chemical Reagent Co., Ltd. Tianjin, China), Na_2SO_4 (Tianjin Zhiyuan Chemical Reagent Co., Ltd. Tianjin, China), KMnO_4 (Tianjin Kemiou Chemical Reagent Co., Ltd. Tianjin, China), H_2SO_4 (18 mol/L, Harbin Polytechnic Chemical Reagent Co., Ltd., Harbin, China), HNO_3 (8 mol/L, Harbin Polytechnic Chemical Reagent Co., Harbin, China), NaOH (Sinopharm Chemical Reagent Co., Ltd. Shanghai, China), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Shanghai Macklin Biochemical Co., Ltd. Shanghai, China), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Shanghai Macklin Biochemical Co., Ltd. Shanghai, China), polytetrafluoroethylene (PTFE, 60%, Shanghai Macklin Biochemical Co., Ltd. Shanghai, China), polyethylene glycol (PEG, 20000, Shanghai Macklin Biochemical Co., Ltd. Shanghai, China), CS_2 (Tianjin Zhiyuan Chemical Reagent Co., Ltd. Tianjin, China), tert-butanol (t-BuOH, Shanghai Aladdin Biochemical Technology Co., Ltd. Shanghai, China), benzoquinone (BQ, Shanghai Macklin Biochemical Co., Ltd. Shanghai, China), tetracycline (TC, Shanghai Macklin Biochemical Co., Ltd. Shanghai, China), a stainless steel mesh (40 mesh, Suzhou Shuertai Co., Ltd. Suzhou, China), p-Phthalic acid (Shanghai Macklin Biochemical Co., Ltd. Shanghai, China), hollow graphite rod (Shanghai Carbon Co., Ltd. Shanghai, China), Specpure graphite powder (1000 mesh), and deionized water.

3.2. Preparation of the $x(y\text{NiO-CeO}_2)\text{-AFS Composite}$

$y\text{NiO-CeO}_2$ nanoparticles with different chemical compositions were synthesized by co-precipitation. Briefly, 0.05 mol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in a PEG solution (0.05 g/L, 50 mL). Then, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with molar ratios of Ni versus Ce of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 was added to the above solution, and mechanical stirring was performed for 2 h. Then, this solution was adjusted with 2 mol/L NaOH until pH = 11, and vigorous mechanical stirring was performed at a constant room temperature for 6 h. The obtained black precipitate was washed with water until pH = 7 and then dried at 60 °C for 24 h, followed by calcination at 450 °C for 2 h in air with a heating rate of 2 °C/min. The prepared samples are denoted as $y\text{NiO-CeO}_2$, where y is 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6, representing the proportion of NiO. Moreover, the CeO_2 (NiO) sample was prepared according to the above-mentioned method without Ni (Ce) addition.

Fullerene soot (FS) was prepared by arc discharge [19]. The prepared FS was washed with CS_2 for 24 h in a Soxhlet extraction device for the removal of soluble fullerene and then dried. On this basis, activated fullerene soot (AFS) was prepared according to a previous report [21]. In brief, KOH (4 g) and FS (0.8 g) were ground in an agate mortar until powder state. The obtained black mixture was calcined at 800 °C for 2 h in Ar atmosphere with a heating rate of 5 °C/min. After natural cooling, this mixture was washed with a mixed acid solution (8 mol/L H_2SO_4 and 8 mol/L HNO_3) for 12 h, repeatedly washed with water until pH = 7, and then dried at 60 °C for 24 h.

For the synthesis of the $x(y\text{NiO-CeO}_2)\text{-AFS composite}$, AFS (0.8 g) was dispersed in water (20 mL). Then, $y\text{NiO-CeO}_2$ powder with a mass ratio of $y\text{NiO-CeO}_2$ versus AFS of 0.2, 0.3, 0.4, and 0.5 was added to the above solution, and vigorous mechanical stirring was performed for 6 h. The separated solid was calcined at 200 °C for 2 h in Ar atmosphere with a heating rate of 2 °C/min. The synthetic samples are denoted as $x(y\text{NiO-CeO}_2)\text{-AFS}$, where x is 0.2, 0.3, 0.4, and 0.5, representing the proportion of $y\text{NiO-CeO}_2$. In addition, CeO_2 , NiO, AFS, $y\text{NiO-CeO}_2$, 0.4NiO-AFS , and $0.4\text{CeO}_2\text{-AFS}$ were also treated by the above process.

3.3. Preparation of the $x(y\text{NiO-CeO}_2)\text{-AFS Composite Electrode}$

The $x(y\text{NiO-CeO}_2)\text{-AFS composite electrode}$ was prepared following a previously reported method [7]. $x(y\text{NiO-CeO}_2)\text{-AFS}$ (0.8 g) was dispersed in ethanol (10 mL). Then, a PTFE (10%, 2.8 g) solution was added to the above solution, and mechanical stirring was performed at 70 °C until this mixture became solid. This solid was repeatedly pressed tightly onto stainless-steel mesh (2 × 7 cm; 40 mesh) using a roller press. The obtained electrode is denoted as the $x(y\text{NiO-CeO}_2)\text{-AFS electrode}$.

3.4. Electro-Fenton Degradation of Tetracycline on the $x(y\text{NiO-CeO}_2)\text{-AFS Electrode}$

The electro-Fenton activity of the $x(y\text{NiO-CeO}_2)\text{-AFS composite electrode}$ was evaluated by electrocatalytic degradation of TC. The degradation experiment was conducted in a 220 mL electrolytic cell. The cathode and anode were $x(y\text{NiO-CeO}_2)\text{-AFS electrode}$ (2 cm × 7 cm) and Ti/IrO₂/RuO₂ electrode (40 mesh, 2 cm × 7 cm), respectively. The distance between the electrodes was 3 cm. A commercial DC power device (UTP3704S, SGMICRO, Suzhou, China) was used as a power source, and the concentration of TC was monitored by a UV spectrophotometer (Shimadzu-UV3600, Shimadzu, Kyoto, Japan). The mineralization percentage of TC was analyzed by a Multi TOC analyzer (N/C2100S, AJ, Berlin, Germany).

3.5. Characterization Methods

Structure and composition were characterized by X-ray diffraction (XRD, D8 advanced diffractometer, Bruker, Berlin, Germany) and X-ray photoelectron spectroscopy (XPS, AXIS Ultra, Shimadzu, Kyoto, Japan), respectively. Morphologies were observed by scanning electron microscopy (SEM, S-4800, Hitachi, Kyoto, Japan) and transmission electron microscopy (TEM, JEM-2010, JEOL, Kyoto, Japan). Raman spectroscopy was carried out on a Lab RAM

HR800: the laser energy was 2.7 eV and the incident wavelength was 458 nm. Brunauer-Emmett-Teller (BET) surface area was calculated by N₂ adsorption-desorption isotherms at 77 K on a Micromeritics ASAP 2010M analyzer. Temperature-programmed desorption (O₂-TPD) was carried out on the AutoChem adsorption analyzer (TP-5080, Finetec, Hangzhou, China) with a thermal conductivity detector. Electron paramagnetic resonance spectra detected the oxygen vacancy information (EPR, EMX plus, Bruker, Berlin, Germany). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on an SP-300 electrochemical workstation (SP-300, Bio-Logic, Seyssinet-Pariset, France) in a three-electrode system with 1 mol/L H₂SO₄ (6 mol/L KOH) as an electrolyte, and the working, reference, and counter electrodes were x(yNiO-CeO₂)-AFS electrode, Hg/HgSO₄ (Hg/HgO) electrode, and Pt plate, respectively. A fluorescence spectrophotometer (FLS920, EI, Edinburgh, England) was used to measure the characteristic fluorescence intensity.

3.6. Calculation Methods

The first-principles calculation was performed using the CASTEP package with GGA-PW91. The project augmented-wave method (PAW) was used to describe the electron-core interactions. The detailed description is presented in Supplementary Materials.

4. Conclusions

The 0.4(0.4NiO-CeO₂)-AFS composite prepared by an impregnation method exhibited excellent electro-Fenton catalytic activity in the degradation of highly concentrated tetracycline. The appropriate porous structure and extremely large specific area of AFS play important roles in the efficient mass transfer and effective adsorption of tetracycline, which facilitate the electro-Fenton reaction on Ni-Ce dual activity centers. Moreover, the pH of wastewater, current density, and aeration velocity are demonstrated to have great effects on the electro-Fenton degradation of tetracycline on the 0.4(0.4NiO-CeO₂)-AFS composite. Additionally, the preparation of the composite catalyst is facile and eco-friendly, and its cost is low. Practical application of the novel composite catalyst to the treatment of various organic wastewater is highly expected. Apart from the catalytic degradation of organic wastewater, it is worth carrying out future investigations on the applications of this novel composite in the fields of energy conversion, energy storage and sensors, etc., which could make full use of fullerene soot.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12050509/s1>, Table S1. The specific surface areas and pore volumes of materials. Table S2. The performance parameters of related electro-Fenton catalysts. Figure S1. The EDS spectrum of 0.4NiO-CeO₂. Figure S2. The survey spectra of 0.4(0.4NiO-CeO₂)-AFS before and after catalytic reaction. Figure S3. The (a) CV and (c) EIS curves in 1 mol/L H₂SO₄ solution and (b) CV and (d) EIS curves in 6 mol/L KOH solution for 0.4(yNiO-CeO₂)-AFS, in which $\alpha - \zeta$ stand for the y values of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 in 0.4(yNiO-CeO₂)-AFS, respectively. Figure S4. The (a) CV and (c) EIS curves in 1 mol/L H₂SO₄ solution and (b) CV and (d) EIS curves in 6 mol/L KOH solution for x(0.4NiO-CeO₂)-AFS (x = 0.3, 0.4 and 0.5). References [43–52] are cited in Supplementary Materials.

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