

# Synergistic effect between Ni and Ce dual active centers initiated by activated fullerene soot for electro-Fenton degradation of tetracycline

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## Calculation Methods

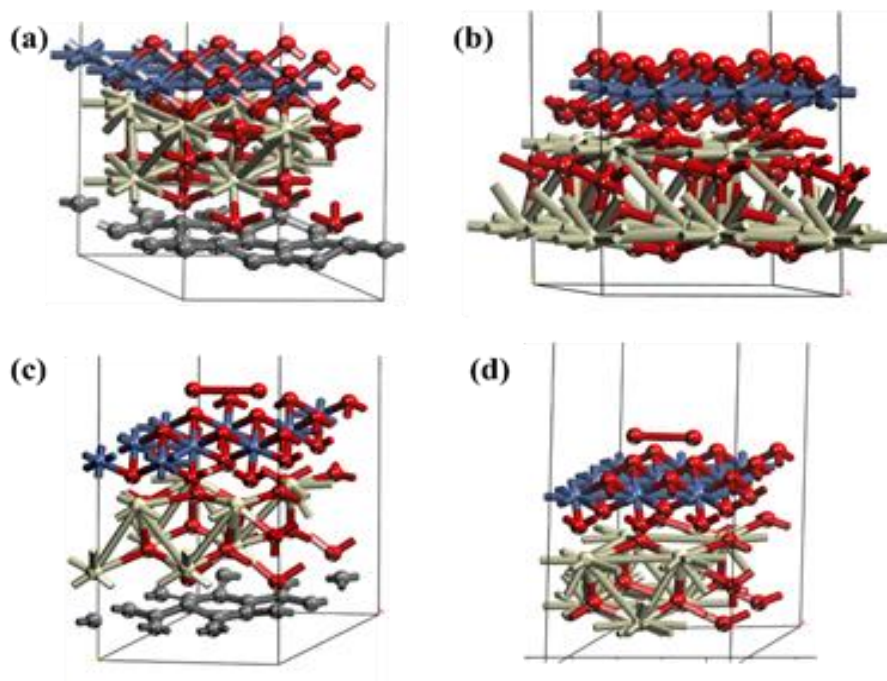
First-principles calculations were performed in the CASTEP package. The exchange-correlation energies were calculated according to the Perdew-Wang 91 (PW91) within the General Gradient Approximation (GGA) framework with the ultrasoft pseudopotentials [43], and Ce (5s, 5p, 6s, 5d, 4f), Ni (3s, 3p, 4s, 3d), O (2s, 2p), and C (2s, 2p) shells were treated as valence orbitals, while the remaining electrons were kept frozen as core states [44].

The DFT-D2 method with the Grimme Van der Waal's force correction was employed to accurately describe the long-range electrostatic interactions and the Coulomb interaction correction was also taken into account with LDA+U method to describe the electronic properties of cerium 4f and nickel 3d orbit [45]. The energy cutoff was 400 eV.

A (4 × 4 × 1) grid treated the integration of the Brillouin-zone, and a vacuum region (15 Å) was added above each slab to avoid the fake interaction along the Z-axis. Stable configurations were obtained by a geometry optimization, and the iterations were repeated until the forces on the atoms were less than 0.03 eV/Å and the energy change less than 1.0×10<sup>-5</sup> eV. The adsorption energy ( $E_{\text{ads}}$ ) is calculated using the following equation:

$$E_{\text{ads}} = E_{\text{surface+oxygen}} - E_{\text{surface}} - E_{\text{oxygen}}$$

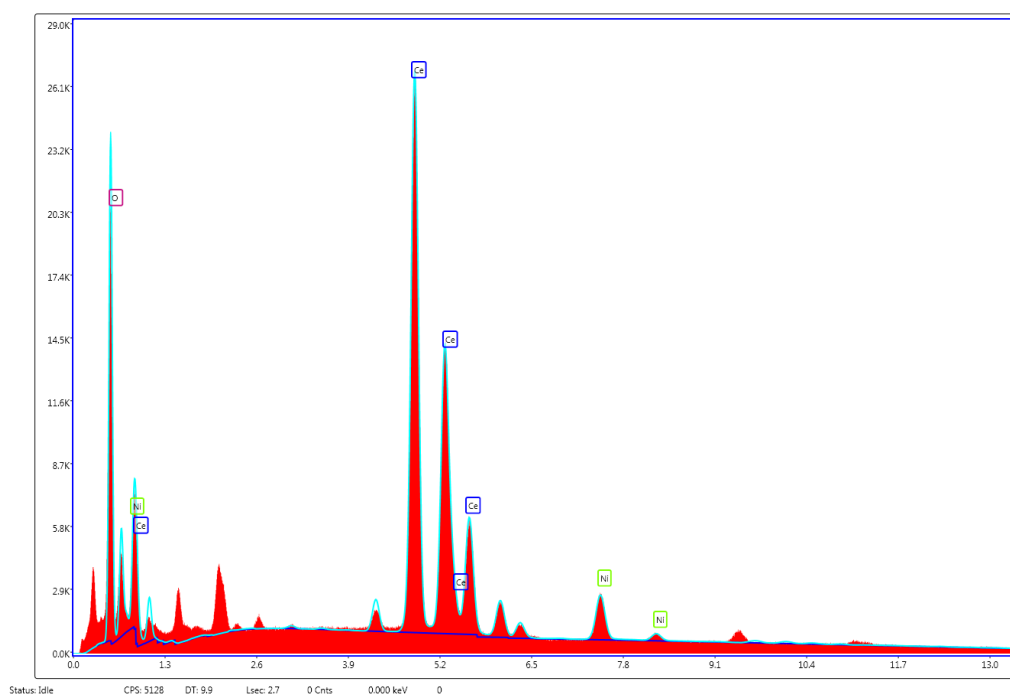
Where the  $E_{\text{surface+oxygen}}$  is the total energy at oxygen adsorbed on the (111) plane,  $E_{\text{surface}}$  is the energy on the individual (111) plane, and  $E_{\text{oxygen}}$  is an oxygen molecule's energy."



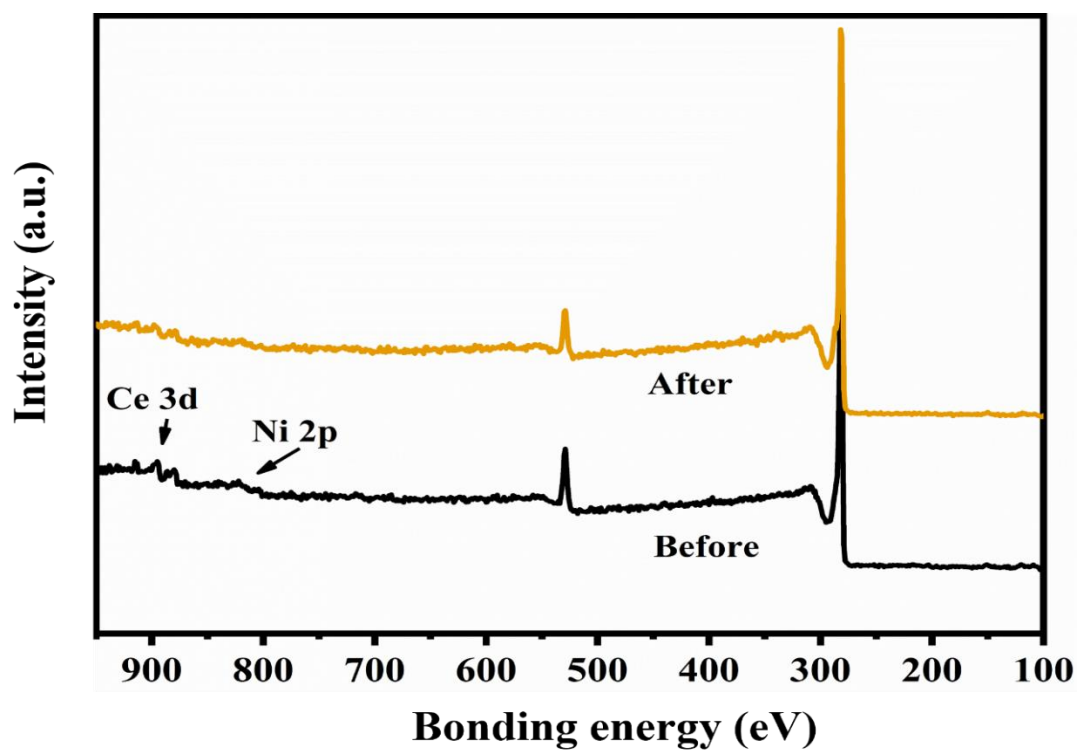
The HRTEM images displayed in Figure 3(e, f) and the XRD patterns shown in Figure 1 (a, b) prove the exposure of the (111) planes of  $\text{CeO}_2$  and  $\text{NiO}$ . And the FT-IR spectrum demonstrated in Figure 1(e) evidences the formation of  $\text{Ce-O-C}$  bond. Thus, we constructed the above figure optimized ball-and-stick models before (a, b) and after (c, d)  $\text{O}_2$  adsorption on  $(\text{NiO-CeO}_2)\text{-AFS}$  (a, c) and  $\text{NiO-CeO}_2$  (b, d), in which the yellow, red, blue and gray balls stand for the cerium, oxygen, nickel and carbon atoms, respectively. The (111) plane of  $\text{CeO}_2$  was set face to face with the (111) plane of  $\text{NiO}$ , and only the  $\text{O}_2$  adsorption on the (111) plane of  $\text{NiO}$  was comparatively studied with (c) and without (d) the existence of AFS.

**Table S1.** The specific surface areas and pore volumes of materials

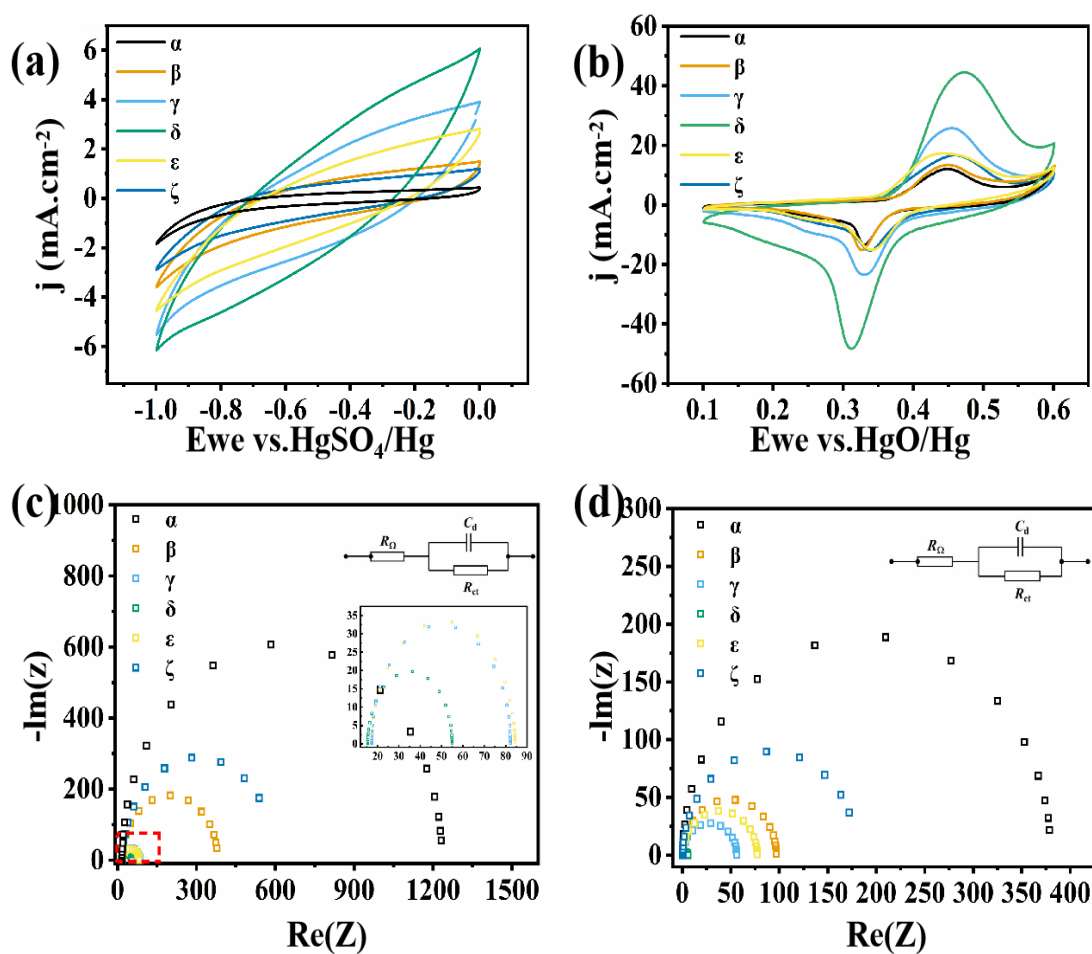
	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{micro}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{micro}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{meso}}$ ( $\text{cm}^3/\text{g}$ )
0.4NiO-CeO <sub>2</sub>	80.2	19.7	0.01	0.01
FS	170.0	65.8	0.1	0.1
0.4(0.4NiO-CeO <sub>2</sub> )/FS	260.1	100.2	0.11	0.1
AFS	1008.3	652.3	0.41	0.30
0.4(0.4NiO-CeO <sub>2</sub> )/AFS	1475.5	959.2	0.45	0.33



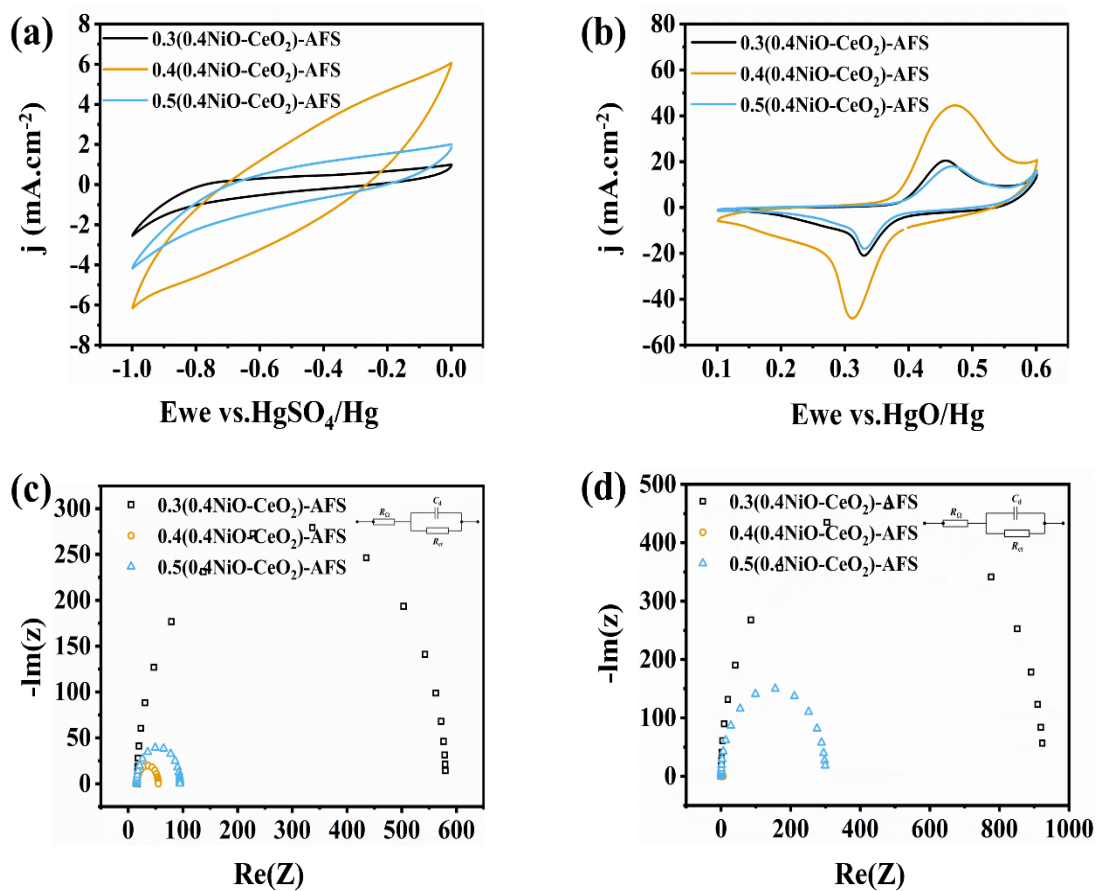
**Figure S1.** The EDS spectrum of 0.4NiO-CeO<sub>2</sub>



**Figure S2.** The survey spectra of 0.4(0.4NiO-CeO<sub>2</sub>)-AFS before and after catalytic reaction



**Figure S3.** The (a) CV and (c) EIS curves in 1 mol/L  $\text{H}_2\text{SO}_4$  solution and (b) CV and (d) EIS curves in 6 mol/L KOH solution for 0.4(yNiO-CeO<sub>2</sub>)-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-CeO<sub>2</sub>)-AFS, respectively.



**Figure S4.** The (a) CV and (c) EIS curves in 1 mol/L  $\text{H}_2\text{SO}_4$  solution and (b) CV and (d) EIS curves in 6 mol/L KOH solution for  $x(0.4\text{NiO-CeO}_2)\text{-AFS}$  ( $x = 0.3, 0.4$  and  $0.5$ ).

**Table S2.** The performance parameters of related electro-Fenton catalysts

Materials	Initial concentration ( $\text{mg}\cdot\text{L}^{-1}$ )	Reaction time (min)	Current density ( $\text{mA}/\text{cm}^2$ )	Degradation efficiency (%)	Mineralization rate TOC/h ( $\%/h$ )	Aeration condition ( $\text{L}/\text{min}$ )	References
Bi-Sn-Sb/ $\gamma\text{-Al}_2\text{O}_3$	20	180	100	86.6	—	0.3	[46]
Ti/ $\text{RuO}_2/\text{IrO}_2$	100	120	200	80	—	—	[47]
ZIF-8/ACF	50	20	32	95	15.5/6	0.6	[48]
Cu-Fe/ $\text{Fe}_2\text{O}_3$	20	120	40	90	85/8	0.1	[49]
Cu-Fe/Biochar	40	360	—	92	—	—	[50]
FPE	50	30	2000	78	—	0.6	[51]
Fe(II)/Graphite	50	100	—	96.1	—	—	[52]
0.4(0.4NiO-CeO <sub>2</sub> )-AFS	200	200	35	96	92/5	0.1	this work