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1 **Bimetallic Carbon Nanotube Encapsulated**
2 **Fe-Ni Catalysts from Fast Pyrolysis of Waste**
3 **Plastics and their Oxygen Reduction**
4 **Properties**

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22 Abstract

23 Carbon-based bimetallic electrocatalysts were obtained by catalytic pyrolysis of waste
24 plastics with Fe-Ni-based catalysts and were used as efficient oxygen reduction reaction
25 (ORR) catalysts in this study. The prepared iron-nickel alloy nanoparticles
26 encapsulated in oxidized carbon nanotubes (FeNi-OCNTs) are solid products with a
27 unique structure. Moreover, the chemical composition and structural features of
28 FeNi-OCNTs were determined. The iron-nickel alloy nanoparticles were wrapped in
29 carbon layers, and the carbon nanotubes had an outer diameter of 20–50 nm and
30 micron-scale lengths. FeNi-OCNT with a Fe/Ni ratio of 1:2 (FeNi-OCNT12) exhibited
31 remarkable electrochemical performance as an ORR catalyst with a positive onset
32 potential of 1.01 V (vs. RHE) and a half-wave potential of 0.87 V (vs. RHE), which were
33 comparable to those of a commercial 20% Pt/C catalyst. Furthermore, FeNi-OCNT12
34 exhibited promising long-term stability and higher tolerance to methanol than the
35 commercial 20% Pt/C catalyst in an alkaline medium. These properties were
36 attributable to the protective OCNT coating of the iron-nickel alloy nanoparticles.

37 **Keywords:** Waste plastics; Catalytic pyrolysis; bimetallic catalysts; Carbon
38 nanotubes; Oxygen Reduction Reaction.

39 Nomenclature

ω	Electrode rotation rate	1/s
A	Electrode area	cm ²

As	Ash	wt. %
B	Levich constant	$A/(s)^{0.5}$
CNTs	Carbon nanotubes	-
C_0	Bulk concentration of O_2	mol/cm^3
D_0	Diffusion coefficient	cm^2/s
E	Electrode potential	V
F	Faraday constant	$A \times \text{s}/\text{mol}$
FC	Fixed carbon	wt. %
J	Measured current density	A
M	Moisture	wt. %
OCNT	Oxidized carbon nanotubes	-
n	Electron transfer number	-
ν	Kinetic viscosity of the electrolyte	cm^2/s
V	Volatile matter	wt. %
Pedices		
ar	As received	-
db	Dry basis	-
L	Diffusion-limited current density	-
K	Kinetic current density	-

40 **1 Introduction**

41 Over the last decades, the sharp increase in the demand for plastics resulted in an

42 estimated annual plastics production of ~400 Mt (380 Mt in 2015) (Geyer et al., 2017),
43 and a consequent growth in the generation of plastic waste, which is currently ~300 Mt
44 per year (Zhao et al., 2018). In China, it is estimated that over 70 Mt of plastic waste were
45 produced in 2017 (Caroline et al., 2018). While most plastic waste is landfilled or
46 incinerated, and only small amounts are recycled, a significant proportion is discarded
47 indiscriminately, resulting in acute environmental pollution (Sharuddin et al., 2016).
48 Given the challenges in the management of plastic waste, the development of novel
49 processes that enable its conversion into high value products is appealing, as it
50 incentivizes plastic waste recycling (Yao et al., 2018b).

51 Pyrolysis is a thermal degradation process through which waste plastics can be
52 converted into gaseous fuels and liquid products, and it has been considered a promising
53 method in plastic waste management (Bientinesi et al., 2009). And pyrolysis or catalytic
54 pyrolysis process has been proved to be an economical way (S.M. Al-Salem, 2017).
55 Furthermore, the catalytic pyrolysis of waste plastics can enhance the calorific value of
56 the gas and the concentration of hydrogen and can deliver high-value-added solid
57 products such as carbon nanotubes (CNTs) (D. Yao et al., 2018; Yao et al., 2018a; Yao et
58 al., 2017). The outstanding physical and chemical properties of CNTs incite research on
59 their extensive applications, such as their use as electrocatalysts in the ORR (oxygen
60 reduction reaction) electrocatalysts. In the preparation of CNTs by catalytic pyrolysis of
61 waste plastics, the choice of the pyrolysis catalyst not only affects the characteristics of
62 the solid products but also significantly impacts the stability and electrical conductivity
63 properties of the CNTs (Sharuddin et al., 2016).

64 At present, iron-(Aboul-Enein et al., 2018; Jonathan et al., 2016) and
65 nickel-based(Ochoa et al., 2017; Wu et al., 2009) catalysts are mainly used in the
66 catalytic pyrolysis of waste plastics. Iron-based catalystscan promote the production of
67 CNTs(Kong et al., 1998; Shen et al., 2014) because of their higher carbon solubility.In
68 contrast, the use of nickel-based catalystscan lead to higher quality of the CNTs due to
69 their ability to cleave C–C and C–H bonds(De et al., 2016; Shen et al., 2014).In
70 previous studies, we found that pyrolysis of waste plastics with an iron-nickel catalyst
71 delivered CNTs in41%yield, which is higher than the yields of iron- (~35%)and
72 nickel-based catalysts (~21%)(Yao et al., 2018a). Moreover, iron- and nickel-based
73 electrocatalystsfind wide applications in electrochemistry. For example, Fe₃C obtained
74 by reforming of hydrocarbons with aniron-based catalyst is an active ORR
75 catalyst(Jiang et al., 2016). However, the low stability of the iron-based electrocatalyst
76 limits its further application. Wu et al. found that a polyaniline–iron–carbon
77 (PANI–Fe–C) electrocatalyst suffered from serious iron sulfide erosion, which led to a
78 decrease in current density of about 50% within 200h(Ferrandon et al., 2013). Nickel is
79 a low-cost metalwith electronic properties which are similar to those of iron, such as the
80 number of electrons and holes in the d-band (Okpalugo et al., 2018), and its reactivity
81 resembles that of palladium or platinum(Stamenkovic et al., 2007), as demonstrated by
82 its use as an alternative to Pt or Pd in the ORR(Lai et al., 2019; Zhao et al., 2015).
83 Furthermore, efficient preparation of Ni-alloyswith most transition metals in different
84 ratios is possible and enables the investigation of the diverse catalytic applications of a
85 wide range of composition-dependent bimetallic nickel systems(De et al., 2016).For

86 instance, Lai et al. prepared ultrathin multimetallic Pt-Pd-Ni material by a co-reduction
87 method, and the Pt₃₂Pd₄₈Ni₂₀ nanosheets exhibited superior catalytic activity to the
88 commercial Pt/C catalyst (Lai et al., 2019). However, studies on the use of bimetallic
89 iron-nickel alloys as ORR electrocatalysts are scarce, and the active sites of
90 carbon-based iron-nickel alloy electrocatalysts remain elusive.

91 Herein, we report the synthesis of Fe-Ni catalysts, the influence of the Fe-Ni loading of
92 oxidized carbon nanotubes (OCNTs) on the electrocatalytic oxygen reduction
93 properties, and detailed mechanistic studies. A highly active and durable catalyst
94 (Fe-Ni-bimetallic-loaded OCNTs) is identified. This work provides a novel strategy
95 to reuse plastic waste, whilst contributing to the development of
96 low-cost, high-performance non-precious metal catalysts for the ORR.

97 **2 Materials and Methods**

98 **2.1 Materials and Chemical Reagents**

99 The employed waste plastic samples consisted of used disposable lunch boxes
100 (polypropylene), which were ground to particles of 0.1–0.5 mm size with a liquid
101 nitrogen grinder. The proximate and ultimate analysis results of the polypropylene
102 waste are presented in Table S1.

103 Catalyst materials: Nickel nitrate hexahydrate (Ni(NO₃)₃·6H₂O), iron nitrate
104 nonahydrate (Fe(NO₃)₃·9H₂O), and aluminum oxide (Al₂O₃) were purchased from
105 Sigma Aldrich (China). Absolute ethanol and methanol were purchased from

106 Sinopharm Chemical Reagent Co. Ltd. (China). 20% Pt/C catalysts and 5% Nafion
107 solution were purchased from Shanghai Hesen Electronics Co. Ltd. (China). All
108 chemicals were analytically pure and used without prior purification. Ultra-pure water
109 ($>18 \text{ M}\Omega \text{ cm}^{-1}$) was obtained from a Millipore system and used to prepare all aqueous
110 solutions. All electrochemical measurements were carried out at 25°C .

111 **2.2 Synthesis of Fe-Ni- Al_2O_3 Catalysts**

112 Bimetallic Fe-Ni catalysts with different Fe/Ni molar ratios were prepared by the
113 impregnation method according to the following procedure: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and
114 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (having different molar ratios 3:1, 2:1, 1:1, 1:2, and 1:3; 1.0 g total
115 mass) were dissolved in 20 mL ethanol, and 10 g $\gamma\text{-Al}_2\text{O}_3$ was added to each solution.
116 The turbid mixtures were stirred for 4 h at 50°C , and subsequently dried in an oven at
117 105°C for 12 h. The dry solids were ground into particles smaller than 0.01 mm
118 and calcined at 800°C for 2 h with a heating rate of $10^\circ\text{C}/\text{min}$ under air atmosphere. The
119 five prepared catalysts were numbered according to their Fe/Ni molar ratio. That is,
120 FeNi31- Al_2O_3 , FeNi21- Al_2O_3 , FeNi11- Al_2O_3 , FeNi12- Al_2O_3 , and FeNi13- Al_2O_3 ,
121 correspond to the Fe/Ni molar ratios of 3:1, 2:1, 1:1, 1:2, and 1:3, respectively.

122 **2.3 Synthesis of FeNi-OCNTs Electrocatalysts**

123 The catalytic vapor deposition method was used to produce the CNTs. The
124 experiments were carried out in a two-stage fixed bed reactor (as shown in Figure S1)
125 consisting of a quartz tube reactor with two heating zones (upper stage for plastic

126 pyrolysis, lower stage for volatile catalytic vapor deposition) that were controlled
127 separately. In each experiment, the reactor was charged with 1 g plastic waste in a
128 ceramic holder(upperstage) and 0.5 g Fe-Ni catalystin a stainless mesh basket (lower
129 stage)(D. Yao et al., 2018; Yao et al., 2018a). Initially, the lower stage was preheated to
130 800 °C(heating rate: 20 °C/min).Once the lowerstage reached the target temperature,
131 the waste plasticsample was pushedto the middle of the upper stage and heated to
132 500 °C (heating rate: 10 °C/min). The system was maintainedunder
133 isothermalconditions for 10 min to ensure complete evolution of the volatiles. The
134 evolving gas was adsorbed with ethanol to avoid environmental pollution. The
135 reactions were conducted under inert atmosphere using nitrogen (99.99% purity) as the
136 carrier gas (flow rate: 100 mL/min). The black solid containing the catalyst (lower
137 stage) was collected and refluxed in 200 mL20 wt.% nitric acid for 4h (100°C)to
138 remove impurities and unstable species, such as metal particles on the outer nanotube
139 surface and part of amorphous carbon,and wassubsequentlywashed with distilled water
140 until the pH of the filtrate was 7.The residuewas dried at 105°C for 12h. The products
141 were numbered according to the used catalyst.For example, the product obtainedfrom
142 FeNi31-Al₂O₃ was named FeNi31-OCNT.

143 **2.4 Characterization of FeNi-OCNTs**

144 The basic surface morphology of the FeNi-OCNT catalysts was studied through field
145 scanning electronic microscope (FSEM, Nova NanoSEM 450) and transmission
146 electron microscopy (TEM, JEM-2100F). High resolution images of the CNTs were

147 obtained by high-resolution transmission electron microscopy (HR-TEM) and
148 distribution of different metals was investigated using high-angle annular dark field
149 detector and energy dispersive spectroscopy (HAADF-STEM-EDS). The specific
150 surface areas, pore volumes, and pore size distribution were investigated through
151 nitrogen adsorption measurement at 77 K (Quantachrome IQ) with the
152 Brunauer–Emmett–Teller (BET) theory, v -T method, and QSDFT methods from 1.7 nm
153 to 33 nm. The crystal structures of the CNTs were determined by X-ray diffraction (XRD)
154 on a Philips X'Pert PRO instrument with a scanning step of 0.026° in the 2θ range from
155 5° to 85° . Raman spectroscopy was performed on a LabRAM HR800 spectrometer at a
156 wavelength of 532 nm with Raman shift from 200 cm^{-1} to 3500 cm^{-1} . Surface chemical
157 states were analyzed by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD,
158 Kratos) using Al $K\alpha$ line (15 kV, 10 mA, 150 W) as the radiation source.

159 **2.5 ORR Catalytic Property Measurements**

160 The electrochemical measurements were conducted on an electrochemical
161 workstation equipped with a rotating disk electrode (RDE, CHI760E, ATA-1B, China)
162 in a three-electrode system. Saturated calomel and Pt wire were used as the reference
163 and counter electrodes, respectively. The working electrode consisted of a 3 mm
164 diameter and 4 mm thickness RDE coated with a FeNi-OCNTs film.

165 FeNi-OCNTs were ground for 30 min prior to preparation of the catalyst ink. For each
166 test, 10 mg catalyst powder was dispersed in 100 μL absolute ethanol and 40 μL of 5 wt.%
167 Nafion was added. The mixture was stirred for 30 min under sonication, yielding a

168 homogenous ink. The working electrode was charged with 2 μ L of the ink and dried
169 overnight. The ORR performance was evaluated in N₂- and O₂-saturated 0.1 M KOH
170 aqueous solutions. The obtained potentials were converted to reversible hydrogen
171 electrode using the equation

$$E(\text{vs RHE}) = E(\text{vs SCE}) + 0.0591 \text{pH} + 0.24 \quad (1)$$

172 where RHE is the reversible hydrogen electrode, SCE is the saturated calomel
173 electrode, and pH is the hydrogen ion concentration.

174 Electron transfer number n for Fe-Ni electrocatalysts was calculated using the
175 Koutecky-Levich equation as follows

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (2)$$

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6} \quad (3)$$

176 where J is the measured current density, J_K is the kinetic current density, J_L is the
177 diffusion-limited current density, ω is the electrode rotation rate, F is the Faraday
178 constant (96485 C/mol), C_0 is the bulk concentration of O₂ (1.2×10^{-3} mol/L for a 0.1 M
179 KOH aqueous solution), D_0 is the diffusion coefficient of O₂ (1.9×10^{-5} cm²/s for a 0.1
180 M KOH aqueous solution), and ν is the kinetic viscosity of the electrolyte (0.01 cm²/s
181 for a 0.1 M KOH aqueous solution).

182 **3 Results and Discussion**

183 **3.1 Physical Porosity of FeNi-OCNTs**

184 Typical FSEM images of the prepared FeNi-OCNTs are shown in Figure 1, and

185 confirm the successful synthesis of CNTs. The images reveal a fibrous structure of
186 interwoven and stacked nanotubes with diameter of approximately 20–50 nm and
187 length ranging from tens of nanometers to several micrometers, dimensions which are
188 similar to those of CNTs prepared by catalytic pyrolysis previously (Yao et al., 2017). The
189 small size of the CNTs imply that the enclosed metal particles are nanoscale and
190 indicate uniformity of metal particle dispersion, significant features of ORR catalysts (Ji
191 et al., 2017). Figure 1a-e shows that iron-rich CNTs are shorter and thicker than those
192 containing a low Fe/Ni ratio. The nanotubes in FeNi12-OCNT and FeNi13-OCNT are
193 longer and thinner than those in the other three samples. It has been reported that a high
194 nickel content leads to more homogeneous and longer CNTs, which is possibly a result
195 of better dispersion of smaller metal particles owing to the stronger interaction between
196 the nickel metal particles and the support, and confirms that the CNTs morphology is
197 related to the particle size of the catalyst (Chung et al., 2005).

198 The isothermal adsorption profile of the solid carbon materials shown in Figure 2a reveals
199 that all FeNi-OCNTs exhibit reversible type IV isotherm and H3 hysteresis loops, the
200 latter at 0.5–1.0 relative pressure, which is the main characteristic of mesoporous
201 materials. The calculated specific surface areas of FeNi31-OCNT, FeNi21-OCNT,
202 FeNi11-OCNT, FeNi12-OCNT, and FeNi13-OCNT are 134.6 m²/g, 162.3 m²/g, 120.4
203 m²/g, 134.6 m²/g, and 126.4 m²/g, respectively. Pore volumes and average diameters of
204 the FeNi-OCNTs are given in Table S2, and indicate that FeNi21-OCNT exhibits the
205 highest total pore volume and average diameter. The pore size distribution, displayed in
206 Figure 2b, shows that all FeNi-OCNTs exhibit four distinguished mesopore distribution

207 peaks at around 9.6 nm, 11.5 nm, 15.0 nm, and 26.1 nm, and that the occurrence of
208 smaller pores correlates with an increase in the nickel content, which is consistent with
209 the SEM results. The mesoporous structure of the catalysts probably corresponds to the
210 inner diameter of the CNTs. Of note, substantial catalyst mesoporosity is regarded as
211 ideal for the ORR, as it correlates with fast mass-transport in the electrolytes and high
212 exposure of active sites (Zhang et al., 2018).

213 **3.2 Chemical Structure of FeNi-OCNTs**

214 From the TEM images of FeNi₁₂-OCNT, it can be observed that the metal
215 nanoparticles are encapsulated in the CNTs (Figure 3a, b). The HR-TEM images reveal
216 that the outer diameter of FeNi₁₂-OCNT ranges from about 10 nm to tens of
217 nanometers, and that the metal nanoparticles of ~20 nm size are wrapped in ~10 nm thin
218 carbon layers (Figure 3b, c). Furthermore, the HR-TEM image for single tube in Figure
219 3c indicates that the 0.202 nm nanoparticle lattice fringe is associated with the (111)
220 plane of FeNi₃ alloy. The TEM-energy-dispersive X-ray (TEM-EDX) shows that
221 FeNi₁₂-OCNT is composed of C with encapsulated Fe-Ni alloy nanoparticles (Figure
222 3d, e, f). The linear profiles obtained by HAADF-STEM of a single particle (Figure 3d,
223 inset) show higher intensity for Ni than Fe, which indicates the presence of more Ni
224 atoms (Figure 3g). And the exact content of the two metals will be studied in the future
225 according to these works (Pierce et al., 1998; Yang et al., 2010).

226 The Raman spectra of FeNi-OCNTs show three characteristic bands at around 1340
227 cm⁻¹ (D band), 1580 cm⁻¹ (G band), and 2670 cm⁻¹ (G' band, Figure 4a), which

228 correspond to the defects in graphene, the planar motion of sp^2 -hybridized carbon
229 atoms in the graphite layers, and the ejection scattering of the two phonons, respectively.
230 The I_D/I_G ratio is commonly used to describe the degree of structural defects of carbon
231 materials. The I_D/I_G ratios for FeNi31-OCNT, FeNi21-OCNT, FeNi11-OCNT,
232 FeNi12-OCNT, FeNi13-OCNT are 0.78, 0.75, 0.82, 0.72, and 0.79, respectively, and
233 are comparable with the values of OCNTs used in commercial applications and those
234 reported in the literature (Kaushik et al., 2014; Wang et al., 2018). In addition, the ratio
235 I_G'/I_G can be used to describe the purity of the CNTs. In this study, the obtained values in
236 the range 0.38–0.50 indicate that the synthesized catalysts have a high degree of
237 graphitization. Moreover, I_G'/I_G sank from 0.49 to 0.38 with the decrease in the Fe/Ni
238 ratio from 3:1 to 1:1, indicating a gradual decrease in the CNT purity with the amount of
239 Fe, until a ratio Fe/Ni of 1:3 at which point I_G'/I_G increased to 0.50.

240 The sharp graphite peaks at $2\theta \sim 26^\circ$ in the XRD patterns of all FeNi-OCNT catalysts
241 (Figure 4b) correspond to the (002) facets of graphite carbon and suggest a high degree
242 of graphitization, which could stem from the CNTs and Fe-Ni alloys. A high degree of
243 graphitization corresponds to good electrical conductivity, which is beneficial to
244 electrochemical applications. In particular, the lower angle of the (002) peak of
245 FeNi12-OCNT indicates a larger inter-layer spacing. This could be explained by
246 the attack of the defective sites by nitric acid, which could intercalate into the CNTs to
247 unzip the tube walls, thus increasing exposure of the active sites (Zhao et al., 2006). The
248 peaks observed at 43° and 75° confirm the presence of a Fe-Ni alloy, which is in
249 accordance with the TEM results. Furthermore, Fe_3C found in the catalysts was

250 generated during the growth of the CNTs (Yao et al., 2018a) and could either serve as an
251 efficient catalytic site (Yang et al., 2015) or boost the activity of other catalytic
252 sites (Jiang et al., 2016). In addition, the detection of residual Al_2O_3 ($2\theta=67^\circ$) implies that
253 it was not entirely removed during concentrated nitric acid washing because of its high
254 stability.

255 XPS characterization was carried out to further determine the components in the
256 prepared composites. As displayed in Figure 5a, the wide-scan spectrum indicates that
257 FeNi-OCNTs mainly consisted of C and O, and peaks corresponding to Fe and Ni were
258 not observed. As shown in Table S3, the amount of C decreased while that of O
259 increased with the rise in the Ni ratio. Only few Fe and Ni atoms were observed on the
260 surface of the samples. These results are confirmed by the XPS spectrum of
261 FeNi12-OCNT shown in Figure 5b. The removal of Ni and Fe from the CNT surface by
262 refluxing with concentrated nitric acid aims at the enhancement of catalyst stability by
263 preventing the direct reaction of the surface-bound metal with electrolyte. Taking
264 FeNi12-OCNT as an example, the C 1s XPS spectrum in Figure 5c shows an intense
265 signal at 285 eV, which corresponds to the graphitic structure (sp^2 hybridization) of the
266 FeNi-OCNTs, and a signal at 285.6 eV, which results from structural defects (Datsyuk et
267 al., 2008). Furthermore, the three signals at 286.4 eV, 287.2 eV, and 289.7 eV
268 correspond to oxygen-bound carbon atoms and can be attributed to C-O-C (mainly from
269 phenols), C=O, and -COOH (mainly from carboxylic acids), respectively (Zhang et al.,
270 2008), whereas the -COOH groups were likely formed during the treatment
271 with concentrated nitric acid (Savilov et al., 2010). The presence of these

272 oxygen-containing hydrophilic groups improves the dispersion of the CNTs in
273 water (Hiura et al., 1995), and therefore favors the exposure of the catalytic active
274 sites. Figure 5d shows the O 1s spectra of FeNi₁₂-OCNT. The peaks at 532.8 eV, 534.3
275 eV, and 536 eV correspond to C=O, C-O, and -COOH, respectively. These functional
276 groups can facilitate the O₂ adsorption and the following O₂ reduction reaction,
277 resulting in improved electrocatalytic performance of the material. In addition, the peak
278 at 537.6 eV corresponds to chemisorbed H₂O (or H-O-H) (Chiang et al., 2011).

279 **3.3 ORR properties**

280 Cyclic voltammetry (CV) results of the FeNi-OCNTs samples are shown in Figure 6a.
281 In contrast to the measurements in N₂-saturated electrolytes, those in an O₂-saturated
282 electrolyte feature sharp reduction peaks in their CV curves, suggesting distinct catalytic
283 activity for the oxygen reduction reaction. In addition, the reduction peak potential of
284 FeNi-OCNTs shifted from 0.77 V to 0.87 V with the increase in the nickel content from
285 25% to 66%, and subsequently decreased to 0.85 V. Linear sweep voltammetry (LSV) of
286 all samples in the O₂-saturated 0.1 M aqueous KOH electrolyte were recorded at 10
287 mV/s and 1600 rpm. The electrocatalytic activities of the five catalysts and commercial
288 20% Pt/C (Figure 6b) reveal that the ORR shift of the onset and half-wave potentials to
289 more positive values coincide with the increase in the ratio of Ni in the catalyst,
290 whereas higher positive potentials suggest an effectively enhanced ORR activity. More
291 specifically, the onset and the half-wave potential increased from 0.94 V to 1.01 V and
292 from 0.79 V to 0.88 V, respectively, with the increase in Ni/Fe ratio (Table S4), and the

293 highest positive potentials were observed for the FeNi12-OCNT catalyst. In addition to
294 the onset and half-wave potentials, the limiting diffusion current also varies with the
295 ratio of Ni in the catalysts. FeNi12-OCNT shows more stable limiting current than the
296 other tested catalysts at the diffusion-controlled region, and its performance was
297 remarkably close to that of the commercial 20% Pt/C catalyst.

298 The Fe-Ni alloy plays a crucial role in the enhanced electrocatalytic activity
299 of FeNi-OCNTs in the ORR in an alkaline solution. LSV of FeNi12-OCNT was
300 measured at rotation rates in the range 800–2000 rpm (Figure 6c), and shows that the
301 limited current density increases with the rotation rate as a result of the faster oxygen
302 diffusion to the catalysts. In Figure 6d, the fitting curves of Koutecky-Levich (K-L)
303 plots obtained at different potentials show nearly linear relationships, which indicate the
304 first-order reaction kinetics with regard to the O₂ concentration in the solution (Dey et
305 al., 2014). The inset in Figure 6d highlights the change in the electron transfer numbers
306 (*n*) calculated from K-L plots from 3.79 to 3.98 over the potential range 0.3–0.6
307 V. Notably, these are close to the theoretical value of 4. The electron transfer numbers
308 of the other catalysts were estimated from the K-L plots and are shown in Figure S2.
309 In conclusion, the Fe-Ni-bimetallic-loaded CNT catalysts display superior oxygen
310 reduction reaction performance under these conditions.

311 High electrocatalytic activity in the ORR is not the only assessment criterion for the
312 replacement of Pt/C by FeNi-OCNTs as cathodic catalysts in commercial fuel
313 cells. Long-term stability and methanol tolerance are equally important for the
314 estimation of the ORR performance in practical applications. Firstly, the durability was

315 evaluated by chronoamperometry in O₂-saturated 0.1M aqueous KOH at 0.6V. As
316 shown in Figure 7a, the FeNi₁₂-OCNT material show superior electrochemical
317 durability to the 20% Pt/C catalyst, retaining 97.6% of the initial current after 40000s of
318 continuous operation in contrast to 95.3% retained by Pt/C under the same conditions. It
319 is known that Pt/C deactivation is due to the loss, susceptible oxidation, or
320 agglomeration of Pt nanoparticles, as well as the corrosion of the carbon black support.
321 Next, the methanol tolerance of FeNi₁₂-OCNT and Pt/C were assessed in O₂-saturated
322 0.1 M aqueous KOH containing 3 M methanol, as the methanol poisoning of catalysts
323 is another important aspect of practical applications. As shown in Figure 7b, a sharp
324 current drop of over 10% of the initial current was observed in the chronoamperogram
325 of the commercial 20% Pt/C electrocatalyst in the presence of methanol. In contrast, the
326 FeNi₁₂-OCNTs exhibit high methanol tolerance with only a slight decrease in the
327 current upon addition of methanol, which indicates that the 20% Pt/C electrocatalyst is
328 farmore prone to methanol poisoning than FeNi₁₂-OCNT. As illustrated in Figure 8, the
329 long-term stability and methanol tolerance of FeNi₁₂-OCNT result from the unique
330 structure of the synthesized CNT materials, in which the encapsulated alloy particles are
331 protected from aggregation and corrosion (Lai et al., 2018). The significant advantages of
332 the prepared catalysts, such as higher stability and methanol tolerance, render them
333 promising candidates for application in the catalytic oxygen reduction reaction.

334 **4 Conclusion**

335 A cost-effective method for the transformation of plastic waste into highly efficient

336 electrocatalysts by a catalytic pyrolysis process has been developed. The variation of the
337 Fe/Ni ratio has a significant impact on the physicochemical properties of the obtained
338 FeNi-OCNTs. While a lower Fe/Ni ratio can lead to longer, smoother CNTs with narrower
339 mesopores, the C/O surface-mass ratio of FeNi-OCNTs increases with the rise in the
340 Fe/Ni ratio. FeNi-OCNT with a Fe/Ni ratio of 1:2 exhibited remarkable ORR catalytic
341 activity, which is comparable to that of a commercial 20% Pt/C catalyst. The onset and
342 half-wave potentials of FeNi₁₂-OCNT were lower than those of the commercial 20%
343 Pt/C catalyst by only 30 mV and 20 mV, respectively. In addition,
344 FeNi₁₂-OCNT showed superior durability and methanol tolerance in an alkaline
345 solution. The outstanding electrocatalytic performance was attributed to the
346 co-existence of the bimetallic Fe-Ni alloy, Fe₃C, and oxygen-containing functional
347 groups in the FeNi-OCNTs. This study not only provides a novel method to reuse
348 plastic waste, but also broadens the design strategies for low-cost, high-performance
349 nonprecious catalysts with controllable bimetallic-species-loaded carbon-based
350 materials.

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358 **Competing interests**

359 The authors declare no competing financial interests with others.

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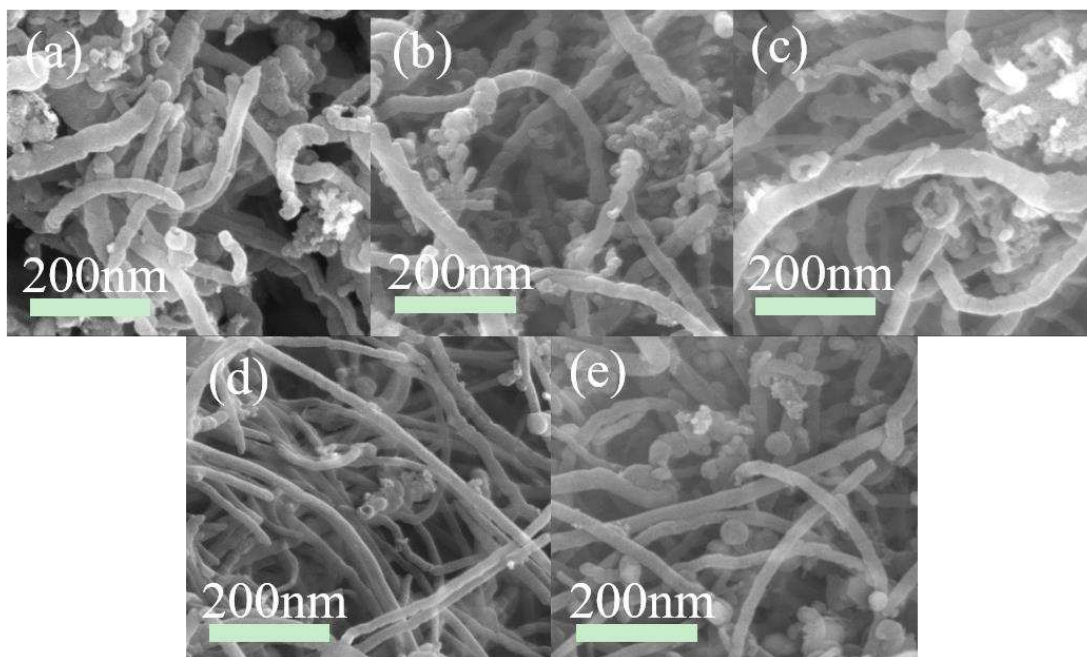
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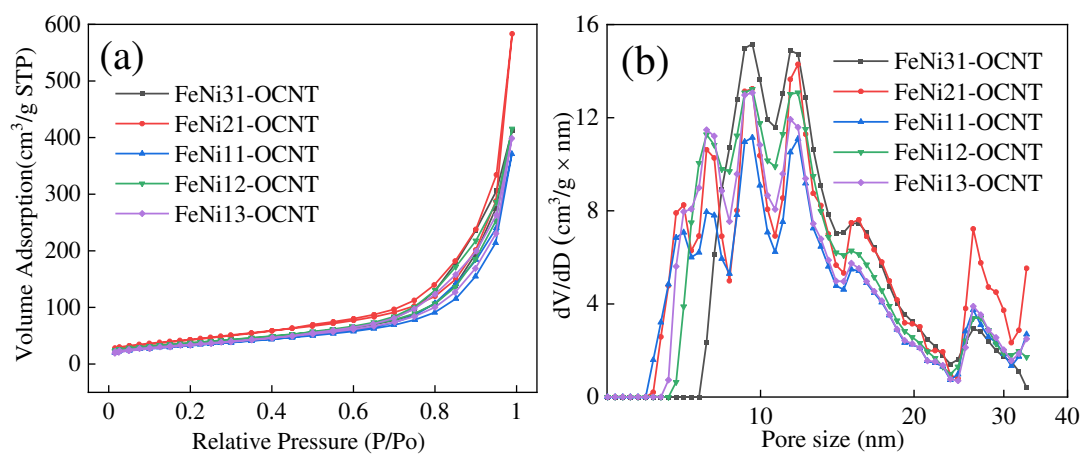
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504 Figure 1 FSEM images of (a) FeNi31-OCNT, (b) FeNi21-OCNT, (c) FeNi11-OCNT,

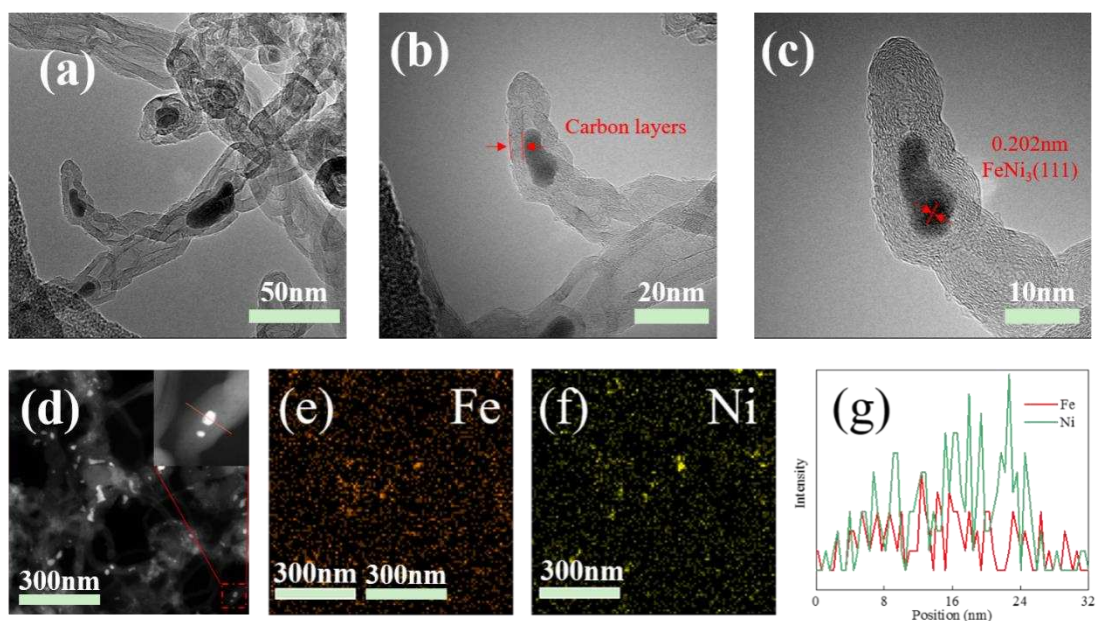
505 (d) FeNi12-OCNT, and (e) FeNi13-OCNT.



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507 Figure 2 (a) N_2 adsorption/desorption isotherms of FeNi-OCNTs. (b) Pore distribution

508 of FeNi-OCNTs.



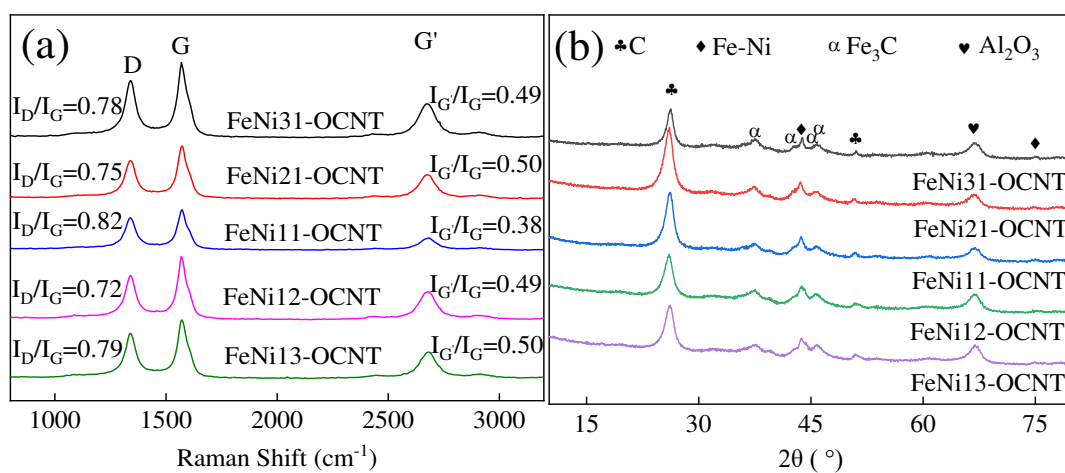
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510 Figure 3 (a)TEM image of FeNi12-OCNT. (b) HR-TEM of Fe-Ni alloy inside. (c)

511 HR-TEM image showing the presence of Fe-Ni alloy. (d) HAADF-STEM images with

512 elemental mapping of Fe (e) and Ni (f). (g) HAADF-STEM cross-sectional

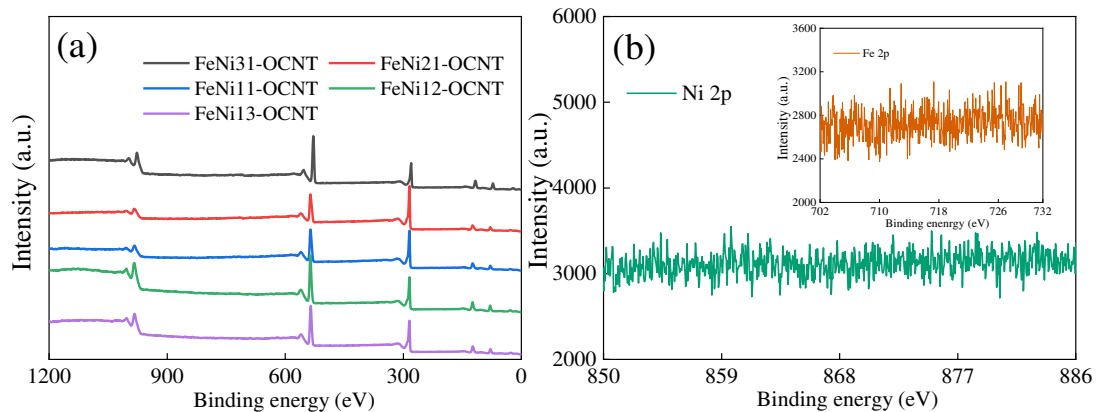
513 compositional profiles.



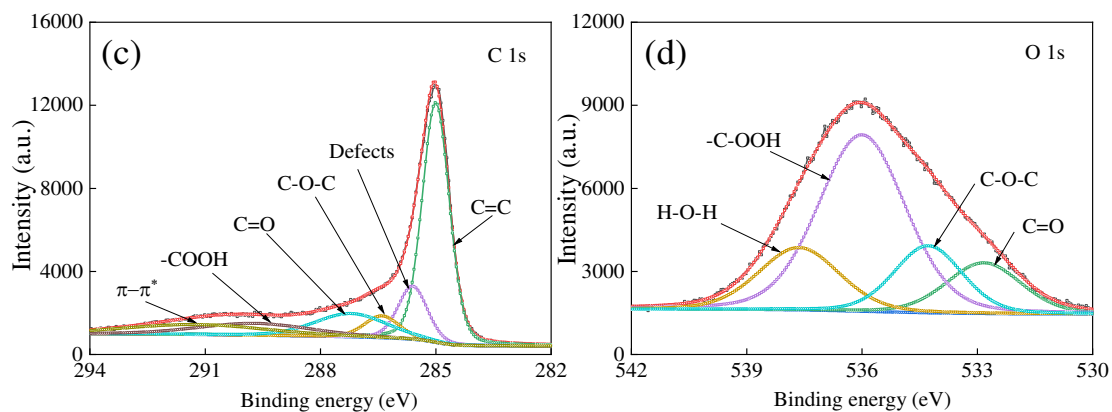
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515 Figure 4 (a) Raman spectra of FeNi-OCNTs. (b) X-ray diffraction patterns of

516 FeNi-OCNTs.



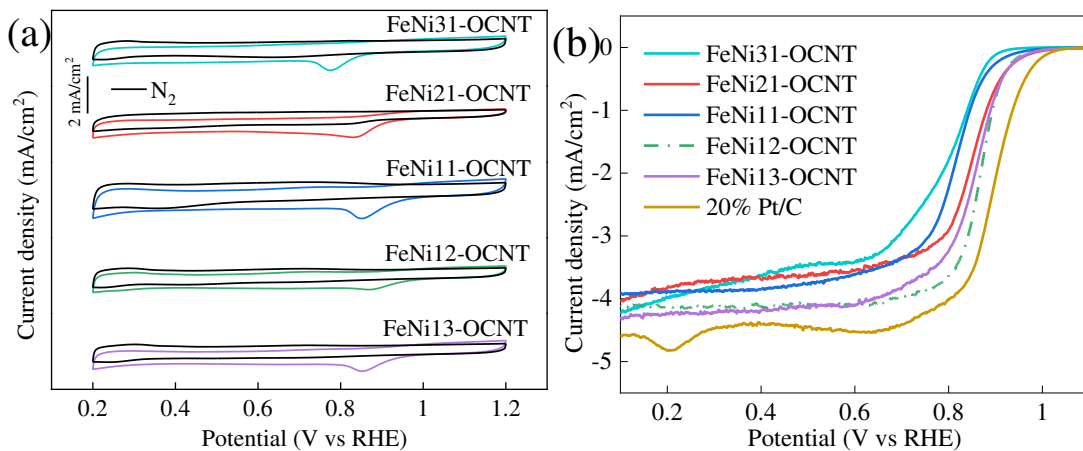
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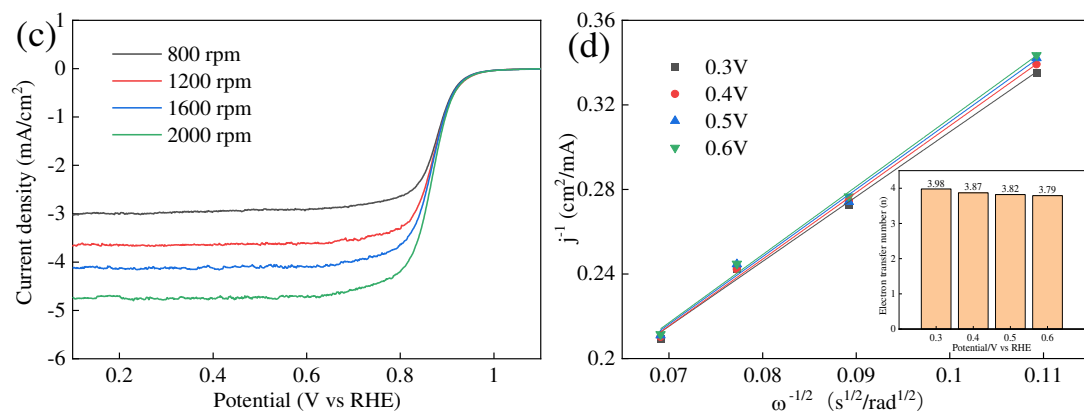
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520 Figure 5 (a) XPS survey spectrum of FeNi-OCNTs and (b) high-resolution XPS
 521 spectrum of Ni 2p and Fe 2p of the FeNi12-OCNT sample. (c) XPS spectrum of C 1s of
 522 the FeNi12-OCNT sample. (d) XPS spectrum of O 1s of the FeNi12-OCNT sample.



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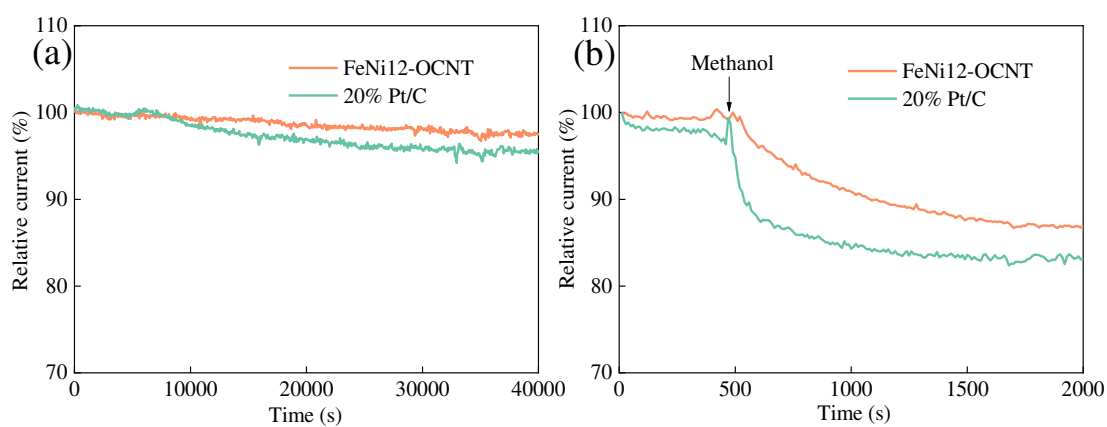
525 Figure 6 (a) CV curves of the FeNi-OCNTs and of 20% Pt/C in O₂-saturated 0.1 M

526 KOH aqueous solutions at 10 mV/s scan rate. (b) LSV curves of FeNi-OCNTs and of

527 20% Pt/C in O₂-saturated solutions at 5 mV/s scan rate and 1600 rpm rotation speed. (c)

528 LSV curves of FeNi12-OCNT at different rotation rates. (d) K-L plots of

529 FeNi12-OCNT at different potentials.



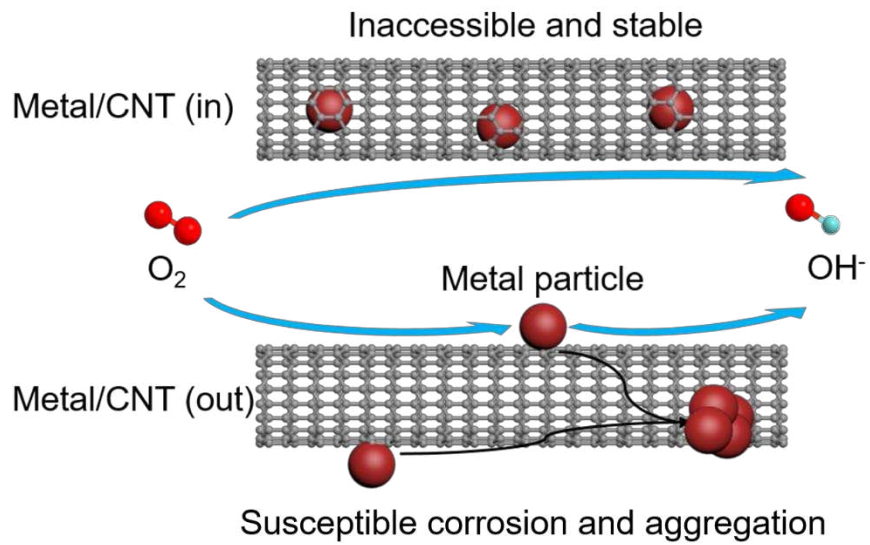
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531 Figure 7 (a) Chronoamperometric responses of FeNi12-OCNT and 20% Pt/C in

532 O₂-saturated 0.1 M aqueous KOH at 0.6 V and 1600 rpm rotation rate. (b)

533 Chronoamperometric responses of FeNi12-OCNT and 20% Pt/C in O₂-saturated 0.1 M

534 aqueous KOH at 0.6 V with and without methanol.



535

536 Figure 8 Schematic illustration highlighting the origin of stability.