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1 ***Operando* Spectroscopic Analysis of Single-Sn-Atom Material for Electrochemical**
2 **CO₂ Reduction**

3 Yachen Deng^{a,b,1}, Jian Zhao^{a,1}, Shifu Wang^{a,c,1}, Ruru Chen^{a,c}, Hsin-Jung Tsai^d, Wen-Jing Zeng^d, Sung-
4 Fu Hung^d, Wei Xu^{e,f}, Junhu Wang^g, Frédéric Jaouen^h, Xuning Li^{a,b,*}, Yanqiang Huang^{a,b,*} and Bin
5 Liu^{i,*}

6 *^aState Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of*
7 *Sciences, Dalian 116023, P.R. China.*

8 *^bUniversity of Chinese Academy of Sciences, Beijing 100049, P.R. China.*

9 *^cDepartment of Chemical Physics, University of Science and Technology of China, Hefei 230026, P.R.*
10 *China.*

11 *^dDepartment of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu 300, Taiwan.*

12 *^eBeijing Synchrotron Radiation Facility, Institute of High Energy Physics, Beijing 100049, P.R. China.*

13 *^fRICMASS, Rome International Center for Materials Science Superstripes, Rome 00185, Italy.*

14 *^gCenter for Advanced Mössbauer Spectroscopy, Mössbauer Effect Data Center, Dalian Institute of*
15 *Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P.R. China.*

16 *^hInstitut Charles Gerhardt Montpellier, University of Montpellier, CNRS, ENSCM, Montpellier 34095,*
17 *France.*

18 *ⁱSchool of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang*
19 *Drive, Singapore 637459, Singapore.*

20 *Corresponding Authors:

21 lixn@dicp.ac.cn (X.L)

22 yqhuang@dicp.ac.cn (Y.H)

23 liubin@ntu.edu.sg (B.L)

24

25 **Abstract**

26 Sn-based materials have been demonstrated as promising catalysts for selective electrochemical CO₂
27 reduction reaction (CO₂RR). However, the detailed structures of catalytic intermediates and the key
28 surface species remain to be identified. In this work, a series of single-Sn-atom catalysts with well-
29 defined structures are developed as model systems to explore their electrochemical reactivity towards
30 CO₂RR. The selectivity and activity of CO₂ reduction to formic acid on Sn single-atom sites are shown
31 to be correlated with Sn(IV)-N₄ moieties axially coordinated with oxygen (O-Sn-N₄). Employing a
32 combination of *operando* X-ray absorption spectroscopy, attenuated total reflectance surface enhanced
33 infrared absorption spectroscopy, Raman spectroscopy and ¹¹⁹Sn Mössbauer spectroscopy, surface-
34 bound bidentate tin carbonate species are precisely captured during CO₂RR. Moreover, the electronic
35 and coordination structure of the single-Sn-atom species under reaction conditions are accurately
36 determined. Density functional theory (DFT) calculations further supports the preferred formation of
37 Sn-O-CO₂ species over the O-Sn-N₄ sites, which effectively modulates the adsorption configuration of
38 the reactive intermediates and lowers the energy barrier for the hydrogenation of *OCHO species, as
39 compared to the preferred formation of *COOH species over the Sn-N₄ sites, thereby greatly
40 facilitating CO₂-to-HCOOH conversion.

41

42

43 **Introduction**

44 The overdependence on fossil fuels leads to an excessive accumulation of greenhouse gas in the
45 atmosphere. It is urgent to develop highly efficient and environmentally friendly technologies to
46 mitigate the depletion of fossil resources, abate carbon emission and to switch to renewable resources.¹⁻
47 ⁵ Electrocatalytic carbon dioxide reduction reactions (CO₂RRs) offer sustainable opportunities to
48 transform CO₂ into value-added chemicals and carbon-based fuels.⁶⁻⁸ While various products can be
49 produced from CO₂RR, some of the C1 products (i.e. formic acid and CO) can be obtained with high
50 selectivity and high energy efficiency, and are of great interest to the chemical industry.⁹⁻¹² Formic
51 acid (HCOOH) is widely explored as a hydrogen storage material and chemical fuel for fuel cells.¹³⁻¹⁵
52 Until now, electrocatalysts developed for reducing CO₂ to HCOOH have included noble metals (e.g.,
53 Pd) and transitional-metal-based materials (e.g., Cu, Bi, Pb, In, Sn etc).¹⁶⁻²²

54 Owing to their unique electronic structure, Sn-based materials have been identified as attractive
55 catalysts for electrochemical CO₂ reduction to HCOOH and/or CO,²³ but suffer from insufficient
56 selectivity and activity, especially at large cathodic current densities.²⁴ To this end, past researches
57 focused on doping Sn crystalline phases with other metal or nonmetal elements to tune the electron
58 density at the Sn active sites and their neighboring dopants to selectively stabilize the reaction
59 intermediates and improve the activity and selectivity of CO₂RR.^{19, 25-29} However, the complex
60 structure model and the complicated coordination environment of metal sites make it difficult to
61 capture the intermediate species and determine the true active sites during the reaction process.

62 Single-atom catalysts (SACs) with well-defined and atomically-dispersed metal sites, tunable
63 coordination environment and high utilization efficiency, have shown promising CO₂RR activity and
64 selectivity towards CO, especially Fe-N-C and Ni-N-C materials.³⁰⁻³¹ This class of materials provides
65 an ideal platform for exploring the structure of active sites and understanding structure-activity
66 relationships.³²⁻³⁷ Beyond 3d transition metal SACs, early studies reported that single-Sn-atom sites in

67 Sn-SACs could selectively reduce CO₂ either to HCOOH or CO.^{2, 10 38} To reveal the intrinsic origin
68 for the different CO₂RR selectivity of Sn-single-atom sites, it is necessary to pinpoint the exact
69 electronic and coordination structure of the catalytic species under CO₂RR conditions. This in turn
70 requires the rational design of single-Sn-atom materials with well-defined sites and the development
71 of advanced *operando* characterization tools with atomic resolution.

72 In this work, a series of Sn-N-C catalysts featuring single-Sn-atoms with tunable and well-defined
73 coordination environments were developed. The average Sn(IV)/Sn(II) ratio could be modulated via
74 the functionalization of carbon nanotubes, modifying the adsorption energy of Sn phthalocyanine
75 (SnPc) molecules. In particular, a model single-Sn-atom catalyst with ~100% axially oxygen
76 coordinated Sn(IV) species (O-Sn-N₄) was obtained using OH-functionalized carbon nanotubes,
77 showing the optimal catalytic activity and selectivity towards HCOOH. Taking advantages of
78 *operando* attenuated total reflectance surface enhanced infrared absorption spectroscopy (ATR-
79 SEIRAS) and Raman spectroscopy, a surface-bound bidentate tin carbonate species was revealed as a
80 key reaction intermediate during CO₂RR. *Operando* ¹¹⁹Sn Mössbauer spectroscopy was applied for
81 the first time to follow changes in the electronic and coordination structure of single-Sn-atom species
82 under CO₂RR. In combination with *operando* X-ray absorption spectroscopy (XAS), the *in situ*
83 generation of the Sn-O-CO₂ catalytic intermediate during CO₂RR was clearly identified. Density
84 functional theory (DFT) calculations further evidenced the dynamic evolution of the electronic
85 structure of O-Sn-N₄ site for CO₂RR and the catalytic mechanism over single-Sn-atom species was
86 unveiled at atomic scale.

87 **Results and discussion**

88 **Characterization of the single-Sn-atom catalysts**

89 A series of single-Sn-atom catalysts were prepared by immobilizing SnPc molecules on CNTs
90 subjected to different functionalization treatments (CNT, CNT-OH and CNT-NH₂) via π - π

91 interaction.³⁹ The respective electrocatalysts are labelled SnPc/CNT, SnPc/CNT-OH and SnPc/CNT-
92 NH₂. The synthesis of SnPc/CNT-OH is schemed in **Fig. 1a**, and fully detailed in **Methods** and
93 **Supplementary Fig. 1**. The X-ray diffraction (XRD) patterns of this series of materials show only one
94 diffraction peak assignable to the diffraction line of carbon nanotubes, suggesting that the SnPc
95 molecules are well-dispersed and therefore cannot contribute to the diffraction patterns
96 (**Supplementary Fig. 2**). In contrast, Raman spectra display signals from both molecular SnPc and
97 CNTs for all materials (**Supplementary Fig. 3**), indicating that SnPc was successfully loaded onto the
98 CNTs. The Sn contents were in the range of 0.37-0.66 wt. % (**Supplementary Table 1**). **Figure 1b**
99 and **Supplementary Fig. 4** show representative scanning electron microscope (SEM) and transmission
100 electron microscope (TEM) images of the catalysts, on which no aggregation of metal species could
101 be observed. The surface morphology of SnPc/CNT-OH is similar to that of CNT-OH, indicating
102 uniform dispersion of SnPc on CNT-OH, which is also confirmed by energy-dispersive X-ray
103 spectroscopy (EDX) mapping analysis (**Supplementary Fig. 5**). Furthermore, high-angle annular
104 dark-field scanning transmission electron microscopy (HAADF-STEM) image of SnPc/CNT-OH in
105 **Fig. 1c** clearly shows Sn atoms dispersed on CNT and the absence of Sn clusters or nanoparticles,
106 further suggesting the successful formation of single-Sn-atom catalysts.

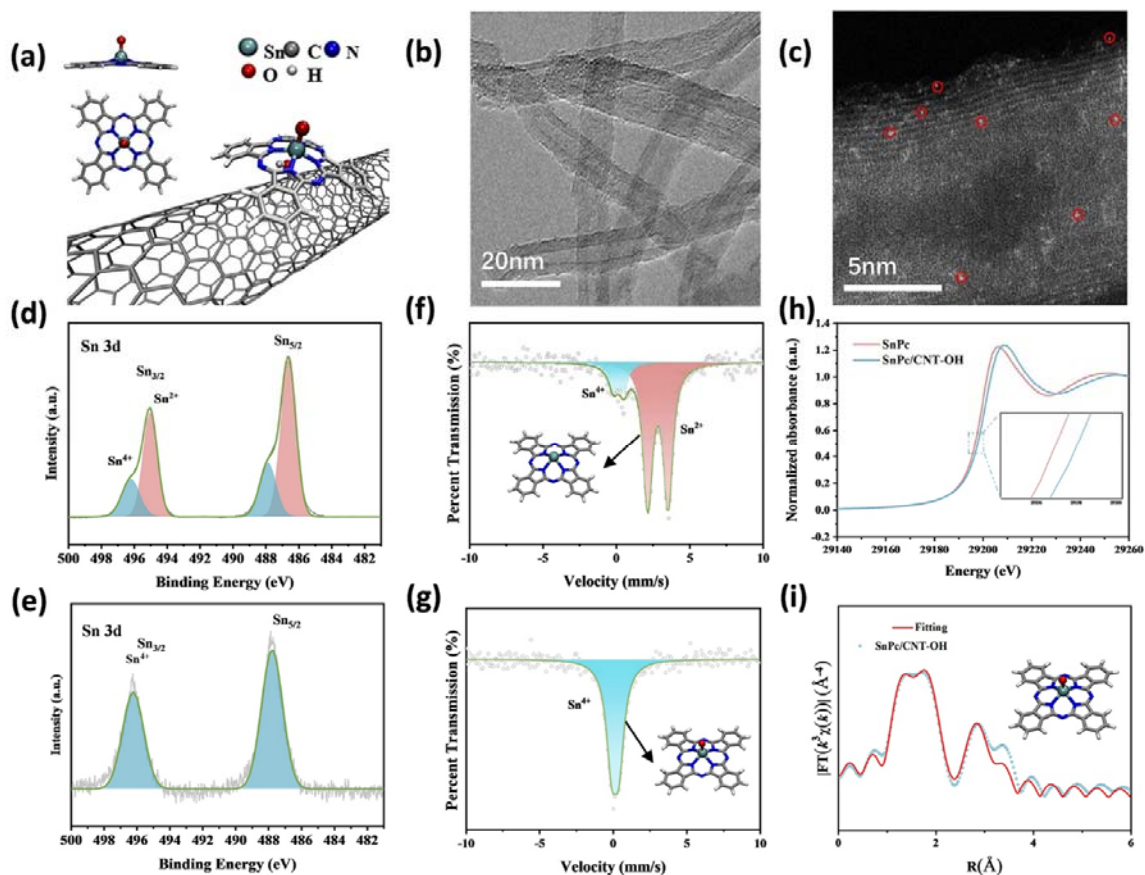
107 X-ray photoelectron spectroscopy (XPS) was performed to examine the elemental compositions
108 and Sn valence states of the single-Sn-atom catalysts. The Sn 3d XPS spectrum of the commercial
109 SnPc can be deconvoluted into two peak groups assigned to Sn(II) (486.6 eV, 495 eV) and Sn(IV)
110 (488.5 eV, 496.4 eV) (**Fig. 1d** and **Supplementary Fig. 6**).⁴⁰ For the series of catalysts, the
111 Sn(IV)/Sn(II) ratio increases strongly in the order SnPc < SnPc/CNT-NH₂ < SnPc/CNT < SnPc/CNT-
112 OH (**Supplementary Table 2** and **Supplementary Fig. 6**), with relative Sn(IV) amounts increasing
113 from 18.1 % to 100 %. In particular, only Sn(IV) is observed for SnPc/CNT-OH (**Fig. 1e**), indicating
114 that OH⁻ functional groups on CNT selectively lead to Sn(IV) possibly due to the strength of
115 electrostatic interactions, which is supported by DFT calculations. As compared in **Supplementary**

116 **Fig. 7**, CNT-OH exhibits an adsorption energy for Sn(IV) species of -2.379 eV, more negative than
117 those of CNT-NH₂ and CNT (-1.946 and -2.229 eV, respectively), suggesting that the CNT-OH surface
118 more likely adsorbs Sn(IV) species than the other two types of carbon nanotubes.

119 To further determine the coordination environment and the electronic structure of the single-Sn-
120 atom species, we conducted room temperature ¹¹⁹Sn Mössbauer spectroscopy measurements. As
121 shown in **Fig. 1f**, the commercial SnPc shows two quadrupole doublets with distinct values of isomer
122 shift (IS) (0.03 and 2.72 mm s⁻¹) and quadrupole splitting (QS) (0.70 and 1.39 mm s⁻¹) (**Supplementary**
123 **Table 3**). The doublets with low and high IS can unambiguously be assigned to Sn(IV) and Sn(II),
124 respectively.⁴¹ Moreover, the IS and QS values for the main high-IS doublet of the SnPc commercial
125 product match well with those reported for Sn(II)Pc.⁴² Interestingly, only one doublet with an IS value
126 of 0.04 mm s⁻¹ and a QS value of 0.50 mm s⁻¹ was observed for SnPc/CNT-OH (**Fig. 1g**), which can
127 be unambiguously assigned to Sn(IV) species. Based on IS and QS values calculated for a set of
128 hypothetical site structures, the fitted parameters of this doublet match well with those calculated by
129 DFT for the axially oxygen coordinated Sn(IV) species (O-Sn-N₄) structure (**Supplementary Fig. 8**).

130 As displayed in **Fig. 1h**, the absorption edge of Sn *K*-edge X-ray absorption near edge structure
131 (XANES) spectrum of SnPc/CNT-OH shifts towards higher energies compared to that of SnPc,
132 suggesting a higher average Sn valence state in the SnPc/CNT-OH catalyst,²⁶ in line with XPS analysis.
133 The Fourier transforms of the extended X-ray absorption fine structure (EXAFS) spectra of both SnPc
134 and SnPc/CNT-OH exhibit the dominant Sn-N coordination at 1.5-1.7 Å, distance not corrected for
135 phase shift (**Supplementary Fig. 9**). No obvious peaks related to Sn-Sn coordination could be
136 observed, confirming the atomic dispersion of all or most of the Sn atoms. In addition, the EXAFS
137 spectra for SnPc and SnPc/CNT-OH could be well fitted with the structural models of Sn-N₄ and O-
138 Sn-N₄ (as optimized from DFT), respectively (**Supplementary Fig. 10**). The fitted parameters are
139 summarized in **Supplementary Table 4**. As depicted in **Fig. 1i** and **Supplementary Fig. 10**, the Sn
140 atom in SnPc is coordinated, on average, with four adjacent N atoms (Sn-N₄), whereas the Sn atom in

141 SnPc/CNT-OH, on average, has four neighbouring N atoms and one axially coordinated O atom (O-
 142 Sn-N₄). All these results clearly show the successful development of a model single-Sn-atom catalyst
 143 with 100% axially oxygen coordinated Sn(IV) species anchored on OH-functionalized carbon
 144 nanotubes.

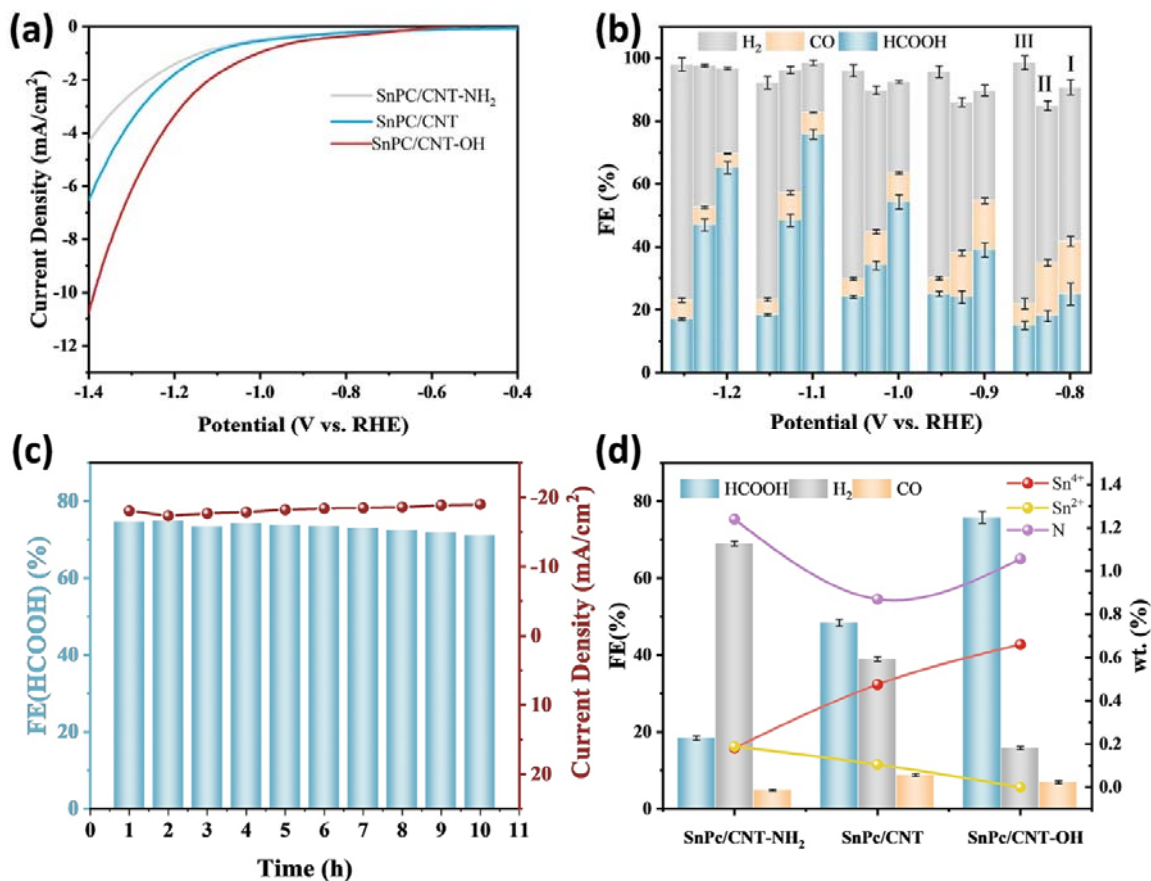


145

146 **Fig. 1 | Structural characterization of the single-Sn-atom catalysts.** **a**, Schematic illustration for
 147 the preparation of SnPc/CNT-OH. **b**, TEM and **c**, HAADF-STEM image of SnPc/CNT-OH. **d-e**, High-
 148 resolution Sn 3d XPS spectrum for SnPc and SnPc/CNT-OH, respectively. **f-g**, Room-temperature
 149 ¹¹⁹Sn Mössbauer spectra for SnPc and SnPc/CNT-OH, respectively. **h**, Normalized Sn K-edge XANES
 150 spectra for SnPc and SnPc/CNT-OH (inset shows the Sn K-edge XANES spectra in a narrow region
 151 sensitive to the Sn oxidation state). **i**, Experimental and fitted EXAFS spectrum of SnPc/CNT-OH in
 152 *R* space.

153 **Electrochemical CO₂RR performance**

154 The electrochemical CO₂RR performance of SnPc/CNT, SnPc/CNT-OH and SnPc/CNT-NH₂ were
155 examined in an H-type cell filled with CO₂-saturated 0.5 M KHCO₃ (pH = 7.3) electrolyte, and the
156 CO₂RR catalyst loading was fixed at 1 mg·cm⁻².⁴³ The CO₂ reduction activity of the single-Sn-atom
157 catalysts was first investigated by linear scan voltammetry (LSV) measurements. As shown in **Fig. 2a**,
158 the current density for CO₂ reduction over SnPc/CNT-OH is the highest among this series of catalysts.
159 **Fig. 2b** summarizes the potential-dependent CO₂RR Faradaic efficiency for SnPc/CNT, SnPc/CNT-
160 OH and SnPc/CNT-NH₂. The main CO₂RR product is HCOOH, along with a small amount of CO,
161 while H₂ is produced in significant quantities on all three catalysts. The HCOOH Faradaic efficiency
162 over SnPc/CNT-OH can reach 75.4% at -1.13 V vs. RHE, which is higher than that over SnPc/CNT
163 (48%) and SnPc/CNT-NH₂ (18%). The same trend is observed at other potentials, SnPc/CNT-OH
164 systematically leading to higher FE towards HCOOH than the other two catalysts. As displayed in
165 **Supplementary Fig. 11**, the SnPc/CNT-OH exhibits an optimal HCOOH partial current density
166 (j_{HCOOH}) of -14.3 mA·cm⁻² at -1.13 V vs. RHE, higher than that over SnPc/CNT (-5.2 mA·cm⁻²) and
167 SnPc/CNT-NH₂ (-2.4 mA·cm⁻²). Besides excellent activity and selectivity, both the FE towards
168 HCOOH and the current density remained nearly constant over SnPc/CNT-OH during 10 h at -1.13 V
169 vs. RHE, indicating promising stability (**Fig. 2c**). The correlation of Faradaic efficiency, partial current
170 density, and relative contents of Sn(II), Sn(IV) and nitrogen species are shown in **Fig. 2d** and
171 **Supplementary Fig. 12**. The data reveals that the catalytic performance towards formic acid
172 formation is positively correlated with the relative content of Sn(IV) (**Supplementary Fig. 12d**). This
173 suggests that the Sn(IV) single atom species is the dominant catalytic site for electrochemical CO₂
174 reduction to formic acid, in line with recent reports.⁴⁴



175

176 **Fig. 2 | Electrochemical CO₂ reduction. a**, LSV curves acquired on a rotating disc electrode in CO₂-
 177 saturated 0.5 M KHCO₃ solution. **b**, Faradaic efficiency of I: SnPc/CNT-OH, II: SnPc/CNT and III:
 178 SnPc/CNT-NH₂ at different applied cathodic potentials. **c**, Stability of SnPc/CNT-OH for CO₂RR at -
 179 1.13 V vs. RHE. **d**, Correlation diagram of the CO₂RR Faradaic efficiency and the relative contents of
 180 Sn(II), Sn(IV) and nitrogen species of SnPc/CNT, SnPc/CNT-OH and SnPc/CNT-NH₂: FE is indicated
 181 as columns (left-hand side y axis), while Sn(II), Sn(IV) and N content are indicated as curves (right-
 182 hand side y axis).

183 Identification of the catalytic intermediates and the surface reaction species

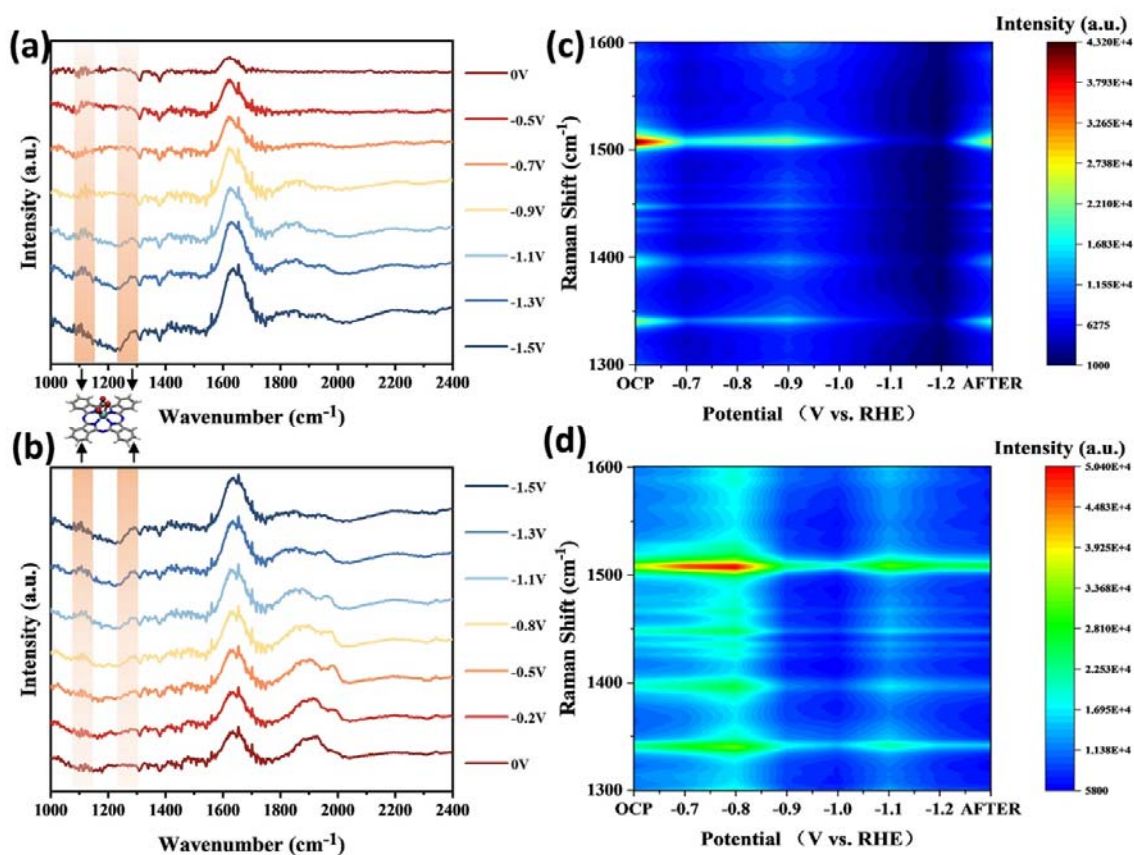
184 XRD, TEM and XPS characterizations of the SnPc/CNT-OH catalyst were performed and
 185 compared before and after CO₂RR, to investigate if an irreversible structural evolution occurred
 186 (Supplementary Fig. 13-15). Interestingly, no obvious morphology and valence state changes were

187 observed, further confirming the high stability of the SnPc/CNT-OH catalyst during the CO₂RR
188 process.

189 To gain insights into the surface reaction intermediates over the single-Sn-atom catalyst during
190 electrochemical CO₂ reduction to HCOOH, *operando* ATR-SEIRAS was carried out.⁴⁵ Control
191 experiments were firstly conducted in Ar-saturated 0.1 M K₂SO₄ solution (**Supplementary Fig. 16**);
192 only one peak centered at 1238 cm⁻¹ was observed, which can be assigned to SO₄²⁻ in the electrolyte.
193 During the potential stepping from 0 to -1.5 V vs. RHE and from -1.5 V vs. RHE to 0 in CO₂-saturated
194 0.1 M K₂SO₄ solution (pH = 4.5), the intensity of the absorption peak at 1650 cm⁻¹ originating from
195 water vibration was observed to slightly increase when stepping the potential from 0 to -1.5 V vs. RHE,
196 and to decrease for the same potential step but in the opposite direction (**Fig. 3a and b**). The weak
197 bands at 1950 and 2000 cm⁻¹ are related to the linearly bonded CO (CO_L) because of the CO₂ to CO
198 reaction pathway on CNT-OH (**Supplementary Fig. 17**). Additional absorption peaks at 1285 and
199 1115 cm⁻¹ appeared at -0.8 V vs. RHE and their intensities increased when further decreasing the
200 potential from -0.8 V to -1.5 V vs. RHE. These peaks can be ascribed to the C-O bond vibration in the
201 bidentate tin carbonate.⁴⁶ The intensity of the tin carbonate peaks slowly decreased and finally
202 disappeared when reverting the potential scan from -1.5 to 0 V vs. RHE. All these results clearly
203 evidence the involvement of bidentate tin carbonate intermediates during the CO₂RR over SnPc/CNT-
204 OH.

205 *Operando* Raman spectra recorded at varying potentials in CO₂- or Ar-saturated 0.5 M KHCO₃
206 solution are shown in **Fig. 3c-d** and **Supplementary Fig. 18-19**.⁴⁷ As displayed in **Fig. 3c**, at open
207 circuit potential (OCP), two characteristic Raman peaks at 1342 cm⁻¹ and 1505 cm⁻¹ were observed
208 on SnPc/CNT-OH, which can be assigned to C=C and C-N vibrations of the phthalocyanine ring,
209 respectively.⁴⁸ With potential decreasing from -0.7 to -1.2 V vs. RHE, the peak intensity of C=C and
210 C-N gradually decreased and eventually vanished, which is most probably due to the generation of
211 surface-bound tin-carbonate (bidentate) species with a symmetric structure. Upon switching the

212 electrode potential back to OCP, the Raman spectrum could almost be restored to that recorded under
 213 the initial OCP condition, suggesting that the potential-induced changes for the SnPc/CNT-OH catalyst
 214 are reversible. Moreover, *operando* Raman spectra measured in Ar-saturated 0.5 M KHCO₃ solution
 215 showed no significant changes in peak intensity, further reflecting that the observed reversible change
 216 of characteristic Raman peaks probably resulted from the *in situ* formation of surface-bound bidentate
 217 tin carbonate species, which was captured by the *operando* ATR-SEIRAS measurements.



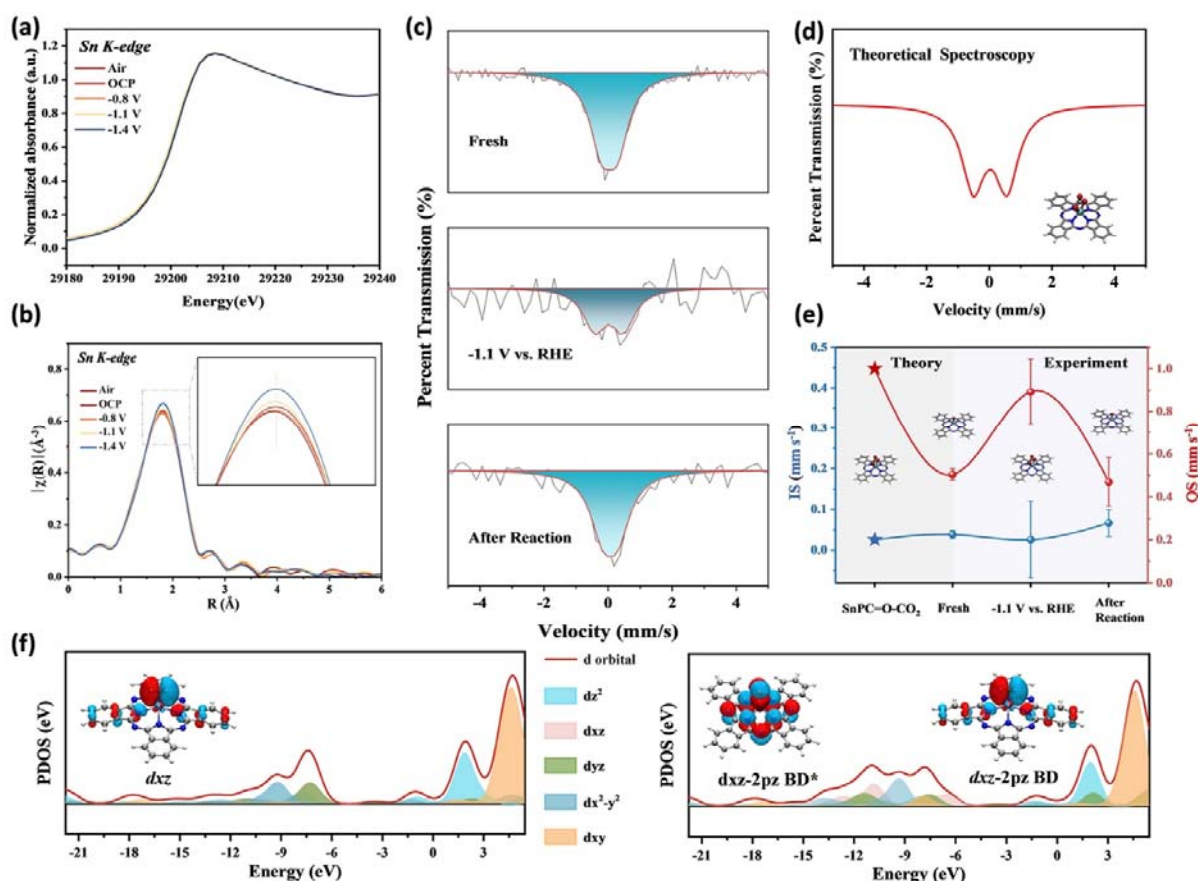
218

219 **Fig. 3 | Identification of the surface reaction species, a-b,** *Operando* ATR-SEIRAS spectra of
 220 SnPc/CNT-OH collected under various applied cathodic potentials (from 0 to -1.5 V vs. RHE and from
 221 -1.5 V vs. RHE to 0) in CO₂-saturated 0.1 M K₂SO₄. *Operando* Raman spectra recorded over
 222 SnPc/CNT-OH at various potentials (V vs. RHE) in **c**, CO₂-saturated and **d**, Ar-saturated 0.5 M
 223 KHCO₃ solution.

224 To further probe the structure of the catalytic intermediates, *operando* XAS measurements were
225 performed. The Sn *K*-edge XANES and EXAFS spectra were recorded in CO₂-saturated 0.5 M KHCO₃
226 solution at various potentials. For the XANES spectra (**Fig. 4a**), a negligible reduction was observed
227 for the Sn *K*-edge of SnPc/CNT-OH during the CO₂RR, revealing that the oxidation state of Sn in
228 SnPc/CNT-OH could be maintained at Sn(IV). In addition, in the EXAFS spectra shown in **Fig. 4b**,
229 the slight increase of the Sn-N (or Sn-C or Sn-O) intensity suggests an increase of the coordination
230 number (CN) of Sn as the CO₂ reduction reaction proceeds. However, negligible changes in the Sn-N
231 bond length were observed, indicating that the coordination environment did not change significantly
232 during the CO₂RR.

233 The electronic and coordination structure of the single-Sn-atom species under CO₂RR conditions
234 ^{47, 49, 50} were further investigated using *operando* ¹¹⁹Sn Mössbauer spectroscopy in a home-made H-
235 type *operando* cell (**Supplementary Fig. 20**). The CO₂-saturated 0.5 M KHCO₃ electrolyte was
236 replaced every ~1.5 h to maintain the pH of the solution. The current-time response of SnPc/CNT-OH
237 during the entire *operando* Mössbauer measurements was quite stable, supporting that the setup
238 performs well and the *operando* spectroscopic data are reliable (**Supplementary Fig. 21**). As shown
239 in **Fig. 4c**, at -1.1 V vs. RHE, the Mössbauer spectrum of SnPc/CNT-OH is different from that of the
240 fresh sample, displaying a symmetric signal with an IS value of 0.03 mm s⁻¹ and a QS value of 0.89
241 mm s⁻¹, matching well with the theoretical Mössbauer spectrum of Sn-O-CO₂ (**Fig. 4d**). The
242 experimental IS and QS values of the catalyst under various *operando* conditions as well as the
243 theoretical IS and QS values of Sn-O-CO₂ are shown in **Fig. 4e** and **Supplementary Table 5**. The
244 results support the *in situ* formation of Sn-O-CO₂ species over O-Sn-N₄ sites during CO₂RR. After
245 removing the applied potential, the Mössbauer spectrum could be fitted by a quadrupole doublet with
246 an IS value of 0.07 mm s⁻¹ and a QS value of 0.50 mm s⁻¹, similar to that of the fresh SnPc/CNT-OH,
247 further suggesting the reversibility of the single-Sn-atom species during the CO₂RR.

248 The dynamic changes observed in the *operando* Mössbauer and XAS measurements could be
 249 further illustrated by the calculated projected density of states (PDOS) of O-Sn-N₄ and Sn-O-CO₂. As
 250 shown in **Supplementary Fig. 22**, similar electron density encloses in the s and p orbital of Sn for O-
 251 Sn-N₄ and Sn-O-CO₂, which results in the negligible changes in the K-edge of *operando* XANES
 252 spectra and IS value of *operando* Mössbauer spectra. However, compared with Sn(IV) in O-Sn-N₄,
 253 the d orbitals (d_{xz} and d_{yz}) of Sn-O-CO₂ change from degeneration to non-degeneration (**Fig. 4f**), which
 254 leads to an increase in the asymmetric distribution of the electrons and thus an increase of QS. All
 255 these results clearly evidenced the *in-situ* formation of Sn-O-CO₂ species over O-Sn-N₄ sites during
 256 the CO₂RR.²⁴



257

258 **Fig. 4 | Identification of the catalytic intermediates.** **a**, Normalized *operando* Sn K-edge XANES
 259 spectra. **b**, FT magnitude of EXAFS spectra of SnPc/CNT-OH during CO₂RR recorded in CO₂-

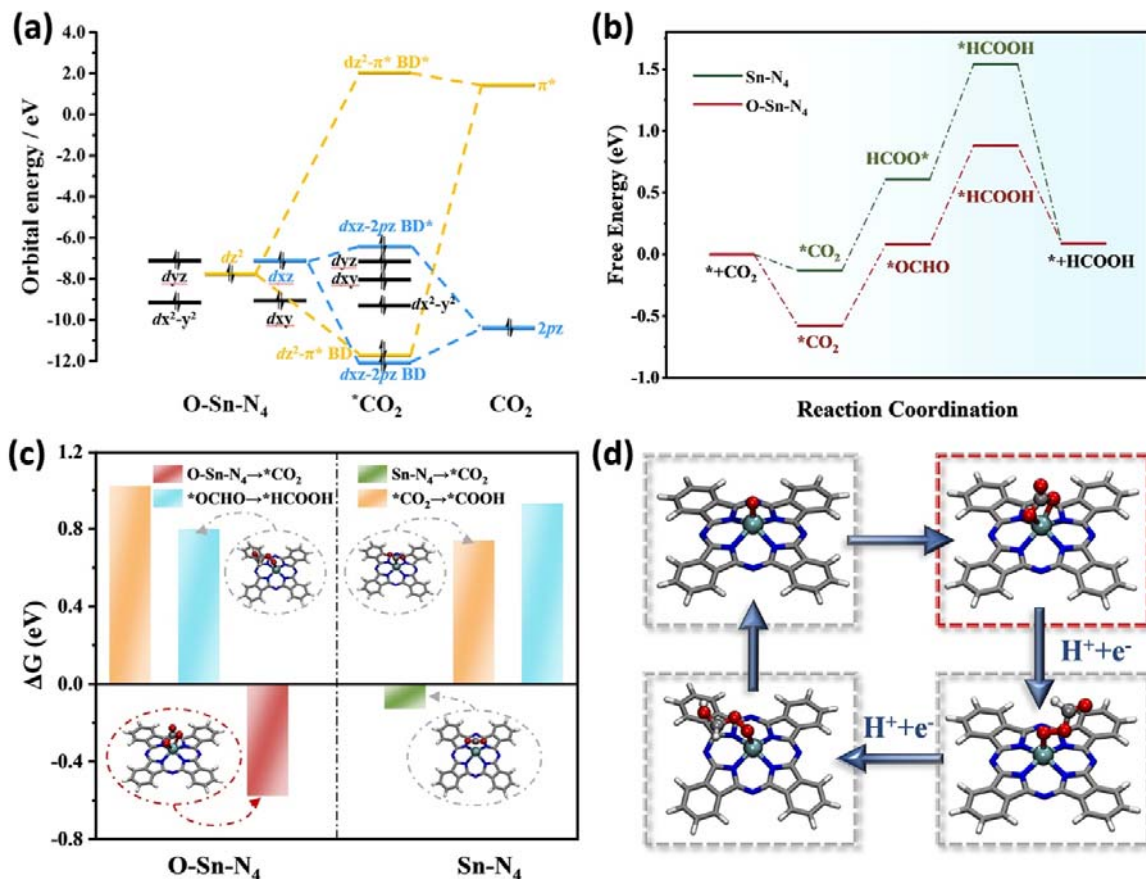
260 saturated 0.5 M KHCO₃ solution. **c**, *Operando* ¹¹⁹Sn Mössbauer spectra for SnPc/CNT-OH recorded
261 before CO₂RR (Fresh), at -1.1 V vs. RHE, and after CO₂RR (After Reaction) in CO₂-saturated 0.5 M
262 KHCO₃ solution at room temperature. **d**; Theoretical ¹¹⁹Sn Mössbauer spectrum of Sn-O-CO₂, **e**,
263 Comparison of the experimental IS and QS values of the catalyst recorded under various conditions
264 and the theoretical IS and QS values of Sn-O-CO₂ structural model (optimized by DFT). **f**, Schematic
265 illustration showing the PDOS of Sn-d orbitals on O-Sn-N₄ and Sn-O-CO₂, respectively.

266 **Theoretical insights into the catalytic mechanism**

267 Theoretical calculations were performed to further investigate the mechanism of CO₂RR over the
268 single-Sn-atom catalysts. The optimized structures of O-Sn-N₄ and Sn-N₄, and the possible adsorption
269 configurations of reaction intermediates are shown in **Supplementary Fig. 23**. **Fig. 5a** shows the
270 Kohn–Sham MO energy-level correlation diagram between CO₂ and the O-Sn-N₄ site during the first
271 CO₂ capture step (* + CO₂ → *CO₂). There exist covalent overlaps between the fully occupied d_{z²}-
272 orbital of the O-Sn-N₄ site and the non-occupied π* orbital of CO₂, generating one fully occupied d_{z²}-
273 π* bonding orbital (BD) and one empty d_{z²}-π* antibonding (BD*) orbital. Similarly, the fully occupied
274 d_{xz} orbital of the O-Sn-N₄ site and the 2p_z orbital of CO₂ also generate two fully occupied d_{xz}-2p_z
275 bonding orbital (BD) and d_{xz}-2p_z antibonding (BD*) orbital. The corresponding MO contour plots of
276 these MOs are displayed in **Supplementary Fig. 24**.

277 We further calculated the Gibbs free energy diagram of CO₂RR to form HCOOH and CO over O-
278 Sn-N₄ and Sn-N₄. As shown in **Fig. 5b**, for the pathway of generating formic acid, the formation of
279 the *HCOOH intermediate via *OCHO/HCOO* hydrogenation is the potential-limiting step; whereas,
280 for producing CO (**Supplementary Fig. 25**), the potential-limiting step is the formation of *COOH.
281 The corresponding energy barriers of CO₂-to-HCOOH and CO₂-to-CO on O-Sn-N₄ and Sn-N₄ are
282 summarized in **Fig. 5c**. Specifically, the downhill energy barrier of the first CO₂-to-*CO₂ step of
283 CO₂RR on O-Sn-N₄ is calculated to be -0.58 eV, while Sn-N₄ exhibits a downhill energy barrier of -

284 0.13 eV, revealing that the CO₂ activation can take place more readily on O-Sn-N₄. Furthermore, O-
285 Sn-N₄ exhibits a relatively lower energy barrier at the formation of *HCOOH ($\Delta G = 0.8$ eV) than Sn-
286 N₄ ($\Delta G = 0.93$ eV), which shall lead to a higher electrocatalytic activity for CO₂RR to HCOOH over
287 O-Sn-N₄. Additionally, Sn-N₄ displays a much stronger adsorption of *COOH with $\Delta G = 0.78$ eV than
288 O-Sn-N₄ with $\Delta G = 1.02$ eV, resulting in a better catalytic ability for the generation of CO over Sn-
289 N₄. As illustrated in **Supplementary Fig. 26-27**, we also assumed that CO₂ approached the single-Sn-
290 atom sites from the back side of O-Sn-N₄ (O-Sn-N₄-inversion). From the Gibbs free-energy diagram,
291 such a convex inversion shows a much higher energy barrier for the formation of both *COOH and
292 *OCHO intermediates, thereby prohibiting both the HCOOH and CO production. Therefore, the
293 reaction pathways of CO₂RR over O-Sn-N₄ and Sn-N₄ sites are presented in **Fig. 5d** and
294 **Supplementary Fig. 28-29**. The O-Sn-N₄ species can regulate the adsorption configuration of *CO₂,
295 which effectively reduces the energy barrier for the formation of *OCHO intermediate and facilitates
296 the CO₂-to-HCOOH conversion.



297

298 **Fig. 5 | Theoretical calculations.** **a**, Schematic Kohn–Sham molecular orbital (MO) energy-level
 299 correlation diagram between CO_2 and the O-Sn- N_4 site during the CO_2 capture step ($* + \text{CO}_2 \rightarrow * \text{CO}_2$).
 300 **b**, Calculated Gibbs free energy diagrams for CO_2RR to HCOOH over O-Sn- N_4 and Sn- N_4 sites. **c**,
 301 Calculated ΔG for HCOOH and CO production over O-Sn- N_4 and Sn- N_4 sites. **d**, Proposed reaction
 302 pathway for CO_2RR over O-Sn- N_4 site.

303 Conclusions

304 In summary, a series of single-Sn-atom catalysts with well-controlled coordination and electronic
 305 structure were developed to explore the CO_2 reduction chemistry. Using a combination of *operando*
 306 spectroscopies and DFT calculations on a model single-Sn-atom catalyst in which all Sn atoms are in
 307 a positive IV oxidation state, situated in a phthalocyanine ring and additionally coordinated to an axial

308 oxygen species (O-Sn-N₄), the *in situ* generation of surface-bound bidentate tin carbonate species (Sn-
309 O-CO₂) in CO₂RR was captured and the dynamic change of the electronic and coordination structures
310 of active sites during CO₂RR was identified. Theoretical studies further revealed that the O-Sn-N₄
311 species could regulate the adsorption configuration of *CO₂ with increasing the asymmetric
312 distribution of the d orbital electrons of Sn(IV), reducing the energy barrier for the formation and
313 hydrogenation of *OCHO species, thus facilitating CO₂-to-HCOOH conversion. The results of this
314 work provide an in-depth understanding of the detailed structures of catalytic intermediates and the
315 key surface species associated with CO₂RR and shall pave the way towards the rational design of high-
316 performance CO₂ electroreduction catalysts.

317

318 **AUTHOR INFORMATION**

319 **Corresponding authors**

320 *lixn@dicp.ac.cn (X.L.)

321 *yqhuang@dicp.ac.cn (Y.H.)

322 *liubin@ntu.edu.sg (B.L.)

323

324 **Author Contributions**

325 Y.C.D., J.Z. and S.F.W. contributed equally to this work. Y.C.D., X.N.L., Y.Q.H. and B.L. designed
326 the study. Y.C.D. synthesized and characterized the materials. J.Z. performed the density functional
327 theory calculations. Y.C.D. and S.F.W. conducted the electrochemical measurements and analysis.
328 Y.C.D. and S.F.W. performed the Raman spectroscopy measurements and analysis. Y.C.D. and J.D.
329 conducted the ATR-SEIRAS measurements and analysis. H.J.T., W.J.Z., S.F.H. and W.X. performed
330 the XAFS measurements and analysis. Y.C.D., S.F.W. R.R.C., J.H.W. and X.N.L. conducted the
331 Mössbauer spectroscopy measurements and analysis. J.H.W. and F.J. participated in the modification
332 of the Results and Discussion section. Y.C.D., X.N.L. and B.L. wrote and edited the manuscript with
333 inputs from all authors. The project was supervised by X.N.L., Y.Q.H. and B.L.

334 **Notes**

335 The authors declare no competing financial interests.

336

337 **ASSOCIATED CONTENT**

338 **Supporting Information**

339 Supplementary data associated with this article is available free of charge via the Internet at
340 www.nature.com/reprints.

341

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