Atomically dispersed Pt–N₄ sites as efficient and selective electrocatalysts for the chlorine evolution reaction

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Chlorine evolution reaction (CER) is a critical anode reaction in chlor-alkali electrolysis. Although precious metal-based mixed metal oxides (MMOs) have been widely used as CER catalysts, they suffer from the concomitant generation of oxygen during the CER. Herein, we demonstrate that atomically dispersed Pt–N₄ sites doped on a carbon nanotube (Pt₁/CNT) can catalyse the CER with excellent activity and selectivity. The Pt₁/CNT catalyst shows superior CER activity to a Pt nanoparticle-based catalyst and a commercial Ru/Ir-based MMO catalyst. Notably, Pt₁/CNT exhibits near 100% CER selectivity even in acidic media, with low Cl⁻ concentrations (0.1 M), as well as in neutral media, whereas the MMO catalyst shows substantially lower CER selectivity. In situ electrochemical X-ray absorption spectroscopy reveals the direct adsorption of Cl⁻ on Pt–N₄ sites during the CER. Density functional theory calculations suggest the PtN₄C₁₂ site as the most plausible active site structure for the CER.
Chlorine (Cl₂) is one of the most important industrial chemicals with an annual production of approximately 75 million tons worldwide. It is used as a key chemical in the production of polymers and pharmaceuticals, pulp and paper industries, and water treatments. The current Cl₂ production is prevalently dependent on the chlor-alkali process, for which the electrochemical chlorine evolution reaction (CER) plays a pivotal role as the anodic reaction. To ensure high efficiency in the chlor-alkali system and the production of high purity Cl₂ gas, CER should be operated in acidic pH saturated with Cl⁻ (ref. 6). The CER is also important for generating active chlorine (AC) as a disinfectant for wastewater and ship ballast water treatments on account of its effectiveness in removing harmful organisms or invasive aquatic species with a long residual time. A disinfectant for wastewater and ship ballast water treatments on industries, and water treatments for the production of polymers and pharmaceuticals, pulp and paper industries.

Density functional theory (DFT) calculations identify the CER selectivity. On the potential scale of reversible hydrogen evolution reaction (OER), the side reaction of CER, shows much lower overpotential than that in acidic pH, leading to low CER selectivity. On the potential scale of reversible hydrogen evolution reaction (OER), exhibiting a scaling relationship between the CER and OER, with Cl⁻ concentration as low as 0.1 M, as well as in neutral media, whereas DSA shows substantially lower selectivity. In situ electrochemical X-ray absorption spectroscopy (XAS) reveals the direct interaction between Cl⁻ reactant and Pt centre of Pt–N₄ sites during the CER. Density functional theory (DFT) calculations identify the PtNi₂C₁₂ structure as the most plausible active site structure with the lowest Gibbs free energy for the CER among the possible structural configurations for the Pt–N₄ sites. The atomically dispersed Pt catalyst comprising Pt–N₄ sites reported herein may broaden the scope of CER catalysts beyond the hitherto-dominated precious metal-based MMOs, with maximised precious metal atom utilisation for the CER.

Results
Preparation and characterisations of catalysts. The preparation of atomically dispersed Pt catalysts consists of mixing a Pt precursor (Pt(II) meso-tetraphenylporphine, PtTPP) with acid-treated CNT (Supplementary Fig. 1a), followed by heat treatment at desired temperatures between 500 °C and 800 °C. The resulting samples were denoted as Pt₁/CNT_X (X = annealing temperature). Among the prepared Pt₁/CNT_X samples, the best CER activity was obtained with the sample treated at 700 °C, which is hereafter denoted as Pt₁/CNT. Inductively coupled plasma optical emission spectroscopy (ICP-OES) and combustion elemental analysis (EA) revealed that Pt₁/CNT comprised 2.7 wt% Pt and 0.7 wt% N (N/Pt atomic ratio = 3.6, Supplementary Table 1). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM; Fig. 1a and Supplementary Fig. 1b) images show uniformly distributed ultrasmall white dots, suggesting formation of atomically dispersed Pt species without Pt NPs. The particle size distribution histogram of Pt₁/CNT (Supplementary Fig. 1c) confirmed the atomic dispersion of Pt species. The electron energy loss spectrum (EELS) of Pt₁/CNT, obtained from a limited area (~5 Å²) comprising an atomically dispersed Pt site in the HAADF-STEM image (Supplementary Fig. 2), indicated the presence of Pt and N. For comparison, the PtNP/CNT catalyst with 2.9 wt% Pt loading (Supplementary Table 1) was prepared by the conventional impregnation-reduction method using H₂PtCl₆·6H₂O as a precursor. The high-resolution TEM (Supplementary Fig. 1d) and HAADF-STEM images (Supplementary Fig. 1e) and particle size distribution histogram (Supplementary Fig. 1f) of PtNP/CNT revealed the formation of Pt NPs with a diameter of 1–6 nm. X-ray diffraction (XRD) results (Supplementary Fig. 3) also suggested the absence of metallic Pt species in Pt₁/CNT and the formation of Pt NPs in PtNP/CNT.

The detailed geometric structure around the Pt atoms was obtained by extended X-ray absorption fine structure (EXAFS) analyses. The k³-weighted Pt L₃-edge EXAFS spectrum of Pt₁/CNT and its fitted curve (Fig. 1b and Supplementary Fig. 4) exhibited a major peak at 1.6 Å, which can be assigned to Pt–N/C bonding with a coordination number (CN) of 3.9 (Supplementary Table 2). A second peak at 2.6 Å could be interpreted as the second shell of Pt–C by way of N. The EXAFS spectrum of Pt₁/CNT remarkably resembles that of PtTPP, indicating that the local structure of PtTPP was nearly preserved in Pt₁/CNT even after the high-temperature treatment. In contrast, the EXAFS
spectrum of PtNP/CNT showed peaks for Pt–Pt and Pt–C bonds, which correspond to metallic Pt and Pt–CNT interaction, respectively. X-ray absorption near-edge structure (XANES) analyses further corroborated the EXAFS results. The Pt L3-edge XANES spectra of Pt1/CNT and PtTPP (Fig. 1c) similarly showed a peak at 11,577.0 eV (peak A), which is a spectral feature of square planar N4-coordinated Pt complexes, such as Pt(II) phthalocyanine and tetraamine Pt(II)46. For the XANES spectra of PtNP/CNT and Pt foil, peaks at 11,580.5 eV (peak B) and 11,595.0 eV (peak C) were observed, which are characteristic peaks for metallic Pt46. Pt 4f X-ray photoelectron spectroscopy (XPS) analyses (Supplementary Fig. 5) revealed that Pt1/CNT consisted almost entirely of Pt2+ species whereas Pt0 was a predominant species in PtNP/CNT with some contributions from Pt2+ and Pt4+ species.

Next, the impact of annealing temperatures on the physico-chemical properties of Pt1/CNT_X catalysts was investigated. The HAADF-STEM images of Pt1/CNT_X (X = 500, 600 and 800 °C) (Supplementary Fig. 6) clearly indicated the formation of atomically dispersed Pt sites irrespective of annealing temperatures, suggesting that annealing temperatures up to 800 °C cannot induce agglomeration of the Pt. XRD patterns of Pt1/CNT_X catalysts (Supplementary Fig. 7) suggested the absence of Pt NPs even the annealing temperature was as high as 800 °C. Pt1/CNT_X catalysts also showed similar EXAFS and XANES spectra (Supplementary Fig. 8) without annealing temperature-dependent peak shifts. Notably, these spectra resemble those of a physical mixture of PtTPP and CNT, indicating that the local structure of PtTPP was preserved after heat treatments up to 800 °C. Deconvoluted N 1s XPS spectra of the series of Pt1/CNT_X samples (Supplementary Fig. 9a) indicated that a large portion of N atoms maintained its chemical state of the PtTPP precursor with a peak at 399.2 eV (Pt–Nx coordination) during annealing at high temperatures. With the samples annealed above 600 °C, peaks for pyridinic N (398.1 eV), pyrrolic N (400.2 eV) and graphitic N (400.7 eV) species emerged, which could be ascribed to the decomposition of surrounding carbons following the van Veen model47. We note that the position of Pt2+-ligated N species was clearly different from those of pyridinic N and pyrrolic N species, which is consistent with the XPS results of heat-treated M–N/C catalysts comprising atomically dispersed Fe–Nx or Co–Nx sites47–50. Deconvoluted Pt 4f spectra (Supplementary Fig. 9b) revealed that Pt1/CNT consisted of Pt2+ species irrespective of the annealing temperatures, which are in accordance with the EXAFS results. Taken together, TEM, XAS and XPS results indicate that the use of Pt-containing macrocyclic compound can yield atomically dispersed Pt catalysts comprising Pt–N4 sites with high Pt loading, which is
Electrochemical CER activity and stability of Pt–N₄ sites. We investigated the electrocatalytic performances of the catalysts using a rotating ring-disk electrode (RRDE) setup in 0.1 M HClO₄ in the presence and absence of 1.0 M of Cl⁻. All electrochemical measurements were conducted at room temperature (RT, ~25 °C) unless otherwise specified. In the RHE scale, the equilibrium potential of CER (E_CER) is dependent on pH, temperature, concentration of Cl⁻ ions, and partial pressure of Cl₂ of the electrolyte. The E_CER was derived by the Nernst equation:

\[
E_{\text{CER}}(T, a(\text{Cl}_2), a(\text{Cl}^-)) \text{vs. RHE} = E_0^{\text{CER}} - \frac{RT}{F} \times \ln a(\text{Cl}^-) + \frac{RT}{2F} \times \ln a(\text{Cl}_2)
\]

where \(T\), \(R\), \(F\), and \(a\) represent the universal gas constant, the temperature, the Faraday constant, and the chemical activity, respectively. The value of \(a(\text{Cl}_2)\) was assumed to be 0.01 for the partial pressure of evolving Cl₂ under Ar purging. \(a(\text{Cl}^-)\) was determined by experimental conditions (i.e., \(a(\text{Cl}^-) = 1.0\) for 1.0 M NaCl). The temperature dependence of \(E_0^{\text{CER}}\) vs. RHE can be calculated from the following Eq. (4):

\[
E_0^{\text{Cl}} = \left[\frac{1.358V + \frac{RT}{F} \times 2.303 \times \text{pH}}{1} - 0.001248 \frac{dE}{dT}\right] \times (T - 298.15K)
\]

Figure 2a displays the CER polarisation curves of the catalysts in the presence of 1.0 M NaCl, which clearly indicate the superior CER activity of Pt₁/CNT compared to CNT, PtNp/CNT and commercial Ru/Ir-based DSA catalysts. Pt₁/CNT started to catalyse the CER at a potential of 1.38 V, which is 30 mV higher than the \(E_{\text{CER}}\) (1.35 V vs. RHE for 25 °C). Pt₁/CNT delivered a current density of 10 mA cm⁻² at an overpotential of 50 mV, which is much lower than those of DSA (105 mV) and PtNp/CNT (120 mV). The evolution of Cl₂ at this potential could be confirmed by Cl₂ reduction on the Pt ring (Supplementary Fig. 10). The CER activity of the catalysts was also assessed by calculating the mass activities and TOFs. At an overpotential of 70 mV, Pt₁/CNT exhibited a mass activity of 1.6 A mgPt⁻¹, which is 6.2 times higher than that of PtNp/CNT. For the calculation of TOFs, all Pt sites in the catalyst layer were considered as active sites for Pt₁/CNT and calculated as 3.46 nmol based on the quantification of Pt by ICP-OES analysis (see Eqs. 8 and 9 in Methods section and Supplementary Table 1). The CO stripping method was used to calculate the electrochemically active surface sites for PtNp/CNT, and the calculated value was 0.96 nmol (see Eqs. 7 and 9 in Methods section and Supplementary Fig. 11). As a result, Pt₁/CNT showed 2.6 times higher TOF than PtNp/CNT at an overpotential of 70 mV (Fig. 2b). The CER activities were also tested on a carbon paper (1 cm × 1 cm). Pt₁/CNT coated on a carbon paper required an overpotential of 70 mV to reach a current density of 10 mA cm⁻² (Supplementary Fig. 12a). The intrinsic catalytic activity of electrocatalysts for the CER was also assessed in terms of exchange current density (\(j_0\)) using Tafel analyses (see Eq. 10 in Methods section). \(j_0\) of Pt₁/CNT was 0.43 mA cm⁻², whereas those of PtNp/CNT and DSA were 0.23 mA cm⁻² and 0.20 mA cm⁻², respectively. Pt₁/CNT loaded on a carbon paper exhibited \(j_0\) of 0.44 mA cm⁻² similar to the value obtained on a RRDE, suggesting that \(j_0\) was invariant on the type of electrode substrates. Because the practical chlor-alkali process is operated at temperatures of 80–90 °C, we also measured the CER activity of Pt₁/CNT and DSA catalysts at 80 °C, which indicated a similar activity trend as that obtained at 25 °C (Supplementary Fig. 13). Significantly, a comparison of CER activity data (Supplementary Table 3) reveals that Pt₁/CNT outperforms previously reported DSA electrodes. The CER activities of Pt₁/CNT on a carbon paper were also compared in neutral pH conditions, 0.55 M NaCl and natural seawater. Pt₁/CNT showed slightly better or similar activity in comparison to DSA in both 0.55 M NaCl solution and natural seawater (Supplementary Fig. 12b and c). Such a high intrinsic CER activity of Pt₁/CNT is noteworthy given that Pt₁/CNT showed much lower surface roughness than DSA, as observed in their cyclic voltammograms (Supplementary Fig. 14).

The CER activities of Pt₁/CNT_IX catalysts and a mixture of PtTPP and CNT were also compared (Supplementary Fig. 15). It is evident that the PtTPP-CNT mixture showed substantially lower CER activity than the annealed catalysts, and the CER activity of Pt₁/CNT_IX catalysts gradually increased with annealing temperatures. To clarify the annealing temperature-dependent activity trend in Pt₁/CNT_IX catalysts, Nyquist plots were obtained at a potential of 1.4 V (vs. RHE) and fitted with an equivalent circuit to assess the charge transfer resistance (\(R_{\text{ct}}\), Supplementary Fig. 16). As the annealing temperature increased, smaller semicircles (Supplementary Fig. 16c) and lower \(R_{\text{ct}}\) of Pt₁/CNT_IX catalysts were obtained (Supplementary Table 4), indicating that more facile charge transfer is achievable for the CER through higher annealing temperature. Overall, the annealing at high temperatures concomitantly enhanced the structural integrity and electrical conductivity between the Pt–N₄ sites and CNT, while preserving the local structure and chemical states of the Pt–N₄ sites.

The stability of Pt₁/CNT was examined by chronoamperometry (CA) at an initial current density of 10 mA cm⁻² (Fig. 2c). Pt₁/CNT retained 72% of its initial current after 12 h of CER operation, which is similar to that of DSA. After the long-term stability test, the polarisation curve of Pt₁/CNT exhibited 75% of its initial current at 1.41 V vs. RHE (Supplementary Fig. 17). In contrast, PtNp/CNT underwent more severe degradation preserving only 50%, which could originate from the dissolution of Pt, because even a trace amount of Cl⁻ accelerates the formation of metastable chloro-Pt complexes. In contrast, the Pt–N₄ sites in Pt₁/CNT could mitigate the formation of chloro-Pt complexes by their strong ligation with N.
catalysts, suggesting that similarly high CER selectivity was obtained irrespective of the annealing temperatures (Supplementary Fig. 23). The universally high CER selectivity of Pt1/CNT in various pH and Cl\textsuperscript{−} concentrations indicates that the Pt–N\textsubscript{4} sites are less sensitive to water activation, unlike MMOs\textsuperscript{5,12,15}.

The kinetic information of the catalysts for CER was obtained from Tafel analyses (Fig. 2e). Pt1/CNT showed a Tafel slope of 38 mV dec.\textsuperscript{−1} at an overpotential range of 30–70 mV, whereas those of PtNP/CNT and DSA were higher with 52 mV dec.\textsuperscript{−1} and 60 mV dec.\textsuperscript{−1} in the range of 40–80 mV, respectively. The Tafel analyses suggest that the CER on Pt1/CNT proceeded with faster kinetics than that on PtNP/CNT and DSA. The Tafel slope of 38 mV dec.\textsuperscript{−1} indicates that the CER on Pt1/CNT may proceed via the Volmer–Heyrovsky mechanism\textsuperscript{13,14,57,58}.

In situ XANES spectroscopy during the CER. We conducted in situ electrochemical Pt L\textsubscript{3}-edge XANES experiments to observe the interaction between the Pt–N\textsubscript{4} sites and Cl\textsuperscript{−} during the CER. The electrochemical in situ XANES was measured while increasing the applied potentials under CER operation conditions in the absence or presence of NaCl (Fig. 3). Two sets of in situ XANES spectra clearly show different trends. In the absence of NaCl, the XANES spectra of Pt1/CNT changed only marginally with applied potentials (Fig. 3a). However, upon the addition of NaCl, their XANES spectra underwent significant changes in white line intensity, particularly at potentials above 1.40 V where CER takes place (Fig. 3b). The marked increase in white line intensity at 1.40 V and 1.50 V indicates that more Cl\textsuperscript{−} species are adsorbed on Pt sites for higher Cl\textsubscript{2} yields. This distinct difference in the XANES spectra elucidates that Cl\textsuperscript{−} ions are absorbed on the Pt–N\textsubscript{4} sites during the CER.

Active site identification by DFT calculations. The origin of excellent CER activity of Pt1/CNT and detailed active site
structure were theoretically elucidated by DFT calculations (Supplementary Note 1). We considered three plausible models representing the atomically dispersed Pt−N4 sites (i.e., PtN4C12, PtN4C10 and PtN2+2C4+4, Fig. 4a), which were identified as the active sites for CER in Pt1/CNT through the EXAFS and in situ XANES analyses. We constructed Pourbaix diagrams, which provide the thermodynamically most stable adsorbate structures under applied electrode potential (U) and pH, by calculating the adsorption free energies (ΔGs) of possible adsorbates (i.e., *, ClO*, Cl*, H*, OOH*, O* and OH*) for Pt−N4 sites.

Fig. 3 In situ electrochemical Pt L3-edge XANES spectra of Pt1/CNT catalyst in the absence and presence of NaCl. XANES spectra a in the absence and b in the presence of 0.1 M NaCl taken under sequentially applied potentials without electrode rotation. The insets show a magnified view of the white line regions.

Fig. 4 DFT calculations of plausible model systems of Pt−N4 sites and PtO2 in CER and OER conditions. a Model system for possible structural configurations of Pt−N4 sites including PtN4C12, PtN4C10 and PtN2+2C4+4 and b PtO2 (110) surface. c Free energy diagrams for CER over Pt−N4 clusters and PtO2 (110) surface at zero overpotential (ηCER = 0 V). d Full free energy diagram along the reaction coordinate of CER over Pt1/CNT catalyst at the respective overpotential for CER (ηCER) of 0 V (black thick lines) and 0.09 V (red thick lines). α1 and α2 represent the transfer coefficients at each transition state (TS), which are determined as 0.83 and 0.58 from the experimental Tafel plots, respectively. The TS with higher free energy at the respective ηCER is indicated by purple line. Orange arrows represent the decreased amounts of free energies by applied ηCER for each state [i.e., first TS (denoted as 'i'), intermediate state, second TS (denoted as 'i'), and final state, respectively]. The free energy change for reaction intermediate at zero overpotential (ΔGTD(CER)) is indicated by blue arrow.
The Pourbaix diagram was constructed using an ab-initio constrained thermodynamics approach; the reactants were adsorbed on the surface while restricting the subsequent formation of product\(^59\). Nevertheless, the active adsorbate structure, identified as the thermodynamically most stable structure, can promisingly serve as a starting point for the investigation of mechanistic pathways. CER is pH-independent on the standard hydrogen electrode (SHE) scale and thus appears as a horizontal line at the equilibrium potential of 1.36 V vs. SHE (Supplementary Fig. 26). In contrast, the equilibrium potential for OER exhibits a decreasing trend with a slope of \(-59 \text{ mV pH}^{-1}\), starting from \(U_{\text{SHE}}\) (theoretical SHE potential) = 1.23 V and \(pH = 0\) (ref. \(^{60}\)). Considering that the present CER operating condition was acidic (pH = 2), the thermodynamic stability by sharing a structure for the CER owing to its lowest thermoneutral state (\(\Delta G = 0\), 0.20 V for \(2O_b^2ClO_c\)) were found to be closer to the thermoneutral state (\(\Delta G = 0\) than \(Cl^*\) species (\(\eta_{\text{TD(CER)}} = 0.09 \text{ V}\) at zero overpotential (i.e., \(\eta_{\text{OER}} = 1.36 \text{ V} - 1.23 \text{ V} = 0.13 \text{ V}\)), to be referenced to the same potential for the CER (i.e., \(\eta_{\text{CER}} = 0 \text{ V}\)). For the PtN\(_{4}\)C\(_{12}\) species, \(OH^+\) adsorption from \(H_2O_l\) was found to be the most endothermic among the reaction steps, corresponding to the potential determining step (PDS) with a large \(\eta_{\text{TDS(OER)}}\) above 0.74 V (Supplementary Table 5). Although the PtN\(_{2}\)C\(_{4}\)C\(_{4}\) site exhibited relatively stable reaction pathways because the value of CN for oxygen-involving intermediates was 4 (Supplementary Fig. 36b) in comparison to other Pt–N\(_4\) sites, it was still considered inactive for OER with very high \(\eta_{\text{TDS(OER)}}\) of 0.62 V, corresponding to the formation of OO\(^-\). This result was in good agreement with experimental observation, where OER did not occur even in the absence of Cl\(^-\) for Pt\(_1\)/CNT (Figs. 2a and 3a). Particularly focusing on the PtN\(_{4}\)C\(_{12}\) site, which most plausibly occurs even in the absence of Cl\(^-\) for Pt\(_1\)/CNT (Figs. 2a and 3a).

To further verify the high CER selectivity as compared to the OER, we obtained the free energy diagrams for CER on the Pt–N\(_4\) sites (Supplementary Fig. 36 and Supplementary Note 3). Note that the thermodynamic overpotentials for CER (\(\eta_{\text{TDS(CER)}}\)) of all Pt–N\(_4\) sites were evaluated at the overpotential of 0.13 V (i.e., \(\eta_{\text{OER}} = 1.36 \text{ V} - 1.23 \text{ V} = 0.13 \text{ V}\)) to be referenced to the same potential for the CER (i.e., \(\eta_{\text{CER}} = 0 \text{ V}\)). For the PtN\(_{4}\)C\(_{12}\) and PtN\(_{4}\)C\(_{10}\) sites, \(OH^+\) adsorption from \(H_2O_l\) was found to be the most endothermic among the reaction steps, corresponding to the potential determining step (PDS) with a large \(\eta_{\text{TDS(OER)}}\) above 0.74 V (Supplementary Table 5). Although the PtN\(_{2}\)C\(_{4}\)C\(_{4}\) site exhibited relatively stable reaction pathways because the value of CN for oxygen-involving intermediates was 4 (Supplementary Fig. 36b) in comparison to other Pt–N\(_4\) sites, it was still considered inactive for OER with very high \(\eta_{\text{TDS(OER)}}\) of 0.62 V, corresponding to the formation of OO\(^-\). This result was in good agreement with experimental observation, where OER did not occur even in the absence of Cl\(^-\) for Pt\(_1\)/CNT (Figs. 2a and 3a). Particularly focusing on the PtN\(_{4}\)C\(_{12}\) site, which most plausibly catalyses the CER in Pt\(_1\)/CNT, a huge difference between \(\eta_{\text{TDS(OER)}}\) and \(\eta_{\text{TDS(CER)}}\) at the PDS (i.e., \(\eta_{\text{TDS(OER)}} - \eta_{\text{TDS(CER)}} = 0.99 \text{ V}\)) further corroborates the excellent CER selectivity of Pt\(_1\)/CNT compared to the OER.

**Discussion**

We synthesised Pt\(_1\)/CNT catalysts comprising dense atomically dispersed Pt–N\(_4\) sites via simple high-temperature pyrolysis of a Pt-porphyrin precursor without the agglomeration of Pt. We demonstrated that Pt\(_1\)/CNT with atomically dispersed Pt–N\(_4\) sites could catalyse CER with high activity and selectivity. Pt\(_1\)/CNT showed superior CER activity compared to PtNP/CNT and commercial Ru/Ir-based DSA. Importantly, Pt\(_1\)/CNT preserved high CER selectivity in acidic pH with low Cl\(^-\) concentration, as well as in neutral pH, where DSA showed...
lower selectivity owing to the concomitant generation of O₂. By combining the in situ electrochemical XANES and DFT calculations, the atomically dispersed Pt₄N₄C₁₂ was identified as the most plausible active site structure for CER. Notably, this work presents the first use of atomically dispersed catalysts for CER. We expect this type of catalyst to be exploited as an alternative to MMO-based catalysts, whose activity and selectivity are intrinsically limited by the scaling relationship between CER and OER. Furthermore, the excellent selectivity of Pt₁/CNT under a wide range of Cl⁻ concentrations and pH suggest its promising applicability in wastewater and ship ballast water treatments.

Methods

**Chemicals.** Sodium chloride (NaCl, ≥99.5%) and sodium iodide (NaI, anhydrous, ≥99.5%) were purchased from Sigma-Aldrich. Multi-walled carbon nanotubes (CNT, MB99) with a diameter of 10 nm and average length of 10 μm were purchased from Carbon Nano-material Technology Co. (Korea). Triton X-100, hydrochloric acid (HCl, 36%), acetic acid (99.7%), ethanol (94.5%), and anhydrous ethanol (99.9%) were purchased from Samchun Chemicals (Korea). Perchloric acid (HClO₄, 70%, Veritas double distilled) was purchased from GPS Chemicals. Hydrogen peroxide (H₂O₂, 30%) was purchased from Junsei Chemical. Carbon paper (Toray, Toray), Sodium perchlorate monohydrate (NaClO₄, ≥99.7%), standardised sodium thiosulfate solution (Na₂S₂O₃, 0.01 N), and soluble starch powder (ACS, for iodometry) were purchased from Alfa Aesar. Pt(II) meso-tetraphenylporphine (PtTPP) was purchased from Frontier Scientific. Dichydrogen hexa-chloroplatinate[IV] hydride (H₂PtCl₆.H₂O, 99.95%) was purchased from Unimicro. Natural seawater, obtained from Ilan beach, Ulsan, Republic of Korea (GPS 35.497005, 129.430996), was used after filtration, whose relative ion concentrations can be found in a previous report. Commercially dimensionable anode (DSA, Ir/Ru atomic ratio = 2) was provided by Sontech Inc. (Korea). All chemicals were used without further purification, except the CNT.

**Acid treatment of carbon nanotube.** Prior to the synthesis of the catalysts, CNT was treated with heat and acids to remove any metallic impurities. CNT (30 g) was calcined in a box furnace at 500 °C for 1 h (ramping rate: 7.9 °C min⁻¹). The heated powder was mixed with a solution of 810 g of 6 M HNO₃ (diluted from 68% HNO₃), and the mixture was stirred at 80 °C for 12 h. The suspension was filtered and washed with excessive amounts of DI water until the filtrate reached a pH of 7. The CNT was then sequentarily treated with 720 g of 9 M HCl (diluted from 36% HCl) as described above, then dried at 60 °C overnight.

**Synthesis of Pt₃CNT-X catalysts.** Five hundred milligram of acid treated CNT and 71 mg of PtTPP were ground in an agate mortar until the colour and texture did not change (for ~20 min). The mixture was heated at a desired temperature between 500 °C and 800 °C under 1 L min⁻¹ N₂ flow (99.999%) for 3 h (ramping rate: 2.1 °C min⁻¹). The resulting catalysts were designated as Pt₃/CNT-X (X = annealing temperature).

**Synthesis of PtN/CNT Catalyst.** Forty four milligram of H₂PtCl₆·6H₂O was dissolved in 5.4 mL of aceton. The solution was mixed with 500 mg of acid treated CNT in a plastic bag by hand scrubbing, then dried at 60 °C overnight. The powder was heated to 200 °C under 0.1 L min⁻¹ H₂ flow (99.999%) for 2 h (ramping rate: 0.6 °C min⁻¹). Subsequently, the temperature was elevated to 350 °C (ramping rate: 2.5 °C min⁻¹) under 1.0 L min⁻¹ N₂ flow (99.999%) and maintained at that temperature for 3 h.

Characterisation methods. The HR-TEM and HAADF-STEM images were taken using an Titan³ G2 60-300 microscope (FEI Company) equipped with a double-sided spherical aberration (Cs) corrector operating at an accelerating voltage of 80 kV and 200 kV, respectively. The size distributions of Pt particles were analysed using the Gatan Microscopy Suite 3 Software. A total of 275 and 295 particles were recorded from two HAADF-STEM images of Pt₃/CNT (17 mm × 17 mm and 24 mm × 24 mm) and PtN/CNT (144 mm × 144 mm and 288 mm × 288 mm), respectively (Supplementary Figs. 1c and f). Scanning electron microscopy (SEM) images were obtained using an S-4800 field emission scanning electron microscope (Hitachi High-Technologies). The XRD patterns were obtained using a high-power X-ray diffractometer (D/MAX2500V/PC, Rigaku) equipped with Cu Kα radiation and operating at 40 kV and 200 mA. The powder sample was ground in an agate mortar until the colour and texture did not change (for ~20 min). The mixture was heated at a desired temperature between 500 °C and 800 °C under 1 L min⁻¹ N₂ flow (99.999%) for 3 h (ramping rate: 2.5 °C min⁻¹). Subsequently, the temperature was elevated to 350 °C (ramping rate: 2.5 °C min⁻¹) under 1.0 L min⁻¹ N₂ flow (99.999%) and maintained at that temperature for 3 h.

**Electrochemical cell construction.** A three-electrode system was built using an H-type cell to separate the working electrode from the counter electrode, in which a reference electrode was placed at the compartment of working electrode. Each compartment of the H-type cell was separated by a Nafion 117 membrane (DuPont). Prior to use, the Nafion membrane was pretreated with 5% H₂O₂ and heated at 60 °C for 1 h. An E7 RRDE (AFET/B9GCPT, Pine Research Instrumentation, the collection efficiency of 0.37), Pt counter electrode, and KCl-saturated Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. An MSR rotator (Pine Research Instrumentation) was used for controlling the rotation speed of the RRDE. The electrolyte were prepared by diluting 70% HCO₃ and by adding 99% NaCl in 18.2 MΩ cm Millipore water. For experiments under different NaCl concentrations, NaClO₄ · H₂O was added into the electrolyte to compensate the total ionic strength. The pH values of the acidic electrolytes were adjusted to 0.90 ± 0.05 by adding NaOH. The pH values of NaOH solutions were measured using a digital pH metre (Orion A211, Thermo Fisher Scientific).

**RHE calibration.** RHE conversion was achieved with a two-electrode setup, where the Pt wire and the reference electrode to be calibrated were immersed. Then, OCP was measured with high purity H₂ gas (99.9999%), which was sparged into the electrolyte. In this setup, the RHE and reference electrode, which was used as the conversion value.

**General electrochemical methods.** Electrochemical measurements were performed on an electrochemical workstation (CHI760E, CH Instruments) at atmospheric pressure. All potentials were converted to the potential scale of RHE, unless otherwise noted. Geometric current density (j, mA cm⁻²) and geometric charge density (μ, C cm⁻²) were calculated by dividing the measured current and the measured charge by the geometric area of electrode, respectively. Before every measurement, the RRDE was polished on a micro-cloth with aqeous suspensions of 1.0 μm and then 0.3 μm alumina to generate a mirror finish. The catalyst ink was prepared by mixing 2.5 mg of catalyst, 50 μL of DI water, 20 μL of 5% Nafion solution (DuPont), and 200 μL of 0.1 M NaCl solution using a micro syringe (Hamilton) and dried at RT. The resulting catalyst loading was 0.1 mg cm⁻². Prior to the electrochemical measurements, the catalyst film was immersed into an electrolyte of 0.1 M HCO₃, which was sparged with Ar gas (99.9999%) for at least 20 min. CV
was conducted to clean and make the catalyst fully wet at a scan rate of 500 mV s\(^{-1}\) for 50 cycles between 0.05 and 1.2 V. Then, the Pt ring electrode (outer diameter = 7.92 mm and inner diameter = 6.25 mm) was cleaned in the same potential range with a scan rate of 500 mV s\(^{-1}\) for 10 cycles. All electrochemical measurements were performed in triplicate, and the averaged values were used.

**Electrochemical CO stripping for active surface area.** For CO stripping experiments, the 0.1 M HClO\(_4\) electrolyte was purged for 10 min with CO gas (30.0%, Ar-balanced), while the constant potential of disk electrode was kept at 0.1 V. The sparging gas was changed to Ar for 30 min to remove the CO from the electrolyte while the disk potential was fixed at 0.1 V. The CO monolayer absorbed on the surface of Pt was stripped off by conducting three sequential CVs from 0.1 V to 1.0 V at 20 mV s\(^{-1}\). The third CV was displayed as a blank. The electrochemical surface area was calculated using the standard charge of the surface coverage of monolayer CO (420 \(\mu\)C cm\(^{-2}\)). The number of active sites \((n)\) of Pt/NP/CNT catalyst could be quantified using the CO stripping charge \((Q_{\text{CO}})\) with the following equation.

\[
n (\text{mol}) = \frac{Q_{\text{CO}}}{2F}
\]

where \(F\) represents the Faraday constant. The factor \(\frac{1}{2}\) is based on the approximation that two electrons are required for the desorption of one CO molecule during CO stripping. For the Pt\(_{65}/\text{CNT}\) catalyst, the number of active sites of Pt\(_{65}/\text{CNT}\) was calculated by the Pt content of Pt\(_{65}/\text{CNT}\) catalyst loaded on the electrode.

**Calculation of turnover frequency.** The number of active sites \((n)\) of Pt\(_{65}/\text{CNT}\) catalyst was calculated by the following equation.

\[
n (\text{mol}) = \frac{m_{\text{Pt}}}{M_{\text{Pt}}} = \frac{m_{\text{Pt}} \times \rho_{\text{Pt}} \times V_{\text{cat}}}{100 \times M_{\text{Pt}}}
\]

where \(m_{\text{Pt}}\) is the amount of Pt in the catalyst layer, \(M_{\text{Pt}}\) is the molar mass of Pt (195.084 g mol\(^{-1}\)), \(\rho_{\text{Pt}}\) is the weight percent of Pt in Pt\(_{65}/\text{CNT}\) (2.7 wt%), \(V_{\text{cat}}\) is the mass concentration of Pt in the catalyst ink (4.17 g L\(^{-1}\)) and \(V_{\text{cat}}\) is the volume of the loaded catalyst ink (6 μL). The turnover frequency (TOF) of Pt\(_{65}/\text{CNT}\) can be calculated as follows.

\[
\text{TOF} (\text{s}^{-1}) = \frac{i_d}{2 \times n \times F}
\]

where \(i_d\) is the disk current during CER measurement in 0.1 M HClO\(_4\) at 20 mV s\(^{-1}\). The CVs were conducted from 1.0 to 1.6 V at a scan rate of 10 mV s\(^{-1}\) with an electrode rotation of 1500 rpm. In a Bode plot, the solution resistance \((R_s)\) was determined as the magnitude of impedance, which is close to zero. The Nyquist plots were obtained at a fixed potential of 1.4 V without \(iR\) compensation to measure the charge transfer resistance \((R_{ct})\) after the CER activity of catalysts was consistently obtained. The Nyquist plots were fitted to obtain \(R_{ct}\) using the ZView software based on the equivalent circuit shown in Supplementary Fig. 16a, which was built on the previous report\(^{18}\). The pseudocapacitance \((C_p)\) and its coupled resistance \((R_p)\) originate from the adsorption and desorption of Cl\(^{-}\) intermediates\(^{19}\). Owing to the uncertain nature of the electrode-solution interface, the double layer capacitance \((C_d)\) and \(C_p\) were fitted with constant phase elements (CPEs) instead of an ideal capacitor. The charge transfer resistances of the catalysts are summarised in Supplementary Table 4. The \(iR\) compensated potentials \((E – iR)\) indicate that the potential was corrected by 85% after measurements with the values of \(R_{ct}\). CVs were conducted from 1.0 to 1.6 V at a scan rate of 10 mV s\(^{-1}\) with an electrode rotation of 1600 rpm, while the ring potential was held at 0.95 V.

**Rotating ring-disk electrode detection of Cl\(_2\) evolution.** For hydrodynamic Cl\(_2\) detection\(^{20}\), the activity of CER was measured in the Ar-saturated 0.1 M HClO\(_4\) with controlled concentrations of NaCl. Before measuring the CER activity, electrochemical impedance spectroscopy (EIS) was conducted at a fixed potential of 0.9 V without \(iR\) compensation from 0.00100,000 Hz to 1 Hz with a potential amplitude of 10 mV. A steady-state electrode rotation speed of 1600 rpm. In a Bode plot, the solution resistance \((R_s)\) was determined as the magnitude of impedance, which is close to zero.

Five sequential CVs of CER were conducted to obtain steady catalyst performance. The forward scan of fifth CV was used for the representative CER polarisation curve. With the above RRDE setup above, Cl\(_2\) generated at the disk electrode was rapidly turned into yellowish brown due to the generation of I\(_2\) from the oxidation of two Cl\(^{-}\) ions to one Cl\(_2\) molecule. The CER yield (in mole) can be calculated from the CA responses using the following equation.

\[
\text{Experimental yield (mol)} = \int_{E_1}^{E_2} \text{dt} \times \frac{2F}{\text{Volume of Na}_2\text{S}_2\text{O}_3 (L)}
\]

where \(E_1\) and \(E_2\) represent the current values, the Faraday constant, and the time, respectively. The factor \(\frac{1}{2}\) is based on the two electrons that were transferred for the oxidation of two Cl\(^{-}\) ions to one Cl\(_2\) molecule.

Immediately after finishing the CA, 10 mL of the anodic electrolyte was moved into 20 mL vial containing a large excess (~100×) of NaI to minimise the equilibrium concentration of volatile I\(_2\). Three titrations were conducted for a single CA measurement. The vial was closed air-tight and the colour of the solution was observed to rapidly turn into yellowish brown due to the generation of I\(_2\) from the following reaction.

\[
\text{Cl}_2 + 2 \text{NaI} \rightleftharpoons \text{I}_2 + 2 \text{NaCl}
\]

I\(_2\) was then titrated with a standardised 0.01 N Na\(_2\)S\(_2\)O\(_3\) solution. When the yellow colour become pale, few drops of 1% (w/v) starch indicator were added, which changed the colour to the solution to dark blue. The titration was completed with additional Na\(_2\)S\(_2\)O\(_3\) solution. Two Na\(_2\)S\(_2\)O\(_3\) molecules are oxidised for the reduction of one I\(_2\) molecule. The experimental Cl\(_2\) yield (in mole) can be calculated with the volume of the Na\(_2\)S\(_2\)O\(_3\) solution used in the titration process from the following equation.

\[
\text{Theoretical yield (mol)} = \frac{0.01 \times \text{Volume of Na}_2\text{S}_2\text{O}_3 (L)}{2}
\]

**Data availability**

The data supporting this study are available from the corresponding author upon reasonable request.

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Author contributions
S.H.J. supervised the project. S.H.J., S.K.K., T.L. and G.Y.J. conceived and designed the experiments and calculations. T.L. conducted synthesis, characterisations and electrochemical analyses. G.Y.J. and S.O.P. performed DFT calculations and analysed the results. J.P. and S.I.K. discussed on the analysis of Cl2 selectivity. H.Y.J and J.H.K. contributed to TEM analysis. Y.-T.K. commented on the paper. T.L., G.Y.J., S.K.K. and S.H.J. co-wrote the paper.

Competing interests
The authors declare no competing interests.

Additional information
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