**Engineering stable electrocatalysts by synergistic stabilization between carbide cores and Pt shells**

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Core–shell particles with earth-abundant cores represent an effective design strategy for improving the performance of noble metal catalysts, while simultaneously reducing the content of expensive noble metals. However, the structural and catalytic stabilities of these materials often suffer during the harsh conditions encountered in important reactions, such as the oxygen reduction reaction (ORR). Here, we demonstrate that atomically thin Pt shells stabilize titanium tungsten carbide cores, even at highly oxidizing potentials. In situ, time-resolved experiments showed how the Pt coating protects the normally labile core against oxidation and dissolution, and detailed microscopy studies revealed the dynamics of partially and fully coated core–shell nanoparticles during potential cycling. Particles with complete Pt coverage precisely maintained their core–shell structure and atomic composition during accelerated electrochemical ageing studies consisting of over 10,000 potential cycles. The exceptional durability of fully coated materials highlights the potential of core–shell architectures using earth-abundant transition metal carbide (TMC) and nitride (TMN) cores for future catalytic applications.

The development of core–shell nanostructures with controllable size, shell thickness, surface facets and composition vastly expands the possibility for engineering noble metal catalysts with enhanced performance. Numerous core–shell systems have been synthesized for catalytic applications, very often with other noble metal cores, such as Ru, Pd, Ag and Ir with marginal cost benefits. Critically, these core–shell materials along with those comprising earth-abundant, metallic cores (for example, Fe, Co and Ni) form intrinsically metastable structures with miscible core and shell elements that degenerate during electrochemical cycling or annealing due to metal leaching or migration. These instabilities result in considerable losses in active surface area and performance over time, imposing major barriers for the broad usage of core–shell architectures in industrial applications, where stability is essential. This is especially true for fuel cell technologies, the commercialization of which has been hindered by the poor durability of ORR catalysts.

Early TMCs and TMNs are ideal core materials due to their thermal and chemical stability, electrical conductivity, low cost and intrinsic ability to bind strongly to noble metals while still being immiscible with them. Unfortunately, the formation of surface oxides or carbon on TMCs and TMNs presents a difficult synthetic challenge for the deposition of atomically thin, uniform noble metal shells. As a result, only a few examples of core–shell systems comprising noble metal shells and TMC or TMN cores have been reported. Recently, we demonstrated a versatile synthetic method that circumvents these challenges via a high temperature self-assembly allowing for the synthesis of Pt shells on titanium tungsten carbide (Pt/TiWC) and titanium tungsten nitride (Pt/TiWN) cores with controllable shell coverage. These core–shell materials display unique catalytic properties resulting from bonding interactions between the shell and the core, including weakened adsorbate binding and extremely high sinter-resistance, but their durability in electrochemical environments has received only minor attention so far.

Here, we conducted a detailed examination of the electrochemical stability of Pt/TiWC and Pt/TiWN nanoparticles (NPs) as a function of two different Pt coverages to help identify possible underlying degradation mechanisms. Specifically, a scanning flow cell with inductively coupled plasma–mass spectrometry (SFC–ICP–MS) was used to measure metal dissolution as a function of potential, and identical location–scanning transmission electron microscopy (IL–STEM) paired with energy dispersive X-ray spectroscopy (EDX) was used to track changes to the structure of individual particles. In addition to possessing exemplary structural stability, fully coated core–shell materials demonstrated durability as ORR catalysts. Together, these results provide important insights on the design of stable core–shell catalysts with earth-abundant elements.

To determine the effect of the Pt shell coverage on the electrochemical stability, we synthesized nominal 0.7 monolayer (ML) Pt/TiWC and 2 ML Pt/TiWC using methods previously reported by our group. The carbon-supported materials (around 20 wt% core–shell particles, Ti/W ratio around 10/90) were characterized by transmission electron microscopy (TEM) (Supplementary Fig. 1) to determine particle size distributions and ICP–MS (Supplementary Table 1) to determine elemental compositions. The particle size distributions for 0.7 ML Pt/TiWC and 2 ML Pt/TiWC were 5.1 ± 1.3 nm and 6.6 ± 1.8 nm, respectively. The average Pt shell thickness was then estimated from the average particle size and the elemental composition.

As a first indication of stability, the dissolution of carbide-based core–shell particle elements was examined in situ via SFC–ICP–MS. To establish a clear relationship between the applied potential and
metal dissolution, a slow cyclic voltammetry (CV) scan was conducted at 2 mV s\(^{-1}\) from 0.0 to 1.5 \(\text{V}_{\text{RHE}}\) (reversible hydrogen electrode) in 0.1 M HClO\(_4\) on the core–shell NPs as well as on bare TiWC NPs supported on carbon (Fig. 1a)\(^{22}\). For the Pt-containing samples, oxidation of Pt occurs around 1.0 \(\text{V}_{\text{RHE}}\) and is accompanied by slight dissolution up to 1.5 \(\text{V}_{\text{RHE}}\), but most Pt dissolution occurs during the cathodic scan when the formed Pt oxides are reduced to Pt\(^0\) near 0.7 \(\text{V}_{\text{RHE}}\), as previously shown by Topalov et al.\(^{23}\). For bare face centred cubic TiWC NPs, the CV scan showed oxidation beginning at roughly 0.6 \(\text{V}_{\text{RHE}}\), coinciding directly with severe W dissolution (Ti dissolution profile in Supplementary Fig. 2). Previous studies on bulk hexagonal WC showed similar behaviour, although at slightly higher potentials being the thermodynamically more stable phase\(^{24,25}\).

The Pt/TiWC core–shell materials displayed a markedly different W dissolution profile compared to the bare carbide. In contrast to the single oxidative W dissolution peak for TiWC, Pt/TiWC showed two smaller dissolution peaks at lower potentials. These peaks below 0.5 \(\text{V}_{\text{RHE}}\) can be attributed to the Pt-catalysed reduction of remaining surface WO\(_3\) from passivation, while the second peak at 0.35 \(\text{V}_{\text{RHE}}\) corresponds to re-oxidation and subsequent dissolution of these reduced surface oxides. This effect is supported by SFC–ICP–MS experiments on Pt NPs deposited onto bulk WC, where the same two peaks were observed in the first scan from 0.0 to 0.5 \(\text{V}_{\text{RHE}}\) but disappeared in later cycles (Supplementary Fig. 3). These peaks only reappeared after severe oxidation of WC while cycling up to 1.5 \(\text{V}_{\text{RHE}}\), thus strongly indicating that the dissolution peaks below 0.5 \(\text{V}_{\text{RHE}}\) are related to the initial state of the surface oxides, rather than to dissolution of WC from the bulk. From thermodynamics, the initial W dissolution occurs in the potential range corresponding to a transition from WO\(_3\) to lower W oxides\(^{26}\), yet similar experiments on bulk WO\(_3\) showed much less dissolution at these potentials\(^{27}\). Since these peaks appear more noticeably in the presence of Pt, it is likely that Pt catalyses the reduction of surface WO\(_3\), leading to the observed dissolution at low potentials. Notably, almost no W dissolution was observed for the Pt/TiWC samples above 0.6 \(\text{V}_{\text{RHE}}\) where bare TiWC dissolves severely. This difference is strong evidence that the Pt shell protects the carbide core from dissolution at these elevated potentials, and no further W dissolution was measured during the cathodic scan or the second cycle (Supplementary Fig. 4).

To obtain a more extensive overview of the stability performance, harsh galvanostatic measurements were performed with the SFC–ICP–MS switching between constant oxidative and reductive current densities of 0.1 mA cm\(^{-2}\). Potentials ranged from −0.5 \(\text{V}_{\text{RHE}}\) under reductive currents up to 2.0 \(\text{V}_{\text{RHE}}\) under oxidative currents, depending on the sample (Supplementary Fig. 5). The dissolution profiles for the galvanostatic measurements revealed the same general features as in the single CV experiments for all the samples, namely dissolution during reduction of surface oxides and during oxidation of unprotected TiWC (Fig. 1b). However, integration of the dissolved elements over the whole galvanostatic sequence indicated that the sample with sub-ML Pt coverage experienced almost complete core dissolution under these aggressive conditions, while the thicker Pt shell was able to substantially suppress dissolution of the carbide core (Fig. 1c). The synthesis was extended to TiWN cores with 0.7 and 2 ML Pt shells, which showed the same stabilizing trend with increased shell coverage (Supplementary Fig. 5b). At potentials surpassing 1.9 \(\text{V}_{\text{RHE}}\), much higher than the potentials at which bare TiWC and TiWN NPs undergo oxidative dissolution, only 17 and 31% of W dissolved for 2 ML Pt/TiWC and 2 ML Pt/TiWN, respectively. In comparison, roughly 80% of W dissolved for both 0.7 ML Pt/TiWC and 0.7 ML Pt/TiWN, demonstrating the critical importance of the Pt shell coverage and thickness for...
protecting the core from dissolution and therefore on the overall stability of the core–shell particles. The sub-ML Pt samples displayed even more dissolution than bare TiWC and TiWN NPs, particularly for Ti (Supplementary Fig. 5c). We suggest that Pt may accelerate the dissolution of exposed core surfaces at the interface through Pt-catalysed reduction or oxidation, further emphasizing the importance of complete, uniform shell coverage.

In addition to the dissolution behaviour, we followed the structural and compositional evolution of individual 2 ML Pt/TiWC NPs before and after an accelerated stress test (AST) with IL–STEM–EDX. The AST consisted of 10,800 cycles between 0.4 and 1.0 VRHE in Ar-sat 0.1 M HClO₄ at a scan rate of 1 V s⁻¹. Scale bars, 5 nm (a), 4 nm (b) and 2 nm (c).

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d, Change in elemental composition (x) measured by EDX of individual particles with complete Pt shells and the whole map after the AST.

e, IL–STEM–EDX of 2 ML Pt/TiWC as prepared, after electrolyte contact, after one cycle and after ten cycles in 0.1 M HClO₄. Scale bars, 4 nm.

f, Schematic showing the evolution of partially and fully coated core–shell particles during potential cycling.
change between cycles one and ten. Particles with greater core exposure dissolved more rapidly, confirming the influence of Pt coverage on the rate of core dissolution (Supplementary Fig. 7).

To evaluate the suitability of Pt/TiWC core–shell materials for ORR applications, we conducted additional long-term durability tests in O₂-sat electrolyte and at elevated temperatures. In situ SFC–ICP–MS experiments measured the dissolution of 2 ML Pt/TiWC over 1,000 cycles between 0.4 and 1.0 V \text{RHE} at 3 V s⁻¹ in both Ar-sat and O₂-sat 0.1 M HClO₄, at either room temperature or 60 °C. Neither the presence of O₂ nor the increase in temperature resulted in a considerable increase in dissolution. For each condition, only around 3% of W and 0.1% of Pt dissolved in total during the 1,000 cycles (Supplementary Fig. 8b), most of which occurred during the first 400 cycles, probably due to the presence of core–shell particles with incomplete Pt coverage (Fig. 3a).

Following this initial period, minimal dissolution occurred with 0.1% or less of W and undetectable amounts of Pt dissolving in total over the last 100 cycles. These results suggest that homogeneously coated 2 ML Pt/TiWC particles are completely stable in O₂-sat electrolyte at elevated temperatures. This was further confirmed by STEM–EDX, which showed preservation of the core–shell structure after the AST consisting of 10,800 cycles between 0.4 and 1.0 V \text{RHE} in O₂-sat 0.1 M HClO₄ at 60 °C (Fig. 3b).

The durability of 2 ML Pt/TiWC as an ORR catalyst was further evaluated by comparing its activity and electrochemical surface area (ECSA) before and after 10,800 cycles in O₂-sat electrolyte to those of a commercial Pt/C catalyst (TKK, 46 wt%, 3 nm) (Fig. 4).

The ORR activity was obtained via thin film rotating disc electrode (RDE) measurements at 1,600 r.p.m. in O₂-sat 0.1 M HClO₄, and the Pt ECSA was measured by CO stripping (Supplementary Figs. 11 and 12). Initially, 2 ML Pt/TiWC displayed an enhanced specific activity of 0.69 mA cm⁻² over Pt/C (0.47 mA cm⁻²), which may be attributed to a weaker oxygen binding energy resulting from its slightly downshifted Pt d-band centre relative to pure Pt²⁸.

After the AST with O₂, the Pt/C control showed a 19% loss in ECSA, 36% loss in mass activity and 22% loss in specific activity, similar to previous work by Hasché et al.²⁹. In contrast, 2 ML Pt/TiWC showed only a 9% loss in ECSA, 22% loss in mass activity and 14% loss in specific activity. For Pt/C, multiple mechanisms have been reported to contribute to the sizeable decrease in ECSA after cycling, including agglomeration, Ostwald ripening, dissolution and particle detachment.³⁰ For 2 ML Pt/TiWC, the losses in performance can all be linked to the corrosion of imperfect core–shell particles, as other degradation mechanisms were not observed in the IL–STEM–EDX or in situ SFC–ICP–MS experiments. When these imperfect
particles restructured and collapsed, the ECSA decreased slightly from the loss of Pt surface sites into the bulk of the newly formed Pt NPs, while the specific activity dropped more substantially due to the lower activity of Pt NPs compared to 2 ML Pt/TiWC. Thus, further optimization of the synthesis method to produce more uniform core–shell particles should result in even greater improvement in performance. Evidently, these results demonstrate the enhanced catalytic stability of the core–shell material over traditional monometallic Pt/C catalysts.

In summary, we have shown how nanostructured core–shell materials with TMC or TMN cores can be engineered to have high stability in harsh, oxidative electrochemical environments. SFC–ICP–MS and IL–STEM–EDX experiments revealed the ability of atomically thin Pt shells to protect the TiWC and TiWN cores against dissolution while emphasizing the need for complete, uniform shell coverage. Notably, 2 ML Pt/TiWC NPs with a homogeneous Pt coating exhibited no degradation in the core–shell structure or atomic composition during ASTs with over 10,000 potential cycles in O₂-sat electrolyte at elevated temperatures. This unique performance, including the absence of leaching, alloying and agglomeration, arises specifically from the stabilizing interaction between the noble metal shell and the TMC core. In addition, the increased catalytic durability compared to Pt/C for ORR highlights potential industrial applications. These results provide a detailed insight into the underlying degradation mechanisms that affect the stability of core–shell nanomaterials and also illustrate promising design strategies using earth-abundant TMC and TMN cores to develop low-cost, ultradurable core–shell catalysts.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41563-019-0555-5.

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Methods

Materials synthesis. Silica encapsulated titanium tungsten oxide NPs coated with a desired amount of Pt salt (denoted as $\text{SiO}_2/(\text{NH}_4)_2\text{PtCl}_6/\text{TiWNO}$) were synthesized using a reverse microemulsion (RME) method by first mixing $n$-heptane, Brili-L4 surfactant, ultrapure water and $0.1 M$ HClO$_4$, followed by $0.1 M$ NaOH solution, tungsten isopropoxide and titanium isopropoxide. The mixture was stirred for 4h to allow the $\text{Ti}_x\text{W}_y\text{O}_{z}$ NPs to form. Afterwards, a separate RME containing $n$-heptane, Brili-L4 and chloroplatinic acid dissolved in water was added dropwise to the first RME causing the precipitation of the Pt salt onto the TiWNO NPs. After another 4h, tetraethyl orthosilicate was added and left to react for 16.5h, encapsulating the particles in a $\text{SiO}_2$ shell. Then, methanol was added to precipitate the $\text{SiO}_2/(\text{NH}_4)_2\text{PtCl}_6/\text{TiWNO}$ NPs, which were recovered after centrifugation and washing with acetone. $\text{SiO}_2$/Pt/TiWOC core–shell particles were formed by heating the oxide powder up to $900^{\circ}C$ at a ramp rate of 2 $^\circ$C min$^{-1}$ under a gas flow of 15% CH$_4$–85% H$_2$ and held for 5h. After cooling to room temperature under H$_2$, the samples were passivated using 1% O$_2$–99% H$_2$. The $\text{SiO}_2$ was removed by dissolution in a mixture of degassed ethanol and aqueous HF solution for 18h at room temperature with dispersed carbon black added as a support. The carbon-supported Pt/TiWOC NPs were recovered through centrifugation, washed thoroughly with degassed ethanol and water, and dried under vacuum. To synthesize Pt/TiWON NPs, the Pt/TiWOC powder was heated up to 800°C at a ramp rate of 2 $^\circ$C min$^{-1}$ under NH$_3$ flow and held for 3h. After cooling to room temperature under NH$_3$, the samples were passivated.

Complete synthetic details are provided in ref. 30. Pt NPs were synthesized via the ethylene glycol route described in literature. Here, 3.13 ml of a $0.1 M$ H$_2$PtCl$_6$ solution in water (8 w/o, Sigma-Aldrich) were dissolved in 22 ml of ethylene glycol and mixed with 25 ml of a 0.5 M NaOH solution in ethylene glycol. The mixture was heated up to 150°C while stirring and held there for 1.5h after its colour turned from orange to brownish black. After the completion of the reaction, 3 ml of a 1 M HCl solution were added to precipitate the NPs, which were recovered through centrifugation and washing with 1 M HCl. Once dried, the Pt NPs were dispersed in acetone along with WC particles ($d=190 nm$, Sigma-Aldrich) using ultrasonication while evaporating the solvent. The deposition on WC was confirmed via TEM imaging on a JEOL JEM 2020FS operating at 200 kV. For the SFC measurements, Pt NPs/bulk WC was re-dispersed in water and deposited on a glassy carbon plate with a total loading of 1 and 0.25 $\mu g$ of W and Pt, respectively. The dissolution was measured during a potential cycle sequence at 2 mV s$^{-1}$ consisting of two cycles up to 0.5 $V_{RHE}$ followed by one cycle up to 1.5 $V_{RHE}$ and ending with one more cycle up to 0.5 $V_{RHE}$.

Characterization. Powder X-ray diffraction was performed on a Bruker D8 diffractometer using Cu Kα radiation with a step size of 0.02° and step time of 0.2 s. TEM was performed on a JEOL 2010F equipped with a field emission gun operating at 200 kV. Sample elemental composition was measured on an Agilent 7900 ICP–MS. IL–STEM was performed on a FEI Titan 80–200 (ChemiSTEM) with a Cs− corrector (CEOS GmbH) and a high angle annular dark field detector. The microscope was operated at 80 kV to minimize beam damage. ‘Z-contrast’ conditions were achieved using a probe semi-convergence angle of 24.7 mrad and a probe current of 0.7 nA. An SEM-EDS (Tschurl modification) was used to avoid chloride contamination. The reference electrode was calibrated against a RHE before each measurement and all potentials are reported versus RHE. Catalyst suspensions were prepared by sonicking the samples in 1 ml ultrapure water (Elga PURELAB Plus, 18 MΩcm, TOC <3 ppb) for 30 min with the concentration of Pt and W as 0.05 and 0.1 g l$^{-1}$, respectively. Then, 20 µl of this suspension was loaded onto a polished 5 mm GC RDE tip and then dried to form the working electrode. The Pt loading was 5 $\mu g$, 2 $\mu g$, and 0.2 $\mu g$ for 2 ML Pt/TiWOC and 20 µg, 2 $\mu g$, and 0.2 $\mu g$ for Pt/C (KK, 46 wt%). The 0.1 M HClO$_4$ electrolyte was prepared from ultrapure water and 70% HClO$_4$ (Merck Suprapur).

The catalyst surface was first pretreated in Ar-sat electrolyte with 20 CV conditioning scans from 0.05 to 1.0 $V_{RHE}$ at 200 mV s$^{-1}$. Afterwards, ORR polarization curves were recorded in O$_2$-sat electrolyte at 50 mV s$^{-1}$ and 1,600 r.p.m. with iR compensation. A background was recorded in Ar-sat electrolyte using identical conditions and subtracted to obtain the ORR current. CO stripping and hydrogen underpotential deposition (HUPD) measurements were performed to calculate ECSA values using the CO voltammograms. The electrolyte was held at 0.05 $V_{RHE}$ as the electrolyte was purified with CO for 7 min to saturate the surface and then with Ar for 25 min to remove excess CO. Immediately after, a CV was recorded from 0.05 to 1.0 $V_{RHE}$ at 200 mV s$^{-1}$. The CO stripping did not lead to enhanced degradation or restructuring (Supplementary Fig. 9). The catalytic stability was evaluated using an AST protocol consisting of 10,800 cycles between 0.4 and 1.0 $V_{RHE}$ at 1 V s$^{-1}$ in O$_2$-sat 0.1 M HClO$_4$, at room temperature.

Data availability

Experimental data are available from the corresponding authors on reasonable request.

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Author contributions

D.G., A.G., Y.R.-L. and M.L. conceived this study. A.G. synthesized the materials and performed physicochemical characterization. D.G. conducted the electrochemical stability measurements via SFC–ICP–MS. P.P. carried out IL–STEM measurements accompanied with EIDX elemental mapping. D.G. and A.G. conducted ORR activity
measurements via RDE. The manuscript was written by A.G., Y.R.-L., D.G. and M.L. All authors discussed the manuscript and the results.

Competing interests
The authors declare no competing interests.

Additional information
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