Engineering of a Low Cost, Highly Active and Durable Tantalate-Graphene Hybrid Electrocatalyst for Oxygen Reduction

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Abstract: Oxygen reduction reaction (ORR) is one of the most important reactions in renewable energy conversion and storage devices. The full deployment of these devices highly depends on the development of highly active, stable and low-cost catalysts. Herein, we report a new hybrid material consisting of $\text{Na}_2\text{Ta}_8\text{O}_{21-x}/\text{Ta}_2\text{O}_5/\text{Ta}_3\text{N}_5$ nanocrystals grown on N-doped reduced graphene oxide. This catalyst shows a significantly enhanced ORR activity by ~ 4 orders of magnitude in acid medium and by ~ 2 orders of magnitude in alkaline medium compared to individual $\text{Na}_2\text{Ta}_8\text{O}_{21-x}$ on graphene. Moreover, it has excellent stability in both acid and alkaline media. It also has much better methanol tolerance than the commercial Pt/C, which is relevant to methanol fuel cells. The high ORR activity arises not only from the synergistic effect among the three Ta phases, but also from the concomitant nitrogen doping of the reduced graphene oxide nanosheets. A correlation between ORR activity and nitrogen content is demonstrated. Deep insights into the mechanism of the synergistic effect among these three Ta-based phases, which boosts the ORR's kinetics, were acquired by combining specific experiments and density functional theory calculations.

1. Introduction

The worldwide fossil energy shortage and relevant environmental issues urgently require renewable and clean energy technologies. Oxygen reduction reaction (ORR) is one of the most important reactions in renewable energy conversion and storage devices, such as fuel cells and metal-air batteries.^[1-8] Especially, the polymer electrolyte membrane fuel cells (PEMFCs), used in automotive applications, have already achieved the level of commercialization.^[5] Although the Pt group metal (PGM) catalysts can efficiently address the kinetics-related challenges, the high cost and the limited resource of PGM greatly hinders the widespread commercialization of these energy conversion and storage devices. Therefore, the development of low cost, highly active and stable PGM-free catalysts, to replace the PGM ones, towards ORR, is highly desired. Over the past decades, extensive research was devoted to the development of alternative and low-cost catalysts, including i) non-precious Fe and Co-based metal catalysts,^[3,4,9-11] ii) metal oxides, nitrides and oxynitrides,^[12-14] and iii) metal-free catalysts such as carbon-based materials.^[15]

Oxides from metals belonging to groups 4 and 5 (Ti, V, Zr, Nb, Hf, Ta) have attracted interest in these fields, mainly due to their low cost compared to PGM catalysts, environmental compatibility and excellent stability in acid medium.^[12,16-19] It has been demonstrated that these oxides can have some activity toward ORR, if their stoichiometry is conveniently tailored to generate a high concentration of defects such as oxygen vacancies.^[12,19-22] As illustrated in Table S1,^[16,18, 21-35] the activity of this class of materials is still low, i.e., they require high overpotential even to achieve a modest current density, and do not reach the limiting current value expected for the reduction of oxygen to water by the four-electron pathway:

In spite of some progress, the exact nature of the active sites of catalysts based on these oxides has not yet been fully elucidated. Moreover, the semiconducting properties of these oxides require their dispersion as nanoparticles on conductive substrates. This also represents an opportunity to add another functionality in order to create a synergy for the oxygen reduction. In this regard, nitrogen moieties in PGM-free Fe, Co-based catalysts have already shown a relevant role.^[3,36]

Herein, we demonstrate how the phase composition and structure of Ta-based oxide materials supported on nitrogen-containing graphene can be engineered to obtain a hybrid catalyst with excellent activity for ORR, stability and methanol tolerance in both acid and

alkaline media. By involving the work function of the Ta-based catalytic phases, density functional theory (DFT) calculations demonstrate that the electron transfer among the nanocrystals leads to a charge accumulation layer at their interface, which boosts the activation of O_2 molecule, leading to an enhanced ORR performance. This type of hybrid catalyst offers great flexibility, as they can be used in 1) fuel cells in combination with protonic or anionic membranes, and in the presence of different fuels spanning from hydrogen to alcohols, which can be obtained through renewable routes such as renewable energy-fed electrolysis or co-electrolysis of CO_2 and water; and 2) other devices such as metal-air batteries including Zn-air, Li-air, Na-air, etc.

2. Results and discussion

2.1. Synthesis and characterization

All catalysts investigated in this study ($Na_2Ta_8O_{21-x}/GP$, $Na_2Ta_8O_{21-x}/Ta_2O_5/GP$ and $Na_2Ta_8O_{21-x}/Ta_2O_5/Ta_3N_5/GP$, where GP stands for the thermally reduced graphene oxide support) and their respective synthesis parameters are summarized in Table S2. The main phase in these catalysts consists of a sub-stoichiometric sodium tantalate ($Na_2Ta_8O_{21-x}$, $x \sim 6$)^{27,28} which is characterized by a high number of oxygen vacancies while showing excellent chemical and electrochemical stability in the acid environment. The other phases are obtained through specific treatments and, to a certain extent, they behave as ORR promoters by the effect of a synergistic mechanism. The dependence of the chemical composition and structure of the catalysts on the synthetic conditions (time of treatment in oven at 60 °C and pyrolysis time at 900 °C), and the impact on the catalytic activity for ORR are summarized in the Supplementary information and in Figure S1 and S2.

Here, we will focus on four representative samples named T1 to T4. As shown in **Figure 1**, Figure S3 and S4, sample T1 is composed of $Na_2Ta_8O_{21-x}$ supported on GP sheets. The $Na_2Ta_8O_{21-x}$ oxide nanoparticles have a rod-like shape, are 70 nm long and their width is fairly constant (ca. 15-20 nm). Samples T2 and T4 are formed by $Na_2Ta_8O_{21-x}$ and Ta_2O_5 on GP, but T4 has a higher fraction of Ta_2O_5 ; and sample T3 is composed of $Na_2Ta_8O_{21-x}$, Ta_2O_5 and Ta_3N_5 on GP. The three compounds ($Na_2Ta_8O_{21}$, Ta_2O_5 and Ta_3N_5) involved in these materials have crystal structures that belong to the orthorhombic crystal system. The crystal shapes of samples T1 and T2 resemble to golden yellow topaz (Figure S5e^[37]), while the crystal shapes of T3 and T4 look more like cerussite formed by crystals of various forms and sized (Figure S5f^[38]). The average length of the nanoparticles progressively decreases with the formation of the other phases: 50 nm for T2, 20 nm for T4 and 10 nm for T3. A detailed

discussion on the formation and the downsizing of the crystal structures is provided in **section 2.3**.

2.2. Electrochemical performance and stability.

The rotating ring-disk electrode (RRDE) is extensively used as a characterization tool to evaluate the activity of electrocatalysts for the oxygen reduction reaction, and simultaneously their selectivity toward the four-electron pathway (Equation 1) versus the unwanted two-electron pathway that leads to the formation of H_2O_2 .^[39] As illustrated in **Figure 2a, b** (lower panels), the activity of these catalysts for ORR in both acid and alkaline media is strongly dependent on their structure and composition. A systematic increase of activity, characterized by a higher disk current at potentials closer to the reversible potential for oxygen reduction, is observed from catalysts T1 to T2 and to T4. This increase in activity can be, in a first approximation, related to a decrease of the $\text{Na}_2\text{Ta}_8\text{O}_{21-x}$ crystal size and the formation of Ta_2O_5 (higher fraction in the case of T4). However, a further enhancement of the activity is observed when the additional Ta_3N_5 phase is present, as in the T3 electrocatalyst. The polarization curve of T3 in HClO_4 is remarkably shifted to even more positive potentials and reaches the limiting current plateau expected for the ORR's $4e^-$ pathway according to the Levich Equation (Equation S1). This has not been reported yet for Ta-based oxides or oxynitrides catalysts in both acid and alkaline media.^[16,18,21-30,35] Furthermore, this catalyst shows excellent activity in alkaline medium almost reaching the activity of a commercial 20% Pt/C catalyst.

In more detail, the onset potential (herein defined as the potential required to generate an ORR current density of 0.1 mA cm^{-2} in a steady-state RRDE experiment, in order to minimize the effect of residual currents) shifts from 0.40 V (T1) to 0.65 V (T3) in acid, and from 0.8 V (T1) to 0.90 V (T3) in alkaline. Similarly, the potential in the mixed kinetic-diffusion control region (here taken at 2 mA cm^{-2}) shifts from 0.13 V (T1) to 0.45 V (T3) in acid, and from 0.72 V (T1) vs 0.82 V (T3) in alkaline. The Tafel slope values extracted from the polarization curves are close to 60 mV dec^{-1} (Figure S6), which is similar to that of Pt electrodes. These shifts in potential correspond to an increase in the ORR activity by ~ 4 and ~ 2 orders of magnitude in acid and alkaline conditions, respectively, going from T1 to T3.^[40] The ORR activity of the T3 hybrid catalyst in acid medium is indeed excellent when compared to that of other Ta-oxide based electrocatalysts and metal oxide catalysts reported so far from groups 4 and 5 (Table S1 and Figure S7) which show very low activity in the mixed kinetic-diffusion control region, and do not reach the limiting current expected for the 4 electrons process (Figure 2e).^[22,39,41] The excellent selectivity of T3 catalyst for the reduction of oxygen to

water is also demonstrated by the low intensity of the ring current (j_{Ring}) with respect to the disk current (j_{Disk}) (Figure 2a, b), and consequent low H_2O_2 yield. This is below 20% and the number of exchanged electrons (n) is above 3.7 (Figure 2c, d).

Besides the high electrocatalytic activity, an excellent chemical/electrochemical stability is mandatory for the operation in the harsh environment of ORR based devices, such as fuel cells.^[42] In the case of direct methanol (alcohol) fuel cells, the so-called “methanol tolerance” is also required for the ORR catalysts.^[43] When methanol is used as a fuel, it permeates in part from the anode to the cathode through the polymer electrolyte membrane and is oxidized at the cathode, resulting in a depolarization of the cell and a lower electrical efficiency.^[44] Thus, we performed the evaluation of the stability and methanol tolerance in both acid and alkaline media for our hybrid catalyst T3 and the commercial Pt/C. As illustrated in **Figure 3**, $\text{Na}_2\text{Ta}_8\text{O}_{21-x}/\text{Ta}_2\text{O}_5/\text{Ta}_3\text{N}_5/\text{GP}$ and Pt/C catalysts exhibit similar stability in acid (22 vs 29% decrease in the current, respectively). Interestingly, in alkaline medium, $\text{Na}_2\text{Ta}_8\text{O}_{21-x}/\text{Ta}_2\text{O}_5/\text{Ta}_3\text{N}_5/\text{GP}$ shows only a 10 % current loss, which is three times lower than that of Pt/C. If methanol is injected into the O_2 -saturated electrolytes, the oxygen reduction current density on Pt/C decreases of about 50 % in acid, and it even becomes positive in alkaline medium due to the high activity of Pt toward methanol oxidation. Instead, the ORR activity of the hybrid catalyst is almost unaffected in both acid and alkaline electrolytes.

2.3. Surface and bulk composition analysis, and corresponding catalytic performance.

Bulk and surface chemical analyses were conducted on the selected samples to unravel the origin of the high activity of the $\text{Na}_2\text{Ta}_8\text{O}_{21-x}/\text{Ta}_2\text{O}_5/\text{Ta}_3\text{N}_5/\text{GP}$ catalyst. The X-ray photoelectron spectroscopy (XPS) survey scans are presented in Figure S8. Table S3 summarizes the bulk and surface elemental compositions of the catalysts. Besides C, Na, Ta, O, other elements such as N and S were also found. The traces of sulfur (~ 0.03 at. %) from the sulfuric acid used during the graphene synthesis are present in all samples and cannot explain the differences in the activity. Instead, the N content and type varies significantly across the catalysts, and it is well established that the electrocatalytic activity of N-doped graphene materials for ORR is higher than that of the undoped materials. The high-resolution N 1s spectra revealed that almost no N was present on pristine GP nanosheets, but its content increased when it was subjected to the hydrothermal process and oven treatment at 60 °C for 10 days (**Figure 4**). This resulted from the physical adsorption of N_2 from air on the surface of the carbon material, which, during the subsequent pyrolysis in Ar at 900 °C, led to its chemical doping. In fact, the longer the oven time, the higher N content in the catalysts (Table S3). Furthermore, the catalyst $\text{Na}_2\text{Ta}_8\text{O}_{21-x}/\text{Ta}_2\text{O}_5/\text{Ta}_3\text{N}_5/\text{GP}$ (T3) had the highest N content,

indicating that exposition to air at 60 °C for 7 days between two pyrolysis treatments (Table S2) resulted in additional adsorption of N₂ molecules and further insertion of N during the second pyrolysis treatment. Accordingly, by exposing the catalyst to air or to a pyrolysis treatment, the growth of the nanocrystals is restrained and the nanoparticles are more prone to break via cleavage, parting and fracture, thus becoming smaller. The deconvolution of N 1s spectrum of T3 catalyst is shown in Figure 4b. There are three nitrogen peaks, attributed to 1) pyridinic N and N from Ta₃N₅ both at 398.0 eV (42.9 at%), 2) graphitic N at 401.0 eV (28.2 at%), and 3) N from NO_x at 410.8 eV (5.5 at%). The N 1s spectrum overlaps with Ta 4p_{3/2}, thus the two contributions related to Ta₃N₅ at 404.4 eV (15.3 at%) and Na₂Ta₈O_{21-x}/Ta₂O₅ at 407.0 eV (8.2 at%) were also considered in the deconvolution of the spectra. The resolved N 1s / Ta 4p_{3/2} spectra for the other samples are presented in Figure S9. The Ta 4f spectrum of sample T3 confirmed the existence of Ta⁵⁺ ions in two different chemical environments. Ta⁵⁺ bound to oxygen anions in Na₂Ta₈O_{21-x} and in Ta₂O₅ (27.1 and 29 eV) and bound to nitride anion in Ta₃N₅ (25.9 and 27.8 eV)^[45,46] (Figure 4c, d). The C 1s, O 1s, S 2p and Na 1s spectra for the four catalysts are reported in Figure S10. The spectra of each element are very similar in terms of shape and binding energy (BE) values, demonstrating an identical chemical environment. The only exception is the Na 1s spectrum of sample T3 that shows a peak shifted to lower BE consistent with the presence of Ta₃N₅.

As reported in the literature, pyridinic N in N-doped graphene materials offers higher ORR activity than the other nitrogen species such as graphitic, pyrrolic and oxidized-nitrogen.^[47,48] Carbon atoms next to pyridinic N can behave as Lewis bases to adsorb oxygen molecules and to initiate ORR.^[47] On the other hand, due to its suitable band structure and electronic characteristics, Ta₃N₅ is used as the catalyst for the oxygen evolution in photocatalytic water splitting.^[46,49] These properties are also appropriate for the reverse process, the oxygen reduction reaction.^[50] However, Ta₃N₅ has been considered less promising than tantalum oxynitrides (TaO_xN_y), because of the higher ionization potential.^[29] In T3 catalyst, a synergy occurring among Ta₃N₅ nanoparticles, the Ta-oxide phases and the graphene support, appears to promote the oxygen reduction process overcoming this drawback. Ta₃N₅ seems to work as a booster for the ORR and graphene allows for a rapid electron transfer.^[51]

The catalysts' ORR activity in both acid and alkaline media was also correlated with total nitrogen content (N_{total}) and with the nitrogen signal at 398 eV (N_{398eV}, i.e., species from both pyridinic N and Ta₃N₅) in **Figure 5**. Remarkably, the ORR activity increases with increasing N_{total} and N_{398eV} in both media, with a higher slope for activity vs N_{398eV} (at.%) demonstrating

that these N species contribute to form the most active sites or act as anchoring sites for the Ta-species. The potential and current values measured with the Pt/C catalyst were included in Figure 5. These were used to extrapolate the values for surface N_{total} and $N_{398\text{eV}}$ that would confer to these catalysts the same ORR activity as of Pt/C catalyst. At present, the N_{total} (1.35 at%) and $N_{398\text{eV}}$ (0.42 at%) contents in sample T3 are sufficient to achieve an ORR activity close to Pt/C in alkaline medium. However, they are still lower than the target values in acid medium (3 at% for N_{total} and 1 at% for $N_{398\text{eV}}$). While it is evident that more N_{total} and $N_{398\text{eV}}$ sites are needed to improve the catalysts' ORR activity in acid medium, the correlations presented in Figure 5 provide benchmarking values for the nitrogen content to further improve the ORR activity of this type of catalysts and to reach the activity of Pt/C.

To further prove that Ta_3N_5 is in part responsible for the high ORR activity of sample T3, we subjected a $Na_2Ta_8O_{21-x}/Ta_2O_5$ catalyst (sample T4) to an additional thermal treatment at 850 °C under NH_3 atmosphere. Ta_3N_5 can be formed according to the chemical reactions described in Equation (2) and (3):

The XRD pattern and XPS analysis confirmed that after the treatment with NH_3 the main component of this sample is Ta_3N_5 and a very small fraction of $Na_2Ta_8O_{21-x}$, **Figure 6a, b**. High-resolution TEM image is presented in Figure S11. As illustrated in Figure 6d, the formation of Ta_3N_5 resulted in a catalyst with higher ORR activity in acid medium compared to the non-treated one, i.e., at -2 mA cm^{-2} , the polarization curve is shifted of about 42 mV to more positive potentials and the beginning of the limiting current expected for the 4 electron pathway is clearly observed. However, this catalyst (mainly Ta_3N_5 on N-doped reduced graphene oxide) does not outperform our best catalyst ($Na_2Ta_8O_{21-x}/Ta_2O_5/Ta_3N_5$ on N-doped reduced graphene oxide). The comparisons of the potential at the current density of 2 mA cm^{-2} in acid medium, for sample T1-T5 with different crystal compositions, is shown in Figure 6e. This undoubtedly illustrates the existence of a synergistic effect between the two oxides and the nitride phase, which results in a hybrid catalyst with a high ORR activity. The oxygen vacancies resulting from the Na doping of tantalum oxide^[28] and those which are intrinsically present in Ta_2O_5 are expected to play a relevant role for the ORR.^[52] However, the presence of a large number of oxygen vacancies and defects in these tantalate and oxide systems, acting as adsorption sites and catalytic reaction centers, is not sufficient to approach the level of activity of Pt. According to our results, it is required to combine the oxygen vacancies with other functionalities like the Ta-N and pyridinic species. Finally, these phases are assisted by the

graphene support which facilitates the electron transfer, resulting in electronic properties similar to noble metals, like Pt, Pd, etc., both in terms of chemisorption and charge transfer.

2.4. DFT calculations and interfacial synergy effect. To understand the synergic effect among the different Ta-based nanocrystals leading to an enhanced ORR activity, density functional theory (DFT) calculations were carried out. As well known, there are two final products for the oxygen reduction: H_2O and H_2O_2 . If the catalytic phases can provide sufficient electrons to activate the oxygen reduction along the four electrons route or if they can efficiently capture the reaction intermediates and break the O-O bond, H_2O formation will be dominant. Otherwise, a two-electron reaction may very likely occur with consequent formation of H_2O_2 . From a fundamental point of view, the materials' work function is an effective parameter that characterizes their electron donation ability. A material with a small work function is characterized by a low energy barrier for electron donation from its surface to the adsorbed oxygen species, thereby facilitating their activation. As a consequence, the work function values of the three Ta components and graphene with different N dopants were calculated using first-principle methods. The bulk models based on an orthorhombic crystal system were selected on the basis of the XRD results, and the exposed surfaces were built according to the HR-TEM micrographs. For the $\text{Na}_2\text{Ta}_8\text{O}_{21}$ model, the structure was obtained from NaTaO_3 as they share the same orthorhombic crystal structures. More details regarding these models and computational methods are given in the Supplementary Information.

From **Figure 7**, it is seen that $\text{Na}_2\text{Ta}_8\text{O}_{21}$ has the largest work function value (6.41 eV) among the three Ta phases, which hinders the electron transfer from the catalyst surface to O_2 and consequently the activation of O-O bond, contributing to a high H_2O_2 selectivity. In comparison, Ta_2O_5 has a relatively smaller work function (5.24 eV) leading to a higher Fermi level occupancy. When the crystals are in contact, the two components will have the same Fermi level since electrons would flow from Ta_2O_5 to $\text{Na}_2\text{Ta}_8\text{O}_{21}$ to reach the charge balance (**Figure 8a**). The charge transfer between Ta_2O_5 and $\text{Na}_2\text{Ta}_8\text{O}_{21}$ will produce a charge accumulation layer at their interface, which can more easily overcome the activation barrier for O_2 reduction thus boosting the catalysis of the electrochemical process. In terms of the role of graphene substrate, our calculations (Figure S12) show that the work functions of pristine graphene (4.2 eV), graphene with graphite-N (3.55 eV), pyridine-N (4.82 eV) and pyrrole-N (4.69 eV) are all beneficial for the electron transfer towards the active phase $\text{Na}_2\text{Ta}_8\text{O}_{21}$.

Based on the above calculations, it is evident how such unique interface improves the catalytic performance (Figure 8). On one hand, the inflowing electrons will upward shift the

valence band bottom (V_{BM}) of $\text{Na}_2\text{Ta}_8\text{O}_{21}/\text{Ta}_2\text{O}_5$ and hence the energy gap between the V_{BM} of the catalyst and lowest unoccupied molecular orbital (LUMO) of O_2 is increased, leading to a large orbital splitting to form bonds and antibonds during these interactions. A strong interaction will accelerate the activation and dissociation of O_2 and therefore the reaction will proceed mainly along the four-electron pathway. Ta_3N_5 possesses an even smaller work function (4.01 eV) and bandgap with respect to the Ta_2O_5 and $\text{Na}_2\text{Ta}_8\text{O}_{21}$, which facilitates the accumulation of electrons on the $\text{Na}_2\text{Ta}_8\text{O}_{21}$ and further boosts the ORR performance of the composite catalyst. On the other hand, the charge transfer from Ta_2O_5 or Ta_3N_5 to $\text{Na}_2\text{Ta}_8\text{O}_{21}$ makes the $\text{Na}_2\text{Ta}_8\text{O}_{21}$ surface an electron-rich region (Figure 8b). The excess of electrons at the $\text{Na}_2\text{Ta}_8\text{O}_{21}$ surface will also accelerate the reaction kinetics through the electrons transfer to adsorbed oxygen species, leading to an enhanced ORR performance. N-doped graphene has a work function of 4.5 eV which is smaller than that of $\text{Na}_2\text{Ta}_8\text{O}_{21}$. Thus, the role of graphene is to provide electrons to the active phase $\text{Na}_2\text{Ta}_8\text{O}_{21}$ to boost the ORR.

3. Conclusion

The approach of combining several functionalities in a stable non-platinum group metal Ta-based catalyst provides a promising route to replace Pt in various ORR applications. A new hybrid material consisting of $\text{Na}_2\text{Ta}_8\text{O}_{21-x}/\text{Ta}_2\text{O}_5/\text{Ta}_3\text{N}_5$ nanocrystals grown on nitrogen-doped reduced graphene oxide showed a remarkable high oxygen reduction performance in acid environment, an electrocatalytic activity comparable to Pt in alkaline medium, and superior stability and methanol tolerance than Pt in both electrolytes. A linear correlation between the occurrence of metal nitrides and pyridinic nitrogen and the activity for oxygen reduction was demonstrated. These species contribute to form the active sites, and when combined with the substoichiometric Ta-oxide phases characterized by oxygen vacancies, create a synergy through such functionalities that increase the adsorption and dissociation of oxygen molecules. The concept presented in this work - hybrid catalyst formed by metal oxide and nitride functionalities supported on graphene to form a highly active and stable ORR catalyst – is a promising alternative to precious metal-based catalysts. This strategy based on tailored surface modification of specific catalytic phases to form hybrid materials can be extended to other formulations providing an avenue to develop new electro-catalysts for various applications.

4. Experimental Section

Materials. Tantalum chloride (TaCl_5 , 99.99%) and graphite flakes (99.8%, metals basis) were purchased from Alfa Aesar. Potassium permanganate (KMnO_4 , 99.8%) and sodium nitrate (NaNO_3 , > 99.0%) were purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4 , 95.0-98.0%

w/w), nitric acid (HNO_3 , 70 % w/w), potassium hydroxide (KOH, 87.1%) and sodium hydroxide (NaOH, 99.2%) were purchased from Fisher Scientific. All chemicals were used as received and solutions were prepared with deionized (DI) water (Millipore Milli-Q, 18.2 M Ω cm). 20% Pt/C (HiSPEC® 3000) was purchased from Alfa Aesar.

Synthesis of the catalysts. Thermally reduced graphene oxide (GP) nanosheets were prepared using the procedure described in our previous paper.^[39] Briefly, natural graphite flakes were oxidized by potassium permanganate in a mixture of concentrated sulfuric acid and sodium nitrate. The suspension was subsequently filtered and washed several times, then dried in a vacuum oven at 60 °C. To obtain the GP nanosheets, the as-synthesized graphene oxide was heated in a tubular furnace at 1050 °C in Ar atmosphere for 2 min.

The Ta-based catalysts were synthesized by the hydrothermal method followed by thermal treatment at high temperature. First, TaCl_5 (163 mg) was dissolved in 15 ml H_2O and 5 ml isopropanol under stirring for 2 hours. In parallel, GP nanosheets (100 mg) were dispersed in 30 ml isopropanol and in 5 ml H_2O for 1 hour. The amount of TaCl_5 was calculated to obtain a nominal composition of 50 wt% of Ta_2O_5 on graphene. Then, the TaCl_5 aqueous solution was added to GP suspension followed by sonication for about 45 min. Afterwards, the pH was adjusted to 10.2 with 1 M NaOH solution, and the mixture was left stirring for 10 min. Then, the solution, and additional 5 ml of DI water used to wash the beaker, were transferred into a three-neck reaction flask equipped with a condenser, and left under stirring for 8 h at 80 °C. The pH was adjusted again to 10.2 with 1 M NaOH solution, and then the solution was transferred (with the aid of 7 ml of DI water) into an autoclave (100 ml volume) for hydrothermal treatment at 150 °C for 3 hours. Next, the product was filtered, thoroughly washed with DI water, and left to dry at room temperature for 3 days.

After the drying step, the powders were subjected to a first thermal treatment in an oven at 60 °C for 0, 6, 10 or 12 days, followed by pyrolysis at 900 °C for 30, 90 or 120 minutes. One sample was subjected to a second oven treatment with 7 days between two pyrolysis steps at 900 °C. Two additional samples were prepared for comparison purpose. The first one consisted of graphene sheets subjected to the same processes as Ta-based samples, i.e., a hydrothermal process in NaOH solution, followed by a thermal treatment in oven at 60 °C for 10 days, and then a pyrolysis at 900 °C in Ar atmosphere for 90 minutes. The second one consisted of a Ta oxide-based sample, subjected to a second pyrolysis at 900 °C in NH_3 atmosphere for 10 minutes. Table S2 summarizes all catalysts investigated in this work.

Physicochemical characterization. The morphology and crystal structure of the catalysts were determined by high-resolution transmission electron microscopy (HR-TEM, JEOL 2010F,

operating at 200 kV) and powder X-ray diffraction (XRD, Bruker D8, with Cu K α radiation (λ = 0.154 nm)). Elemental composition was determined by energy dispersive X-ray analysis (EDAX) equipped in an FEI XL30 instrument. Since EDAX analysis is less accurate in determining the content of light elements, a commercial bulk Ta₂O₅ sample was analyzed under the same conditions to calibrate for the oxygen content. The oxygen sub-stoichiometry in the sodium tantalate was quantified with respect to its crystallographic structure determined from X-ray analysis (Na₂Ta₈O₂₁ JCPDS 28-1137). The surface composition was analyzed by X-ray photoelectron spectroscopy (XPS, Physical Electronics (PHI) 5800-01 spectrometer with monochromatic Al K α X-ray source). The C1s peak (BE = 284.6 eV) was used as the reference line to calibrate the positions of other spectral lines. The fine structure of the photoelectron lines was analyzed using CasaXPS software. The total content of the nitrogen element in the samples was measured by CHNS elemental analysis (CHNS-O Model EA 1112 Thermo Fischer).

Electrochemical measurements. The activity of the catalysts toward the oxygen reduction reaction was evaluated by linear sweep voltammetry using a rotating ring-disk electrode (RRDE). The RRDE consisted of a glassy carbon disk (5.61 mm diameter), surrounded by a Pt ring (6.25 and 7.92 mm inner and outer diameters, respectively). The following ink formulation was used for the Ta-based catalysts: 10 mg of catalyst was dispersed in 350 μ L of ethanol and 95 μ L of 5 wt% Nafion® perfluorinated resin dispersion. A 9 μ L volume was deposited on the glassy carbon disk, resulting in a PGM-free catalyst loading of 817 μ g cm⁻². The state-of-the-art 20 wt% Pt/C (HiSPEC® 3000, Alfa Aesar) was used as an internal reference. In this case, 5 mg of catalyst was dispersed in 85 μ L of DI water, 1650 μ L of ethanol and 50 μ L of 5 wt% Nafion® perfluorinated resin dispersion (Aldrich). Then, 9 μ L of ink was deposited on the glassy carbon disk, resulting in a catalyst loading of 20.4 μ g_{Pt} cm⁻².^[39]

The RRDE measurements were performed at room temperature in a three-electrode single compartment cell filled with 0.1 M HClO₄ or 0.1 M KOH electrolyte solution. The linear sweep voltammograms (LSVs) were recorded at 10 mV s⁻¹ with a Pine potentiostat (model AFRDE4), under N₂- or O₂-saturated electrolyte. The ring electrode was held at 1.3 V vs Reversible Hydrogen Electrode (RHE) during the ORR measurements, and the RRDE rotation rate was set at 1600 rpm. The net ORR Faradic current was obtained by subtracting the voltammogram recorded under N₂ from the one recorded under O₂. Only Faradic currents are presented in the figures.

For a four-electron process, mass transfer-limited current densities close to the theoretical values ($\sim 5.5 \text{ mA cm}^{-2}$ at 1600 rpm in either 0.1 M HClO_4 or 0.1M KOH) are expected. These values are obtained from the Levich equation for the mass transfer-limited current for a perfect smooth disk electrode rotating with an angular velocity of ω :

$$I_l = 0.62nFAD_{O_2}^{2/3}\nu^{-1/6}\omega^{1/2}C_{O_2} \quad (4)$$

where n , F , D , ν , ω , C , and S refer to the number of electrons transferred in ORR (mol^{-1}), Faraday's constant (C mol^{-1}), diffusion coefficient of the analyte ($\text{cm}^2 \text{ s}^{-1}$), kinematic viscosity of the electrolyte ($\text{cm}^2 \text{ s}^{-1}$), angular velocity of the rotating electrode (rad s^{-1}), concentration of the analyte (mol cm^{-3}), and electrode surface area (cm^2).

The following equations were used to calculate the apparent number of electrons transferred during ORR (n) and the percentage of H_2O_2 formed during ORR ($\% \text{H}_2\text{O}_2$):

$$n = \frac{4I_D}{I_D + I_R/N} \quad (5)$$

$$\% \text{H}_2\text{O}_2 = 100 * \frac{2I_R/N}{I_D + I_R/N} \quad (6)$$

where I_D is the disk current, I_R is the ring current and the $N = 0.37$ is the RRDE collection efficiency.^[39]

Computational details. All spin-polarized total energy calculations were carried out using the Vienna *ab initio* simulation package (VASP).^[54] The electron-ion interaction was described by projector augmented-wave (PAW) pseudopotentials.^[55] For the exchange and correlation functional, the Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA)^[56] was employed. The energy cutoff of 550 eV was adopted for the wave functions expansion. The Brillouin zone integration was sampled with a $9 \times 9 \times 7$, $9 \times 5 \times 5$, and $9 \times 7 \times 9$ k-grid mesh for geometry optimizations of Ta_2O_5 , Ta_3N_5 , and NaTaO_3 bulk, respectively. The lattice constants obtained from these settings were tabulated in Table S4, which are comparable to the previous literature.^[57-59] The surface models and the correspondingly work function were treated in Figure S1. The periodic structure of the three crystallographic phases were decoupled by a vacuum thickness larger than 20 Å. Then Gamma points were used for the surface optimization and a $3 \times 3 \times 1$ k-grid mesh was utilized for work function calculations. All the geometries were fully optimized until the atomic forces and energy were smaller than 0.02 eV Å^{-1} and 10^{-6} eV , respectively. The bulk models based on an orthorhombic crystal system were selected on the basis of the XRD results, and the exposed surfaces were built according to the HRTEM micrographs. For the $\text{Na}_2\text{Ta}_8\text{O}_{21}$ model, the exact structural information is still unavailable. So the NaTaO_3 with perovskite structure is employed to model the $\text{Na}_2\text{Ta}_8\text{O}_{21}$ as 1) they share the same

orthorhombic crystal structures, 2) the key physical and geometrical natures of $\text{Na}_2\text{Ta}_8\text{O}_{21}$ can be preserved by NaTaO_3 according to the rule of valance states equilibrium. Regarding the work function calculation for different graphene systems, the Brillouin zone integration was sampled with a $9 \times 9 \times 3$ and $3 \times 3 \times 1$ k-grid mesh for geometry optimizations of the unit cell and supercell, while $9 \times 9 \times 1$ k-grid mesh was employed to calculate the work function. The obtained lattice constant of 2.462 Å is in good agreement with previous reports.^[60,61] Then a 4×4 supercell with the vacuum layer thickness of about 16 Å along *z*-direction was constructed to calculate the work function of doped systems. The work function value of 4.24 eV for the pristine graphene is in good agreement with previous calculations and experiments,^[62-64] indicating the validity of the calculations.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of interest

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Figure 1. High-resolution transmission electron microscopy (HRTEM) images of the four representative Ta-based catalysts, a-d) T1-T4. All oxides and nitride phases are crystalline and were indexed to orthorhombic crystal structures (JCPDS: 28-1137; JCPDS: 25-0922; JCPDS: 19-1291). The lattice plane identification in the HRTEM images is in white for $\text{Na}_2\text{Ta}_8\text{O}_{21-x}$, in yellow is for Ta_2O_5 , and in green is for Ta_3N_5 .

Figure 2. Electrochemical activity for the oxygen reduction reaction in both acid and alkaline media. a,c) Rotating ring (top panel) and disk (lower panel) polarization curves recorded at 10 mVs⁻¹ and 1600 rpm; and b,d) yield of H₂O₂ (top panel) and number of electrons transferred (lower panel) as a function of the disk potential in 0.1 M HClO₄ (a,b) and in 0.1 M KOH (c,d). e) Comparisons of maximum current density of T3 with the reported representative catalysts (based on groups 4 and 5) in literature, in acid medium. The catalysts are identified as following: T1 refers to Na₂Ta₈O_{21-x}/GP, T2 to Na₂Ta₈O_{21-x}/Ta₂O₅/GP, T3 to Na₂Ta₈O_{21-x}/Ta₂O₅/Ta₃N₅/GP and T4 to Na₂Ta₈O_{21-x}/Ta₂O₅/GP; the relative content of Ta₂O₅ in sample T4 is higher than that of in sample T2. Experimental data obtained with a commercial 20 wt% Pt/C (HiSPEC® 3000, Alfa Aesar) are included for comparison.

Figure 3. a,b) Stability and c,d) methanol tolerance tests carried out by chronoamperometry with Na₂Ta₈O_{21-x}/Ta₂O₅/Ta₃N₅/GP (T3) at 0.2 V vs RHE and with 20% Pt/C at 0.6 V vs RHE in O₂-saturated 0.1 M HClO₄, and at 0.75 V vs RHE for both catalysts in O₂-saturated 0.1 M KOH. The arrows in (c,d) indicate the addition of methanol into the electrolyte. The concentration of methanol in the electrolyte was 3 M.

Figure 4. Surface chemical analysis. a) High resolution N 1s/Ta 4p_{3/2} spectra of samples T1 to T4, pristine GP, and GP subjected to the hydrothermal process in NaOH, followed by oven treatment at 60 °C for 10 days and pyrolysis at 900 °C (GP NaOH 10 days). b) Deconvolution of the N 1s / Ta 4p_{3/2} spectrum of sample T3. c) High resolution Ta 4f spectra of samples T1 to T4. d) Deconvolution of the Ta 4f spectrum of sample T3. T1 refers to Na₂Ta₈O_{21-x}/GP, T2 to Na₂Ta₈O_{21-x}/Ta₂O₅/GP, T2 to Na₂Ta₈O_{21-x}/Ta₂O₅/Ta₃N₅/GP and T4 to Na₂Ta₈O_{21-x}/Ta₂O₅/GP; the relative content of Ta₂O₅ in sample T4 is higher than that in sample T2.

Figure 5. Correlation between the activity for the oxygen reduction reaction and the nitrogen content in the catalysts. a-d) Disk potential (at 2 mA cm^{-2}) and current density (at 0.3 V vs RHE) in 0.1 M HClO_4 (a,b) and in 0.1 M KOH (c,d). The red symbols and the green symbols are data obtained from the forward scan of Pt/C catalyst.

Figure 6. Structural, surface and electrochemical characterization of the control sample T5. a) X-ray diffraction pattern; b,c) N 1s and Ta 4f spectra and d) Linear sweep voltammetry recorded at 10 mVs^{-1} and 1600 rpm in O_2 -saturated 0.1M HClO_4 recorded for a $\text{Na}_2\text{Ta}_8\text{O}_{21-x}/\text{Ta}_2\text{O}_5/\text{GP}$ catalyst (sample T4) after being subjected to a thermal treatment in NH_3 atmosphere (sample T5). e) Comparisons of the potential at current density of 2 mA cm^{-2} in acid medium, for sample T1-T5 with different crystal compositions.

Figure 7. Density functional theory calculations. a-c) The geometries and the corresponding work function of NaTaO₃ (a), Ta₃N₅ (b), and Ta₂O₅ (c). d) The schematic band position of Ta₂O₅ and Ta₃N₅ from the literature.^[53] C_{BM} , V_{BM} and E_F refer to conduction band bottom, valence band maximum and Fermi level, respectively.

Figure 8. Schematic illustration of the change of the band level positions of Ta_xM_5 ($x=2$, M=O; $x=3$, M=N) and $\text{Na}_2\text{Ta}_8\text{O}_{21}$ before and after an atomic contact (a), and the schematic charge transfer from Ta_xM_5 to $\text{Na}_2\text{Ta}_8\text{O}_{21}$ after this contact (b).

The table of contents

New hybrid material $\text{Na}_2\text{Ta}_8\text{O}_{21-x}/\text{Ta}_2\text{O}_5/\text{Ta}_3\text{N}_5/\text{Graphene}$ shows a significantly enhanced ORR activity. The experiment and DFT calculation demonstrated the cause from the synergistic effect among the three Ta phases and the N-doped graphene.

Keyword

oxygen reduction reaction, groups 4 and 5, metal oxide, metal nitride, hybrid catalyst

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Title

Engineering of a Low Cost, Highly Active and Durable Tantalate-Graphene Hybrid Electrocatalyst for Oxygen Reduction

ToC figure