One-step route to a hybrid TiO₂/TiₓW₁₋ₓN nanocomposite by \textit{in situ} selective carbothermal nitridation

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Abstract

Metal oxide/nitride nanocomposites have many existing and potential applications, e.g. in energy conversion or ammonia synthesis. Here, a hybrid oxide/nitride nanocomposite (anatase/TiₓW₁₋ₓN) was synthesized by an ammonia-free sol–gel route. Synchrotron x-ray diffraction, complemented with electron microscopy and thermogravimetric analysis, was used to study the structure, composition and mechanism of formation of the nanocomposite. The nanocomposite contained nanoparticles (<5 nm diameter) of two highly intermixed phases. This was found to arise from controlled nucleation and growth of a single oxide intermediate from the gel precursor, followed by phase separation and \textit{in situ} selective carbothermal nitridation. Depending on the preparation conditions, the composition varied from anatase/TiₓW₁₋ₓN at low W content to an isostructural mixture of Ti-rich and W-rich TiₓW₁₋ₓN at high W content. \textit{In situ} selective carbothermal nitridation offers a facile route to the synthesis of nitride-oxide nanocomposites. This conceptually new approach is a significant advance from previous methods, which generally require ammonolysis of a pre-synthesized oxide.

Keywords: oxide/nitride nanocomposite, sol–gel, carbothermal nitridation, Ti–W–N, synchrotron XRD

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1. Introduction

Transition metal nitrides and carbides (e.g. WC, Fe₃N and Co₃Mo₃(N)) are important materials with diverse applications in electronics, catalysis, electrochemistry and hard coatings [1]. As catalysts, they are undergoing a recent revival due to the need for materials based on earth-abundant elements [2–7]. They can exhibit noble-metal-like behavior [8] and therefore have the potential to replace scarce and costly noble metals such as platinum in fuel cell electrodes or as cocatalysts in photocatalytic water splitting [9, 10]. To enhance activity and also prevent sintering, it is desirable to produce a composite with a metal oxide support [11–13]. Other key requirements are small particle size, high interdispersion and good connection between the carbide/nitride and metal oxide particles. However, the synthesis of mixed oxide/carbide or oxide/nitride nanocomposites with such properties presents a considerable challenge. A further question is how to achieve this goal without traditional but inherently
hazardous techniques such as ammonolysis. In this paper, we present a conceptually new approach: in situ selective carbothermal nitridation to synthesize a hybrid oxide/nitride nanocomposite, TiO$_2$/Ti$_x$W$_{1-x}$N.

Nanoparticulate metal nitrides are typically synthesized by ammonolysis of oxide, metal or molecular precursors [14, 15]. While effective, this method poses substantial hazards and technical disadvantages of operating a high-temperature stream of ammonia. As a sustainable alternative, ammonia-free methods have become increasingly popular. They generally use a nitrogen-containing organic precursor such as urea or gelatin to stabilize a metal salt solution and form a homogeneous gel-like precursor. On heating under nitrogen, the precursor decomposes to form a metal nitride nanomaterial. This method is very flexible and has been used to synthesize nanostructures of many different nitrides, e.g. GaN, WN, TiN and Fe$_3$N [16–18]. The advantage of the gel precursor is that reagents can be mixed on a molecular level, which leads to lower reaction temperatures and a much smaller particle size.

For nitridation of an oxide, the nitridation temperature varies depending on the stability of the metal oxide [19]. This principle has been used to achieve selective nitridation in the synthesis of mixed oxide/nitride composites. Generally, this involves pre-synthesis of a composite or solid-solution oxide precursor followed by selective nitridation of the oxide under a stream of ammonia [20–22]. Alternatively, a metal oxide support can be impregnated with a nitrogen-rich precursor solution of a second metal followed by decomposition under ammonia or an inert gas [23, 24]. However, these methods have only been applied to a limited number of systems. Furthermore, the use of a preformed metal oxide means that the resulting particles tend to be relatively large. No attempts of a direct synthesis of a nitride/oxide nanocomposite from a homogeneous gel precursor have been reported.

In this paper, we demonstrate a one-step synthesis of an oxide/nitride nanocomposite, anatase/Ti$_x$W$_{1-x}$N, using a sol–gel method. The use of a gel precursor ensures that the particle size of both phases is kept very small (<5 nm). The biopolymer alginate was selected as the organic gel precursor. Alginate is the structural component of many types of seaweed and comprises a carboxylate-functionalized polysaccharide, which is strongly cross-linked by metal polysaccharide, which is strongly cross-linked by metal cations in water. This metal-binding ability has been shown to make alginate an effective template for synthesizing nanostructures of metal oxides and carbides [25–27]. Electron microscopy and scanning energy-dispersive x-ray analysis revealed that the synthesized oxide and nitride particles are highly interspersed. We investigated the synthesis using synchrotron x-ray diffraction (XRD) over a wide range of temperatures and Ti:W compositions to identify the necessary conditions for nanocomposite formation. A study of the mechanism suggests that the reaction proceeds through nanoparticles of a W-doped anatase intermediate, which phase-separates into W-rich and W-poor domains. The organic component decomposes to a carbon-rich matrix around the oxide nanoparticles and then induces selective carbothermal nitridation of the W-rich oxide to a ternary Ti$_x$W$_{1-x}$N solid solution while leaving the W-poor anatase unchanged.

2. Experimental details

Nanocomposites of anatase/Ti$_x$W$_{1-x}$N were prepared via an aqueous sol–gel method. Titanium ethoxide (Ti(OEt)$_4$, 12.5 g) was first stabilized against oxidation by mixing with acetylacetone (5 g) in ethanol (20 g) [28]. An aliquot of the resulting clear solution was added to a solution of ammonium alginate and ammonium metatungstate in water with fast stirring. More details can be found in supplementary information (table S1 available online at stacks.iop.org/STAM/13/035001/mmedia). The mixture initially became cloudy yellow but then changed to deep orange. Thickening occurred very rapidly, as the alginate polymer was strongly cross-linked by the Ti$^{4+}$ cation and the mixture formed a gel on standing. At high W content, the mixture was much less viscous owing to the low affinity of alginate for the tungstate anion. Furthermore, the high-W mixture remained cloudy, possibly due to the precipitation of poorly soluble tungsten oxide from the ethanolic solution. Drying the gel in an oven at 100 °C produced a brittle glassy solid with an orange color. Samples of the gel were calcined in capped crucibles in a muffle furnace in N$_2$ flow, with the temperature increased to 900 °C at a rate of 10 °C min$^{-1}$. The furnace was then cooled under a continuous N$_2$ flow before the iridescent blue–green solids were removed. All the samples were ground to black powders in a mortar for analysis. To find the optimum conditions for producing an oxide/nitride composite, several parameters were varied including calcination temperature, Ti:W molar ratio (100:0, 90:10, 75:25, 50:50 and 0:100), carbon content (low (10 g), medium (20 g) and high (30 g) alginate content, based on mass of a 10% polymer solution) and calcination rate. The complex mixtures of crystalline phases resulted in a large number of XRD peaks that sometimes overlapped with each other. The XRD pattern was further complicated by considerable line broadening due to the small particle size. Therefore, the samples were analyzed using the Spring-8 BL15SU synchrotron beamline equipped with imaging plates [29] to maximize peak resolution and signal-to-noise ratio. Additionally, the low divergence of the x-ray beam from the synchrotron reduced the line broadening. Extra samples (quenched at 100 °C intervals for study of the reaction mechanism) were analyzed using a Rigaku Ultima + x-ray diffractometer with Cu K$_\alpha$ radiation (~8 h per sample). Additional characterization details are provided in supplementary information.

3. Results and discussion

Figure 1 shows the powder XRD (PXRD) pattern of an optimized sample (10 mol% W), together with reference lines for anatase (ICDD 01-070-7348), rutile (ICDD 01-072-4812) and a ternary Ti$_{0.5}$W$_{0.5}$N phase. From the pattern, it is clear that the primary Ti-phase in this sample is anatase with some small sharp peaks corresponding to rutile. The presence of this minor rutile phase can be ascribed to an imperfect N$_2$ atmosphere in the muffle furnace used for calcination. The peak positions for the second phase lie between those of...
cubic TiN and WN. Ti\(_x\)W\(_{1-x}\)N was previously described with various compositions [30]; this phase is characterized by a lattice expansion and subsequent peak shift from cubic tungsten nitride (WN) toward cubic TiN, as well as a change in the relative peak intensities [31]. This lattice expansion was modeled using Carine 3.1 Crystallography software, assuming a linear change of the lattice parameters with composition (tables S2 and S3 available online at stacks.iop.org/STAM/13/035001/mmedia). Comparing the experimental data with the reference patterns for WN, TiN and the simulated Ti\(_{0.5}\)W\(_{0.5}\)N ternary phase, it is clear that the sample peak position and intensity can be best attributed to a Ti\(_x\)W\(_{1-x}\)N solid solution (figure S1). The particle size was estimated using the Scherrer equation as 2–3 nm (table S4) for both the anatase and ternary nitride phases. This result is consistent with scanning and transmission electron microscopy (SEM and TEM) images of the sample (figure 2), which show agglomerated nanoparticles, typically <5 nm in size. Nitrogen porosimetry (BET) indicated a relatively high surface area of \(\sim 190\,\text{m}^2\text{g}^{-1}\), which is consistent with the small particle size. High-resolution TEM images show lattice fringes for each nanoparticle crystallite. The lattice fringe spacings and interplanar angles for each particle can be assigned to either anatase or titanium tungsten nitride. An example of a Ti\(_x\)W\(_{1-x}\)N crystallite is shown in the inset in figure 2(d). Black lines in this image correspond to an interplanar angle of 90°, which is consistent with the angle between the (220) and (−110) planes. Energy-dispersive x-ray analysis (EDXA) line scans (figure 2(c)) show Ti-rich and Ti/W-rich regions, supporting the identification of a biphasic TiO\(_2\)/Ti\(_x\)W\(_{1-x}\)N system. The elemental composition (wt%) was measured as Ti (25.5%), W (10.6%), C (33.9%), N (2.3%) and O (25%). This is approximately in agreement with the theoretical composition, calculated for a mixture of anatase and Ti\(_x\)W\(_{1-x}\)N. The high carbon content is a result of decomposition of the organic biopolymer, and it is likely a mixture of amorphous and graphitic phases. There is evidence in TEM images of stacked layers characteristic of graphitic carbon wrapping parts of the sample (figure S2).

Examination of the PXRD data over a range of Ti/W ratios offers more insight into the formation and composition of the TiO\(_2\)/Ti\(_x\)W\(_{1-x}\)N system (figure 3(a)). The anatase peak progressively weakens with increasing W content and almost disappears at 50 mol% W. Meanwhile, Ti\(_x\)W\(_{1-x}\)N emerges as the dominant component, indicating that at 50 mol% W, almost all the Ti is contained within a Ti\(_x\)W\(_{1-x}\)N ternary nitride phase. In figure 3(b), a magnified section of this PXRD profile is plotted together with a control pattern of tungsten nitride (100 mol% W, prepared using the same sol–gel method at 800 °C), reference lines for TiN and WN, and the simulated pattern for Ti\(_x\)W\(_{1-x}\)N. The shift to a smaller d-spacing with increasing W content is consistent with a shift from a Ti-rich ternary nitride to a W-rich ternary nitride. It should be noted that the shoulder at \(\sim 15\)° is due to TiO\(_2\) (rutile), and the broad peak at 2θ = 18° for 0 mol% W is attributed to a titanium monoxide (TiO) phase. The Ti\(_x\)W\(_{1-x}\)N peak for 50 mol% W appears at a very similar position to the control sample, supporting the prediction of a W-rich ternary nitride phases. This phase separation becomes more apparent at higher diffraction angles (figure S3), although full deconvolution of the peaks at 2θ \(\sim 25.5°\) and 30° is complicated by the presence of W\(_2\)C as a minor phase. Intrinsic instability in solid solutions is well known and can lead to phase separation into isostructural components, in this case, Ti-rich and W-rich cubic Ti\(_x\)W\(_{1-x}\)N [32]. Further evidence for the separate phases comes from heating the 50 mol% W sample for an additional 3 h at 900°C. PXRD (figure S4) shows that additional heating causes a shift in the Ti\(_x\)W\(_{1-x}\)N peaks back to a larger d-spacing, indicating that Ti-rich Ti\(_x\)W\(_{1-x}\)N becomes the dominant ternary nitride phase. This shift is coupled with a substantial strengthening of the W and W\(_2\)C peaks. These data are consistent with the Ti-rich and W-rich ternary nitrides having different thermal stabilities. Under carbothermally reducing conditions, many interstitial nitrides transform to carbides and finally to the most thermodynamically stable elemental phase. Here, the Ti-rich ternary nitride is more stable and remains unchanged, while the W-rich counterpart transforms to W\(_2\)C/W. Returning to figure 3, at low W content, there is also a slight shift in the anatase peak with increasing W content, suggesting some doping of W into the anatase phase (figure S5). Tungsten doping into anatase is well known and is used to modify the properties of anatase such as the band gap [33]. The minor rutile phase undergoes a more substantial peak shift at 50 mol% W, indicating the formation of Ti\(_x\)W\(_{1-x}\)O\(_2\) with a rutile structure (ICDD 01-085-0270).

The sol–gel synthesis of binary metal nitrides and carbides strongly depends on the metal:carbon ratio [16]. To investigate the effect of carbon content in this mixed oxide/nitride system, a series of samples with 0–100 mol% W were prepared using low and high organic (alginate) content in the precursor. They were compared with the already discussed samples, which are designated as having ‘medium organic content’. XRD patterns show that for
Figure 2. (a) SEM, (b) bright-field TEM and (c) dark-field TEM images with corresponding EDXA line profiles for tungsten and titanium. (d) High-resolution TEM image with the black lines in the inset showing the spacings and relative orientation between the (220) and (−111) planes of Ti$_x$W$_{1-x}$N.

Figure 3. (a) PXRD patterns of samples with different W contents (mol% as total of Ti + W). (b) Section of (a) with added reference pattern for a control sample of WN (100 mol% W) prepared at 800 °C.

samples containing no tungsten or 10 mol% tungsten, the anatase peaks broaden and weaken with increasing organic content (figures 4(a) and S6(a) available online at stacks.iop.org/STAM/13/035001/mmedia). This is because the organic biopolymer decomposes to amorphous carbon, which restricts the growth and sintering of the anatase nanoparticles. At high carbon content, the minor peaks for TiO also become more prominent as a result of increased carbothermal reduction of anatase. For the mixed Ti/W sample of 25 mol% W, XRD data show only minor changes
in composition with increased carbon content (figure 4(b)). This again is coupled with reduced peak intensity and peak broadening of the primary anatase and Ti$_x$W$_{1-x}$N phases. For samples containing 50 mol% W, XRD patterns show a weakening of the elemental tungsten peak with increasing carbon content (figure 4(c)). This is coupled with a change in the peak shape for the primary Ti$_x$W$_{1-x}$N phase (figure 4(d)). As discussed above, the ‘skewed’ shape of the Ti$_x$W$_{1-x}$N peaks indicates the presence of separate Ti-rich and W-rich phases. In this case, the peak maximum shifts from Ti-rich to W-rich Ti$_x$W$_{1-x}$N phase with increasing carbon content, and the elemental W peak weakens. This indicates that a high carbon content stabilizes the W-rich ternary Ti$_x$W$_{1-x}$N phase against decomposition to elemental W, which is consistent with observations in binary nitride systems [18]. At 100 mol% W, a high carbon content also appears to stabilize W$_2$C against decomposition to the more thermodynamically stable elemental W phase (figure S6(b) available online at stacks.iop.org/STAM/13/035001/mmedia). Interestingly, the Ti$_x$W$_{1-x}$N solid solution is considerably more stable than the pure WN phase. A control sample of tungsten nitride could only be isolated by reducing the heating temperature to 800 °C and using a high organic content (figure S7). However, the Ti-doped tungsten nitride was stable over a wide range of conditions and compositions.

To investigate the formation mechanism of the anatase/Ti$_x$W$_{1-x}$N nanocomposite, a series of samples were quenched from 600, 700, 800 and 900 °C and analyzed by PXRD. For samples with a low tungsten content (0, 10 or 25 mol%), the primary phase up to 800 °C is anatase (figures 5(a) and (b) and S8(a)). The broad peaks indicate a very small particle size. The size increases slightly for all the samples from <1 nm to approximately 3–4 nm with the temperature increasing from 600 to 900 °C, as calculated using the Scherrer equation (table S5). The very small particle size is related to the strong templating effect of the biopolymer precursor. Alginate is a negatively charged carboxylate-rich polysaccharide that binds very strongly to multivalent metal cations [34]. In this system, addition of the Ti-acetylacetone precursor to alginate considerably increased the viscosity, showing cross-linking of the biopolymer by the Ti cation. This templating effect has been shown many times to constrain the nucleation and growth of crystalline materials in the sol–gel synthesis of metal-oxide and carbide nanostructures [25–27]. For samples containing 10 or 25 mol% W, the ternary Ti$_x$W$_{1-x}$N phase begins to emerge at 800 °C with a substantial increase in the Ti$_x$W$_{1-x}$N:anatase peak intensity ratio between 800 and 900 °C. This suggests that direct nitridation of a W-doped anatase is the mechanism of formation of the Ti-rich Ti$_x$W$_{1-x}$N. A question arises at this point: why are these low-W-content samples not completely transformed to a ternary Ti$_x$W$_{1-x}$N? This is possibly due to phase separation in the W-doped anatase leading to relatively W-rich and W-poor TiO$_2$ crystallites. Phase separation in mixed Ti–W oxides was previously observed [35]. The W-rich phase then transforms to Ti$_x$W$_{1-x}$N leaving the W-poor phase unchanged as an anatase phase. Further evidence for this comes from holding the 10 mol% W sample at 900 °C for a longer time (figure S9). Rather than all the anatase eventually transforming to Ti$_x$W$_{1-x}$N, the anatase/Ti$_x$W$_{1-x}$N mixture becomes a rutile/Ti$_x$W$_{1-x}$N mixture.

At a higher concentration of W (50 mol%), the XRD data for samples quenched at 600, 700 and 800 °C show a mixture...
of peaks originating from anatase and WO\textsubscript{2} (figure 5(c)). Small peaks for Ti\textsubscript{x}W\textsubscript{1−x}N are present at 800 °C and this is the primary phase at 900 °C. The sharp peaks for WO\textsubscript{2} indicate that this phase has a significantly larger crystallite size than the anatase phase in low-W samples. This is possibly because the tungstate anion would have a much lower affinity than Ti\textsuperscript{4+} for the negatively charged alginate in the precursor gel. This would result in a weaker templating effect of the biopolymer on crystalline WO\textsubscript{x} phases. Another factor could be precipitation of amorphous WO\textsubscript{3} in the precursor gel, since tungstate salts have limited solubility in water and this would be reduced further by the presence of some ethanol. As noted in the experimental section, some cloudiness was observed when preparing mixed Ti/W samples with a high W content, indicating the precipitation of a poorly soluble phase. At 900 °C, the Ti\textsubscript{x}W\textsubscript{1−x}N solid solution prepared from the 50 mol% W sample separated into isostructural Ti-rich and W-rich phases (figure 3). Given the presence of separate titanium and tungsten oxides at lower temperatures, it seems likely that the isostructural nitride phases form via separate mechanisms. The W-poor Ti\textsubscript{x}W\textsubscript{1−x}N probably forms via nitridation of W-doped anatase, as observed for samples with low W content. Formation of the W-rich Ti\textsubscript{x}W\textsubscript{1−x}N is likely to occur via nitridation of WO\textsubscript{2}. There is no clear peak shift with increasing Ti content in the WO\textsubscript{2} phase. However, the peak for W-rich Ti\textsubscript{x}W\textsubscript{1−x}N appeared at a 2\theta value very similar to that of the control WN sample. This suggests a very low level of Ti doping into this phase, which explains the lack of a peak shift for WO\textsubscript{2}. Further evidence of direct nitridation of the WO\textsubscript{2} phase comes from the control 100 mol% W sample. PXRD of a sample quenched at 800 °C (figure S8(b) available online at stacks.iop.org/STAM/13/035001/mmedia) shows a mixture of WO\textsubscript{2} and WN peaks, indicating a mechanism of nitridation of WO\textsubscript{2}. In this case, the nitride has a lower stability than the ternary Ti\textsubscript{x}W\textsubscript{1−x}N and transforms to W\textsubscript{2}C between 800 and 900 °C.

Thermogravimetric analysis (TGA) data offer further insight into the nitridation mechanism (figure 5(d)). All the samples show a characteristic sharp mass loss at approximately 200 °C corresponding to the major decomposition step of the alginate biopolymer matrix. This is consistent with previous thermal decomposition studies of metal–alginate complexes [36]. Above 500 °C, the rate of mass loss increases with increasing W content. The most rapid mass loss occurs for the sample containing 100 mol% W. This is consistent with the WO\textsubscript{2}-to-WN transformation that was observed in the XRD profile of the 800 °C sample since carbothermally nitridation of WO\textsubscript{2} should result in mass loss through the evolution of CO/CO\textsubscript{2}. With increasing Ti content, a larger part of the sample remains in the anatase phase. With less of the sample being carbothermally reduced, the mass loss is correspondingly lower.

The proposed mechanism for the formation of the anatase/Ti\textsubscript{x}W\textsubscript{1−x}N nanocomposite is summarized in figure 6. At low W content, the alginate forms a homogeneous gel, strongly binding the Ti\textsuperscript{4+} cations and dispersing the tungstate

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Figure 5. PXRD patterns for samples containing (a) 10, (b) 25 and (c) 50 mol% W quenched at 600, 700, 800 or 900 °C. (d) TGA profiles (arrow indicates the mass loss trend with increasing W content).
ions. On heating, the gel constrains the nucleation and growth of W-doped anatase nanoparticles before decomposing to an amorphous carbon matrix that prevents sintering of the nanoparticles. Further heating forces phase separation into W-rich and W-poor regions. The carbon-rich matrix then induces selective carbothermal nitridation of the W-rich Ti–W–O phase to Ti₅W₁₋ₓN. The W-poor anatase is more resistant to carbothermal nitridation and so remains as an oxide. At high W content (50 mol% W), a different mechanism is proposed. Firstly, WOₓ is precipitated in the precursor gel. On heating, there are two distinct oxide intermediates: WOₓ and W-doped anatase. They undergo carbothermal nitridation to form WN and Ti-rich TiₓW₁₋ₓN, respectively (figure S10 available online at stacks.iop.org/STAM/13/035001/mmedia).

4. Conclusions

In summary, we have demonstrated a one-step route to a nitride-oxide nanocomposite, anatase/TiₓW₁₋ₓN. This is achieved via a simple sol–gel method yielding a finely dispersed mixture of nanoparticles (<5 nm) of the two phases. Synchrotron x-ray diffraction patterns show that increasing W content resulted in a shift from anatase as the primary phase (0 mol%) to an anatase/TiₓW₁₋ₓN mixture (10–25 mol%), and finally, to a composite of isostructural Ti-rich and W-rich TiₓW₁₋ₓN (50 mol%). The order of thermal stability of the various nitride phases was determined to be WₐN < W-rich TiₓW₁₋ₓN < Ti-rich TiₓW₁₋ₓN. As has been observed in single-component nitride and carbide systems, a higher carbon content stabilizes the nitrides against decomposition to elemental phases. The formation mechanism depended strongly on the Ti/W ratio. At low W content, it appears that a stable W-doped anatase precursor exists as the only phase. This then separates into W-rich and W-poor anatase phases, followed by selective carbothermal nitridation of the high-W anatase to give an anatase/TiₓW₁₋ₓN mixture. If the amount of W in the precursor gel is too high, phase separation occurs from the start, resulting in the precipitation of a WOₓ phase. W-doped anatase nanoparticles then nucleate around this phase and both phases undergo carbothermal nitridation to give a mixed nitride product.

In situ selective carbothermal nitridation offers a facile new route to nitride-oxide nanocomposites based on simple procedures and precursors. This procedure presents a substantial advance over previous methods, which rely on pre-synthesis of an oxide composite or impregnation of a binary oxide with a second precursor, followed by ammonolysis, and tend to produce materials with relatively large grains. This investigation opens many directions for exploring nitride/oxide nanocomposites through phase separation and subtle variations in crystal phase stability. The extension of this synthesis to general oxide/nitride and oxide/carbide nanocomposites is currently under investigation. Furthermore, the presence of conductive graphitic carbon combined with oxide/nitride or oxide/carbide nanoparticles could produce materials of interest for electrocatalysis. For example, metal carbide and metal oxide nanoparticles combined with graphitic carbon are of interest for the oxygen reduction reaction as catalysts and cocatalysts, respectively [37, 38].

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