



Full Length Article

Reduced-graphene-oxide supported tantalum-based electrocatalysts: Controlled nitrogen doping and oxygen reduction reaction



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ABSTRACT

Controlled N-doping is feasible to engineer the surface stoichiometry and the electronic configuration of metal-oxide electrocatalysts toward efficient oxygen reduction reactions (ORR). Taking reduced graphene oxide supported tantalum-oxides (TaO_x/RGO) for example, this work illustrated the controlled N-doping in both metal-oxides and carbon supports, and the contribution to the improved ORR activity. The active N-doped TaO_x/RGO electrocatalysts were fabricated via SiO₂-assisted pyrolysis, in which the amount and kind of N-doping were tailored toward efficient electrocatalysis. The optimal nanocomposites showed a quite positive half-wave potential (0.80 V vs. RHE), the excellent long-term stability, and the outstanding tolerance to methanol crossing. The improvement in ORR was reasonably attributed to the synergy between N-doped TaO_x and N-doped RGO. Elucidating the importance of controlled N-doping for electrocatalysis, this work will open up new opportunities to explore noble-metal-free materials for renewable energy applications.

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1. Introduction

Exploring high-performance and low-cost electrocatalysts for oxygen reduction reaction (ORR) is a major challenge for the large-scale application of fuel cells, metal-air batteries, etc [1–3]. Currently, platinum (Pt) and Pt-based alloys are the most efficient materials [4,5]; however, they cannot meet the demand for the widespread commercialization because of their scarcity, low durability and susceptibility to poisoning [6]. Thus, the ongoing search for Pt-free ORR catalysts has attracted much attention [6,7]. An interesting class of cost-efficient electrocatalysts is the metal oxides of groups 4 and 5 (Ti, V, Zr, Nb, Hf and Ta), due to their good stability and low cost [8–10]. They become active for ORR if the surface stoichiometry is conveniently tailored, and the resulting oxygen vacancies serve as the active sites for O₂ adsorption and activation [11,12]. Many efforts dealing with surface modification have been made, and introducing nitrogen to substitute oxygen is demonstrated feasible [13,14]. Nitrogen doping (N-doping) can create abundant surface oxygen-vacancies to enable O₂ adsorption, and more importantly increase valance band and Fermi level in parent metal oxides [15–17]. This effect is of great importance in electrocatalytic ORR, because it will promote the adsorption, activation, and dissociation of oxygen species.

The low conductivity of metal oxides remains as another bottleneck in electrocatalytic ORR that requires a four-electron process to reduce O₂ to OH⁻. The integration with conducting matrix, e.g., carbon nanotubes (CNT) and graphene, would remarkably improve the conductivity and thus the ORR activity [18,19]. Meanwhile, carbon-based supports also provide large surface for anchoring highly dispersed active oxides, successfully avoiding the sintering of catalysts during N-doping at high temperature. For such carbon-supported electrocatalysts, the N-doping into the both of oxides and carbon supports should be noticed [20]. The former is responsible for the varied electronic property and surface stoichiometry of metal-based active sites, while, the latter makes influences on conductivity, and even creates new active-sites on carbon [21,22]. The pyridinic and pyrrolic N atoms, which have planar structures, are active for electrocatalytic ORR [23]. In contrast, quaternary and oxidized N atoms, possessing a 3D structure, are inactive. Even more, quaternary N atoms lead to the poor conductivity because of the interruption of their π-π conjugation by the 3D structure. More importantly, the effect of oxide-carbon hetero-interface enhanced by N-doping should be taken into account for catalyst design. Recently, the evidenced Co–N bonds were highlighted in N-doped CNT (N-CNT) and reduced-graphene-oxide (N-RGO) supported cobalt-oxides [24], and the resulting electronic interactions between metal oxides and carbon supports, as well as their synergic enhancement, are responsible for the efficient ORR. However, in the most of previous reports, the N-doping in both metals/metal oxides and carbon is unfortunately ignored, prohibiting the further

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improvement in electrocatalysis and the insight into structure-activity relationship. To this end, the precisely-controlled N-doping into both oxides and carbon is thus demanded to explore metal-oxide-based efficient electrocatalysts.

Taking reduced graphene oxide (RGO) supported tantalum-oxides for example, this work demonstrates the controlled N-doping in both metal-oxides and carbon supports, and illustrates their contribution to ORR activity. Improved from our previous work [25], a silica assisted urea-glass route is utilized to control N-doping in both TaO_x and RGO (Scheme 1), in which the varied feeding ratio of urea/ TaCl_5 ($R_{\text{U/Ta}}$) leads to the accordingly varied amount and type of N-doping. The assisting SiO_2 nanoparticles are removed via the treatment with NaOH aqueous solution, and the N-doped TaO_x supported by RGO (denoted as N-TaO_x/RGO-n, n referring the feeding $R_{\text{U/Ta}}$) nanocomposites are finally harvested. With the assistance by SiO_2 , the N-doping into TaO_x is enhanced, which results in the enriched electrons around Ta and the consequently improved ORR activity. Meanwhile, the N-doping into RGO is also affected by SiO_2 , being responsible for the conductivity of electrocatalysts. As expected, the optimal composites present a high ORR activity in an alkaline electrolyte (0.1 M KOH), featured by an onset potential of 0.88 V (vs. RHE), a half-wave potential of 0.80 V (vs. RHE), and excellent long-term stability and methanol tolerance outperforming Pt/C. Elucidating the efficient ORR associated with controlled N-doping, this work will shed some light on the development of cost-effective materials in energy field.

2. Experimental section

2.1. Catalyst synthesis

Typically, 0.125 g of TaCl_5 powder was added to 5 mL of methanol, followed by introducing 0.1 g of SiO_2 , 0.071 g of graphene oxide (GO) and a varied amount of urea. The mixture was let dry to

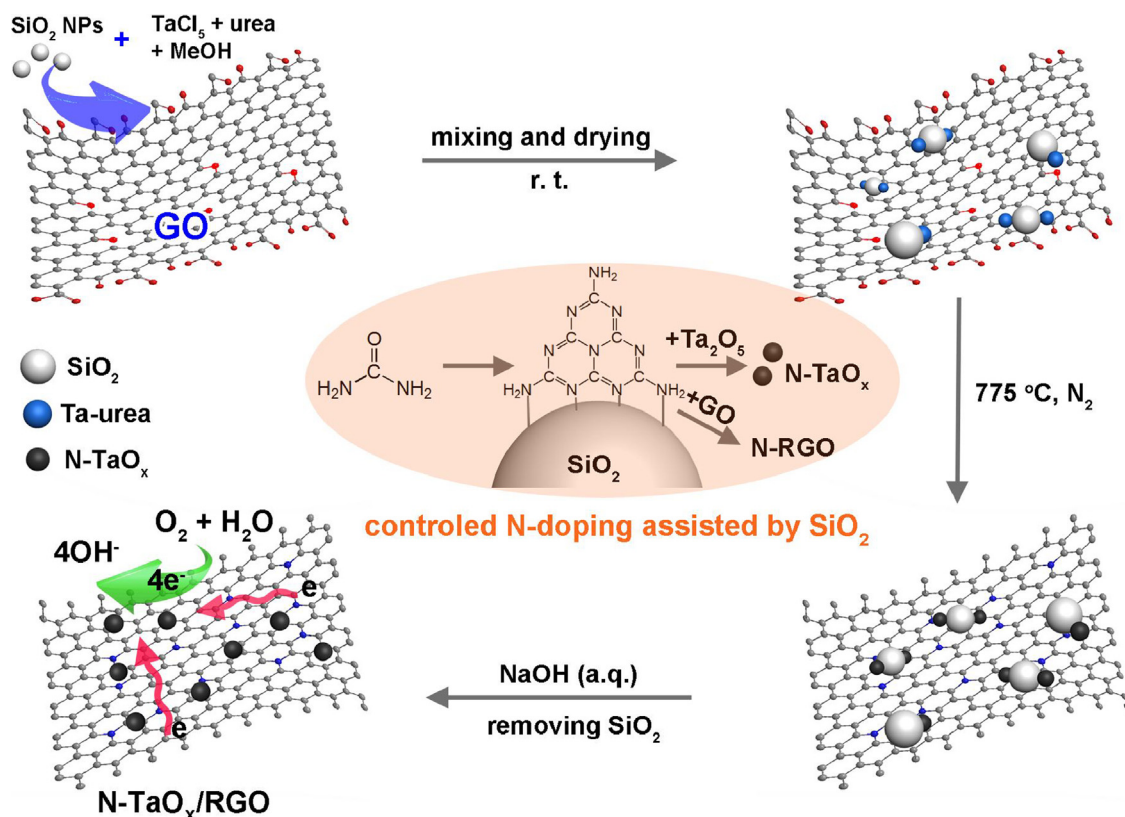
gel under stirring at room temperature, and then transferred into an oven and kept under N_2 flow (250 mL min^{-1}) for 2 h to remove air before heating. Afterwards, it was heated to 775°C with a ramping rate of 5°C min^{-1} , and kept for 5 h. After treating the as-received powders with 2 M NaOH (aq.), the N-TaO_x/RGO electrocatalysts were harvested.

2.2. Physical measurement

X-ray diffraction (XRD) analysis was performed on Bruker D8 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) investigations were taken on a ZEISS ULTRA55 and a JEOL JEM 2100F, respectively. Energy dispersive spectrum (EDS) was carried out on a JEOL JEM 2100F. X-ray photoelectron spectroscopy (XPS) analysis was processed on a Perkin-Elmer PHI X-tool, using C 1s (B. E. = 284.6 eV) as a reference. The N content in the obtained catalysts was determined by CHN elemental analysis using a Vario EL Elementar. Thermogravimetric analysis coupling with differential scanning calorimeter (TGA/DSC) was tested on NETZSCH STA449F3 under N_2 flow. N_2 adsorption-desorption isothermal was conducted on an automatic gas adsorption analyzer (Quantachrome AutosorbIQ-MP). Raman spectra were recorded on a laser confocal Raman microspectrometer (XploRA, Horiba Jobin Yvon, Ltd.), with an excitation laser wavelength of 633 nm.

2.3. Electrochemical tests

Electrochemical analyses were performed in a conventional three-electrode electrochemical system connected with a CHI 760D electrochemical station (CH Instruments, Inc.). A rotating disk electrode (RDE) with a glassy carbon disk (5.0 mm in diameter) was used as the working electrode, which was installed on a RDE system (Princeton Applied Research, US). Ag/AgCl (3 M KCl) and Pt



Scheme 1. Schematic illustration for fabricating N-TaO_x/N-RGO electrocatalysts with controlled N-doping.

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