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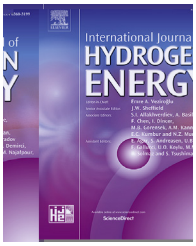

The individual role of pyrrolic, pyridinic and graphitic nitrogen in the growth kinetics of Pd NPs on N-rGO followed by a comprehensive study on ORR

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ABSTRACT

In order to develop and replace the expensive PtC catalyst from the fuel cells, we have attempted to synthesize an efficient catalyst for oxygen reduction reaction (ORR) in an alkaline media. The materials were initially fabricated as follows; (a) synthesizing a nitrogen doped (para-xylylenediamine, nitrogen precursor) graphene oxide (N-rGO); (b) synthesizing palladium nanoparticles on graphene oxide surface (rGO-Pd). The electrochemical analysis showed that the ORR path on the N-rGO catalyst is observed to follow 2-electron mechanism. Conversely, the onset potential, current density and surface area of the rGO-Pd doesn't match with the commercially available PtC catalyst. To overcome these flaws, we have combined the individual effects of each component and fabricated N-rGO-Pd nanocomposite. The covalent interaction between nitrogen part of para-xylylenediamine with oxygenated functionalities of GO, followed by a strong π–π stacking interaction between the aromatic ring of para-xylylenediamine and GO altered the electronic distribution of the carbon support, induced more defects, influenced the size and averted the self agglomeration of the Pd NPs which lead to the astonishing catalytic activity of N-rGO-Pd catalyst. Furthermore, various spectroscopic techniques revealed the individual influence of pyrrolic, pyridinic and graphitic–N on the synthesis, size and extraordinary distribution of Pd NPs.

Introduction

Copious amount of researchers around the world is putting their dedicational efforts in the development of renewable-energy and storage devices such as rechargeable metal-air batteries [1–3], CO_2 electrochemical reduction [4], water splitting cells [5,6] and regenerative fuel cells (FCs) [7]. The commercial development of aforementioned devices is hindered due to sluggish cathodic oxygen reduction reaction (ORR) and anodic oxygen evolution reaction (OER). The complicated multi-electron transfer process resulted in the slow kinetics and high overpotential. Hitherto, Pt-based materials have proved itself to be an excellent catalyst towards sluggish ORR kinetics [8–10], but its vulnerability to poisoning, scarcity of resources, high cost and electrochemical deactivation made us

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look insight for its substitution [11–14]. Amid various candidates, Pd has shown promising electrocatalytic behavior along with resistance to CO poisoning in comparison to Pt-based materials for FCs [14,15]. Furthermore, Pd is cheaper (349.91 $ per gram) than Pt (424.30 $ per gram) [Sigma Aldrich; 2017 Price] along with distinguished electrochemical stability than other 3d transition metals like Co, Ni, and Fe. Therefore, the fabrication of palladium nanoparticles (Pd NPs) have gained massive consideration from the scientific community due to their strong catalytic effects in the redox reaction for a variety of applications including electrochemical sensors [16], biosensors [17], water splitting [18], hydrogen storage [19], lithium-ion batteries [20], lithium air batteries [21] etc. The synthesis and dispersion of Pd NPs require an electrochemically active substrate surface to facilitate their role in the electrochemical process.

Graphene, a three-dimensionally arranged single sheet of carbon in a honeycomb lattice has been the spotlight since its discovery in 2004. The astonishing electrical conductivity, large theoretical specific surface area, good electrochemical stability and a tunable band gap made it a promising substrate [22] in numerous applications such as rechargeable lithium-ion batteries [21], transistors [23], ultra-sensitive sensors and biosensors [24,25], photocatalytic degradation [26,27], supercapacitors [28] and in FCs [29]. However, its derivative, graphene oxide (GO), possesses not only the inherited properties of graphene but also abundant anchoring sites (functional groups, mainly carboxyl, epoxy, hydroxyl) to immobilize various active species. Although, the Sp^3 hybridization of the carbon basal plane with oxygen functionalities brings an insulating character to the GO surface, but it's possible to tune it either by chemical or electrochemical reduction. Thereby, renovating the semimetal or semiconductor like graphenic properties [30–34].

As we all know, in the last decade incorporation of heteroatoms such as nitrogen, boron [35], phosphorus [36], and sulfur [37] into the basal plane of carbon has gathered huge attention. Amid all aforementioned doping elements, N managed the stream light due to its comparable atomic size with carbon and the availability of five valence electrons to get incorporated into the basal plane of carbon [38–42]. In addition, nitrogen doping is believed to influence the growth kinetics of Pd NPs which eventually leads to the small particle size and uniform dispersion [41]. The literature survey suggests that the introduction of nitrogen into carbon plane alters the geometry and the electron donor character of the nanocomposite by redistribution of the electronic density of the adjacent carbon atoms inducing an electrophilic center in the vicinity of heteroatom [38].

By keeping in view the literature survey, herein, we report the synthesis of (N-rGO-Pd), an electrochemically active catalyst from the dual interaction of GO and para-xylylenediamine (a nitrogen precursor) followed by the fine dispersion of Pd NPs. There are two reasons for using para-xylylenediamine as a nitrogen precursor. (i) The linker $-NH_2$ position of para-xylylenediamine will covalently react with oxygen functionalities of GO through condensation reaction (ii) followed by strong π-π stacking interactions between aromatic rings of para-xylylenediamine and GO which will induce the redistribution of the electronic density, thus will eventually create an electrophilic and nucleophilic character in the material. Different types of nitrogen incorporation into carbon nanomaterials have been found in the literature with four distinctive types including pyrrolic, pyridinic, graphitic and pyridinic–N–oxide [42]. Among these nitrogen types, pyridinic–N and graphitic–N are sp^2 hybridized whereas, pyrrolic–N is sp^3 hybridized. The pyridinic–N bonds with two C atoms at the edges or defects of graphene and contributes one p electron to the p system. Pyrrolic–N refers to N atoms that contribute two p electrons to the p system. Whereas, graphitic–N refers to N atoms that substitute for C atoms in the hexagonal ring [30]. The oxidation state of the Pd metal along with its NPs size is strongly affected by the nature of the N species and its surrounding environment. The bonding between an unsaturated N species and a transition metal involves a σ bond formation from the donation of a filled π bonding molecular orbital (unsaturated N species) to the empty $d\sigma$ orbital of the metal followed by the π back-donation from the filled $d\pi$ orbital of metal to the empty π^* antibonding molecular orbital of the (unsaturated) N species. This interaction is characterized by a charge transfer, typical of a covalent chemical bond with the partial ionic character depicting divalent Pd. On the other hand, the graphitic–N sites interact with Pd only through a covalent bond without any charge redistribution. In this case, the electronic state of the Pd corresponds to metallic Pd NPs, which is electronically modified by the interaction of the support [43].

The Pd^{+2} occurs on the functional groups of N-rGO surface as oxo-hydroxo Pd clusters. The existence of oxo-hydroxo Pd species becomes more profound when Lewis basic sites in the form of pyridinic–N species are present, which indicates that the coordination at these sites lowers their reducibility. The reduction of the metal oxide species results in Pd NPs formation which might follow clustering. Clustering occurs due to H spillover of pyrrolic–N by the small metallic NPs. In principle, hydrogenation of the carbon support through activated hydrogen from the Pd NPs preferentially attacks the quaternary nitrogen sites due to the charge localization. In this way, the Pd mobilizes itself gradually, and particle growth is the consequence. Only those Pd species that are unable to activate the hydrogen by hydride formation are safe against this self-destruction of the anchoring sites [44–46].

Amongst aforementioned nitrogen functionalities, pyridinic–N is believed to be associated with ORR activity due to the availability of a single lone pair of the electron which is considered as an active catalytic center by various research groups [47,48]. Furthermore, the presence of Pd NPs coordinated at the N sites will act as an electron transfer mediator along with increasing adsorption sites for O_2. The electrochemical study was performed exclusively by cyclic voltammetry (CV), electrochemical impedance spectra (EIS), rotating ring disc electrode (RRDE) and chronoamperometry (CA) in 0.1 M KOH as a supporting electrolyte. The individual effect of pyridinic, pyrrolic and graphitic–N on the synthesis, size and behavior of Pd NPs was investigated through Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman spectroscopy. The successful synthesis of N-rGO-Pd was analysed using energy dispersive X-ray spectroscopy (EDX).