



Proposed mechanisms for the removal of nitrate from water by platinum catalysts supported on polyaniline and polypyrrole

M. Jesús García-Fernández^a, M. Mercedes Pastor-Blas^a, Florence Epron^b,
Antonio Sepúlveda-Escribano^{a,*}

^a Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica – Instituto Universitario de Materiales de Alicante, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

^b Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), Université de Poitiers – UMR CNRS 7285, 4 rue Michel Brunet – Bâtiment B27, TSA51106, 86073 Poitiers Cedex 9, France

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ABSTRACT

Platinum nanoparticles have been synthesized on polyaniline (PANI) and polypyrrole (PPy) as supports using H_2PtCl_6 as metal precursor and a reducing treatment with cold Ar plasma. The catalytic activity of the polymer-supported catalysts in the reduction of aqueous nitrate with H_2 at room temperature was evaluated. These systems are able to considerably decrease the concentration of nitrate in water in only 5 min. The mechanism of the nitrate abatement process is determined by the nature of the conducting polymer. The nitrogen functionalities in polyaniline are external to the ring system, and favor nitrate retention at the platinum complex either by the formation of an adduct or by nitrate participating as a ligand. In contrast, polypyrrole possesses aromatic nitrogen atoms with a considerably more important steric hindrance. In this case, ion exchange between the counter ions in the doped polymer (SO_4^{2-}) and nitrate from water is produced, followed by reduction of nitrate by hydrogen chemisorbed on the platinum nanoparticles.

1. Introduction

Since the discovery of electrical conducting properties of conjugated polymers (as polypyrrole and polyaniline) promoted by doping, they have been studied for a great variety of applications such as lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, etc. The main issue that is useful for most applications is not the metal-like electrical conductivity itself, but the combination of electrical conductivity and polymeric properties such as flexibility, low density and ease of structural modification that suffice for many commercial applications [1]. However, their use in catalysis has not been extensively studied.

Among conducting polymers, polypyrrole (PPy) and polyaniline (PANI) have attracted great attention. Their hetero-aromatic and extended π -conjugated backbone structure provide them with chemical stability and electrical conductivity, respectively. However, the π -conjugated structure is not enough to produce appreciable conductivity on its own; a doping process, which can be achieved chemically or electrochemically, is necessary. This produces a partial charge extraction from the polymer chain and, depending on the doping degree,

polypyrrole and polyaniline can exhibit multiple inherent oxidation states. Charge carriers are located in the main chain and compensated by counter-ions.

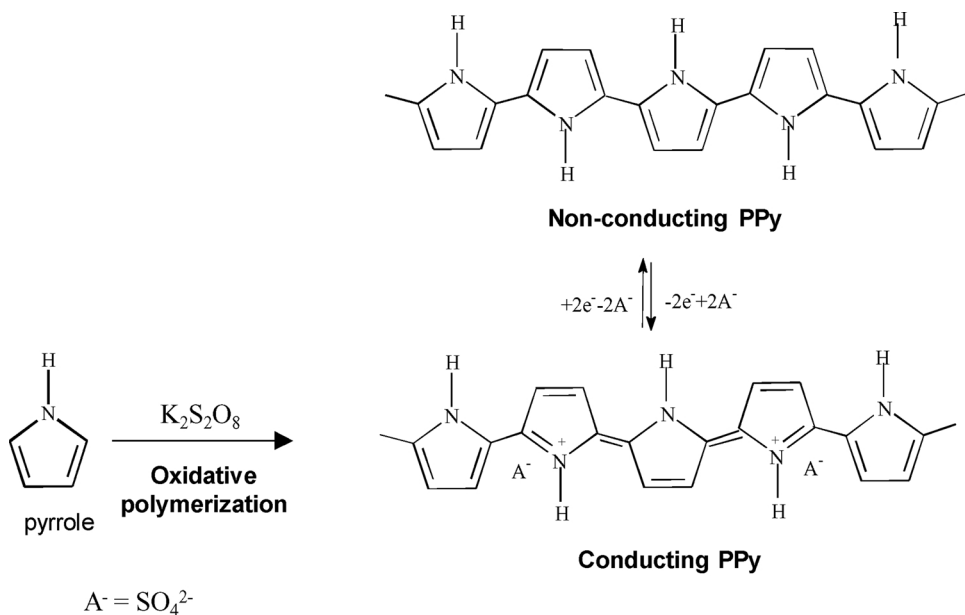
The process of chemical oxidative polymerization of PPy and PANI is usually followed by visible changes in the color of the polymerization solution. PPy appears yellow-green and dark blue-gray in its neutral (non-conducting) and oxidized (conducting) forms, respectively. When the pyrrole monomer is put into contact with an oxidant (Scheme 1), an initially colorless solution turns blue and dark blue after a while, indicating the formation of oligomers. Some time later, the precipitation of a dark blue or black solid polymer is observed, thus corresponding to the conducting PPy [2]. On the other hand, PANI shows the greatest number of characterized forms among the conducting polymers [3]. The polymer is composed of reduced (B-NH-B-NH) and oxidized (B-N=Q=N-B) units where B and Q are benzenoid and quinoid rings, respectively. The variation of the amine and imine ratio in its structure gives rise to several forms: leucoemeraldine, which contains only benzenoid rings and is the completely reduced form, emeraldine containing half benzenoid rings and half quinoids and pernigraniline that only shows quinoid rings. In turn, each of these forms can be found

* Corresponding author at: Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica – Instituto Universitario de Materiales de Alicante, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain.

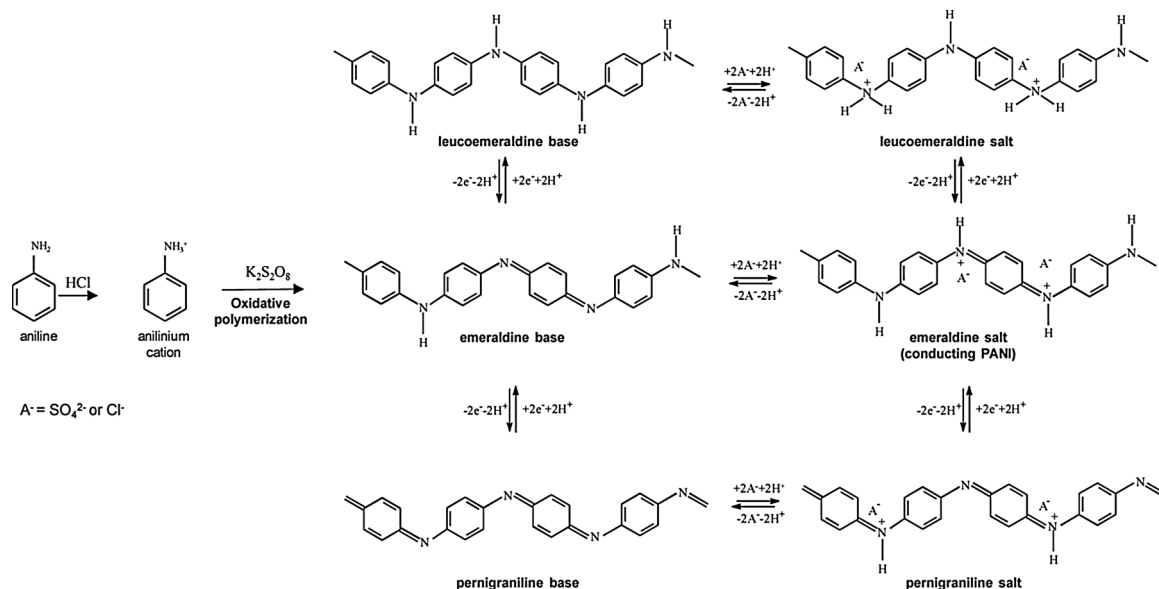
E-mail addresses: asepul@ua.es, a.sepulveda.esc@gmail.com (A. Sepúlveda-Escribano).

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Scheme 1. Scheme showing the oxidative polymerization of pyrrole with potassium peroxydisulfate producing conducting PPy.



Scheme 2. Scheme showing the oxidative polymerization of aniline with potassium peroxydisulfate in acidic aqueous medium producing conducting PANI.

protonated or deprotonated, producing a total of six forms, which can be transformed into one another by reactions of oxidation, reduction, protonation and deprotonation. **Scheme 2** shows the different reactions that take place between the different states of PANI. Protonated forms of PANI are known by the term “salt”, while non-protonated forms are called “base”. They show different colors depending on their oxidation state and their protonation. The leucoemeraldine base is clear yellow, emeraldine base is blue and pernigraniline base is violet. The corresponding protonated forms are leucoemeraldine salt (colorless), emeraldine salt (green) and pernigraniline salt (blue but in a different shade than that of emeraldine base).

The oxidation of aniline in acidic aqueous media using ammonium peroxydisulfate as oxidant has become the most widely synthetic route to produce conducting PANI [3], which is obtained in the form of protonated emeraldine salt, named after its green colour. Emeraldine salt is the one that shows greater electrical conductivity than the rest of states and is highly stable in environmental conditions (presence of air, humidity).

Metal particles (e.g. Au, Ag, Pt, Pd) can be readily deposited on

these polymers by direct chemical or electrochemical redox reactions between the polymer and the oxidative metal cations [4,5]. However, it is not easy to control the size and distribution of the metal particles across the polymer matrix. Many catalyzed reactions require small monodispersed metal particles to achieve a high catalytic activity, so reduction of metal precursors is necessary. The catalytic properties of metal species are closely related to their morphology and particle size, which are normally determined by the reduction conditions. In many cases, catalysts are reduced by flowing hydrogen at elevated temperatures or by chemical reductants, such as formaldehyde, hydrazine or sodium borohydride. Non-thermal Ar plasma has been proposed as an alternative reduction technology operating at room temperature, which complies with the requirements of green chemistry, and is easy to perform [6–8]. The reducibility of metal ions by plasma can be determined by the value of their standard electrode potential; thus, those metal ions with positive standard electrode potential, such as Pd, Pt, Au, Ag, Rh and Ir can easily be reduced by non-hydrogen plasma at room temperature. It is well known that these metals have very interesting applications in catalysis [9].

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