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Synthesis and spectroscopic analysis of polydiphenylamine via oxidation with bentonite clay in the solid state



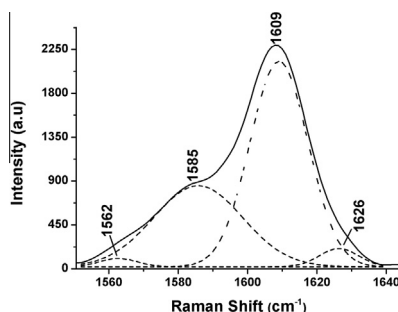
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HIGHLIGHTS

- Developing an innovative synthesis route for diphenylamine oxidative polymerization.
- Comparing the Raman spectra of the prepared chemically with that electrochemically.
- Deconvolution of the band characterizing C=C stretching in the Raman spectra.
- Characteristic frequencies of the aromatic, radical cation and dication segments.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, solids of polydiphenylamine (PDPA) synthesized mechanochemically by reaction with bentonite (PDPAOB) were studied using Raman spectroscopy. It was possible to identify the chemical species in the PDPA–bentonite compound. The spectra obtained were compared to the spectra of PDPA prepared chemically by oxidation of DPA with $K_2S_2O_8$ in the solid state, and PDPA produced electrochemically, with the aim of studying the characteristic frequencies of the aromatic segments (DPB), radical cation (DPB^{•+}) and dication (DPB²⁺) of N,N-diphenylbenzidine (DPB) in the polymer structure of the PDPA. To analyze the segments present, the band characteristic of C=C asymmetric stretching of the aromatic ring in the Raman spectra was deconvoluted because of the widening of the band and shifts observed by irradiation at wavelengths of 532 and 785 nm. This procedure showed that there are three distinct contributions in the spectra which facilitate the monitoring of changes in the contributions of the segments in the materials doped with HCl (PDPAOBD) and de-doped with NH_4OH , (PDPAOBR).

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1. Introduction

The search for composite materials incorporating semiconductor polymers with high electrical conductivity that are easy to process and have good chemical stability has led to various research projects aimed at the application of these composites as the active material in supercapacitors [1], fuel cells [2], batteries [3] and chemical and biochemical sensing devices [4]. For these applications, various materials incorporating polydiphenylamine (PDPA)

as the active material have been prepared [5–8], since PDPA has good redox properties, electrochromic behavior and environmental stability [9].

Polydiphenylamine is usually synthesized using electrochemical methods in which polymer films are produced over conductor substrates [10–12]. However, the need for new materials has led researchers to seek different synthesis methods, such as preparation in a solution of the diphenylamine (DPA) with sulfuric acid [13], potassium persulfate in water–ethanol homogeneous media [14] and oxidation of the DPA in the solid state by $FeCl_3$ [15].

Bypassing the normal route taken to prepare these new materials, better structural characterization has been achieved using

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spectroscopic techniques, and especially Raman spectroscopy and FTIR, combined with UV–visible spectroscopy, thermogravimetric analysis, X-ray diffraction, SEM and TEM [5,16,17].

The aim of this study was to develop an innovative synthetic route for the oxidative polymerization of diphenylamine in the solid state, using a clay as the oxidant and characterizing the composite produced using Raman spectroscopy.

In this study, the various experimental parameters that influence the mechanochemical synthesis of PDPA with bentonite were defined and the materials characterized using Raman spectroscopy at different irradiation wavelengths with the aim of obtaining a semiconductor material with good chemical stability and clearly-defined structural properties.

The Raman spectra of PDPA oxidized by bentonite were compared to those obtained for PDPA prepared chemically by oxidizing DPA with $K_2S_2O_8$ in the solid state and PDPA produced electrochemically, with the aim of studying the characteristic frequencies of PDPA aromatic, radical cation and dication segments present in the polymer matrix. The analysis was improved after subjecting the PDPA to various doping (HCl) and dedoping (NH_4OH) agents, which showed the stabilization of the segments present in the material produced.

2. Experimental

2.1. Chemicals

The diphenylamine ($(C_6H_5)_2NH$) supplied by Allkimia Ltda was recrystallized three times in 99.8% petroleum ether supplied by Labsynth Ltda. The 93.5% bentonite clay (Acros Organics), 37% HCl (Biotec Reagentes Analíticos) and 27% NH_4OH (Synth) were used without further purification.

2.2. Chemical synthesis of solid polydiphenylamine (PDPA) using bentonite and potassium persulfate

The best conditions for synthesizing solid state PDPA were set up using 0.7 g purified diphenylamine (DPA) and 0.3 g clay. The

DPA was first crushed in a porcelain crucible for five minutes and added gradually to the bentonite. This material was mixed and crushed in the porcelain crucible for 45 min to obtain a light green material, designated polydiphenylamine obtained by bentonite oxidation (PDPAOB).

To synthesize the PDPA using 0.8 g solid potassium persulfate, 0.8 g purified DPA was used, following the procedure described above. This material was designated polydiphenylamine obtained by persulfate oxidation (PDPAOP).

2.3. Electrochemical synthesis of PDPA

The supporting electrolyte was 99% pure lithium perchlorate ($LiClO_4$) supplied by Acros Organics. The 99.5% pure, HPLC grade acetonitril (CH_3CN) was obtained from JT Baker.

Electropolymerization was performed in a single-compartment cell with a Pt working electrode, large Pt plate auxiliary electrode and an Ag/AgCl reference electrode. The electrolyte solutions were 0.10 mol L^{-1} DPA and 0.10 mol L^{-1} $LiClO_4$ in ACN. The DPA was polymerized by continuously cycling the potential between 0.40 and 1.50 V until 60 cycles were reached, with a scan speed of 50 mV s^{-1} . The polymer deposited on the electrode surface was retrieved by removing the working electrode from the cell at 1.00 V.

Cyclic voltammetry readings were taken on an Autolab PGSTAT 302 N potentiostat/galvanostat coupled to a microcomputer running NOVA 1.8.

2.4. Doping and dedoping PDPAOB and PDPAOP solids

Hydrochloric acid at 0.10 mol L^{-1} was added to the solid materials obtained (PDPAOB and PDPAOP) and they were crushed for 5 min, washed with ultra-pure water and ethyl alcohol and then filtered. They were then transferred to a petri dish and dried in an oven at $60 \text{ }^\circ\text{C}$ for 3 min. These materials were designated doped PDPA obtained by bentonite oxidation (PDPAOBD) and doped PDPA obtained by persulfate oxidation (PDPAOPD).

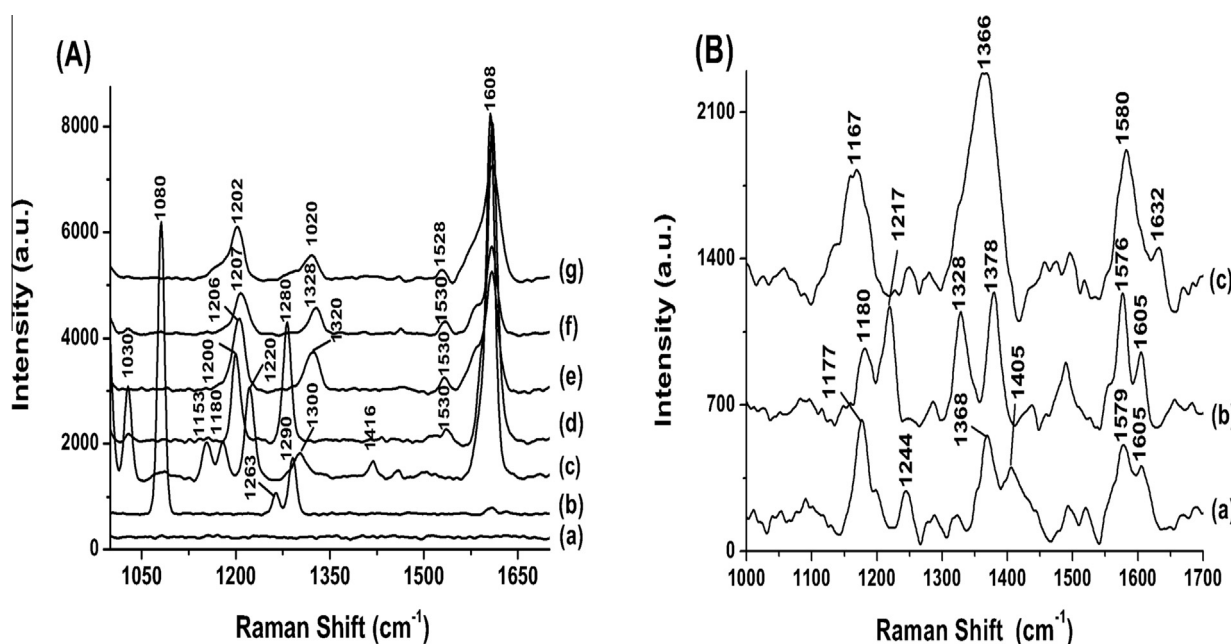


Fig. 1. Raman spectra of the solid samples at an irradiation wavelength of 532 nm (A): (a) bentonite, (b) persulfate, (c) diphenylamine, (d) diphenylbenzidine, (e) PDPA prepared electrochemically, (f) PDPAOB and (g) PDPAOP; and at 785 nm (B): (a) PDPA prepared electrochemically (b) PDPAOB and (c) PDPAOP.

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