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Molecular Modeling of Protonic Acid Doping of Emeraldine Base Polyaniline for Chemical Sensing Applications

Xianping Chen[1,2,3], Cadmus A. Yuan[3,4], Cell K. Y. Wong[1], Guoqi Zhang[1,3,5]
[1] Department of Precision and Microsystem Engineering, Delft University of Technology, Mekelweg 2, 2628 CD, Delft, the Netherlands
[2] The Faculty of Mechanical & Electrical Engineering, Guilin University of Electronic Technology, 541004 Guilin, China
[3] Delft Institute of Microsystems and Nanoelectronics (DIMES), Delft University of Technology, Feldmannweg 17, 2628 CT, Delft, the Netherlands
[4] TNO IenT, Materials Technology, De Rondom 1, 5612 AP, Eindhoven, the Netherlands
[5] Philips Lighting, Mathildelaan 1, 5611 BD, Eindhoven, the Netherlands

Abstract

A combined molecular mechanics and molecular dynamics simulation techniques has been used to modeling the protonic acid doping of emeraldine base polyaniline. The molecular model, which is capable of representing the polyaniline doping with the aqueous hydrochloric acid, was built by Monte Carlo method. The doping process is modeled by a scripted loop control simulation using a doping distance criterion. The radial distribution functions of doped emeraldine salt and the relationships including pK_a/pH and doping percentage/pH, were computed and compared with the experimental data with good agreement. This method contributes a novel molecular modeling approach to predict the pH dependence of conducting polymer in design and evaluation of chemical sensing materials.

Key words: molecular mechanics, molecular dynamics, protonic acid doping, emeraldine base, pK_a

Introduction

Ever since the discovery of conductive polymers (CPs) in 1977 [1], research activities on CPs has been ever-increasing with applications in various fields such as actuators [2], gas sensors and biosensors [3], etc. Amongst the family of CPs, emeraldine base (EB) form of polyaniline (PANI) is especially attractive due to its ease of synthesis, less expensive, environmental stability, and simple doping/dedoping chemistry [3,4]. The doping mechanisms for protonic acid (e.g. HCl) doping of the EB as proposed by Chiang and MacDiarmid is illustrated in Fig. 1 [5]. The protonation involves an insulator-metal transition which results in ten orders of magnitude increase in conductivity (from 10^{-10} S/cm to 10^{0} S/cm). This mechanism has been extensively used to monitor the environmental pollutants, such as NO_2, CO_2, SO_2, H_2S and other greenhouse gases [3]. Using EB–PANI as a sensing material for dissolved gases sensing, is highly dependent on the operating pH range. The understanding and utilization of these pH dependences is important for their application.

Experiments exhibit a trend of improving the material properties by modifying the chemical structure and the chemical composition of the PANI [3,4]. The prediction of pH characteristics in modifications of the structure is a critical issue in design, synthesis and evaluation of new polyaniline polymers for chemical sensing applications. Molecular simulation methods are now routinely used to investigate the structure, dynamics, surface properties and thermodynamics of inorganic, biological and polymeric systems [6]. Recent studies [3-8] show that molecular simulation approaches together with experimental efforts is a key in selecting and developing new materials for chemical & biological sensing applications in a rational way [8]. A molecular simulation methodology that is capable of predicting the doping of EB by protonic acid is essential for the chemical sensing material research of the PANI. If the method can be developed, it would provide a novel computational approach to design and evaluate the new conducting polymers for chemical sensing applications. It could also be brought to the reversible thermodynamic equilibrium with respect to doping in the study of such complex polymer systems.

The objective of this work is to develop a molecular simulations methodology which can describe the protonic acid doping of EB with

percentage of doped polyaniline against the equilibrium pH of the HCl doping solution. Again the calculated values agree well with the experimental results measured by Chiang and MacDiarmid [14] with a mandatory saturation at level of 50% doping was detected in both results. The plot also matches the theoretical analysis curve derived by H. Reiss [13]. These good agreements between experimental data and simulation results on $g(r)$, pK_a/pH and doping percentage/pH suggests our molecular modeling methodology in modeling of protonic acid doping of the EB is realistic and accurate.

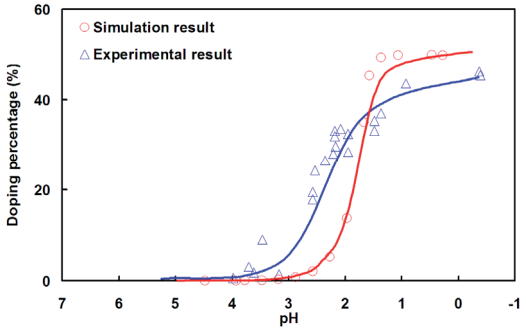

Fig. 5. The relationship between the doping percentage of doped EB and the equilibrium pH of HCl solution in which it was equilibrated: simulations results (read line and circle dots) and experimental data (Ref. 17) (blue line and triangles).

Conclusions

A combined MM and MD method has been used to model the HCl doping of the EB form of PANI for the first time. The method is comprised of two key steps: i) generation of the molecular models using MM/MD equilibrated simulations with the COMPASS forcefield, ii) modeling the doping reaction with a scripted loop control MD simulation using the doping distance criterion. Via this modeling framework, the radial distribution functions were estimated. The relationships of pK_a/pH and doping percentage/pH, were predicted. The accuracy of our method has been confirmed by the agreement with the experimental data. This method contributes a novel molecular modeling approach to predict the pH dependence of conducting polymer in design and evaluation of chemical sensing materials. It also provides yet another molecular model of a conducting polymer system that could be brought to reversible thermodynamic equilibrium with respect to doping.

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