SYNTHESIS OF CONDUCTIVE POLYANILINE NANOPARTICLES BY OXIDATION OF ANILINE WITH CERIUM(IV) SULFATE

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Abstract

The conductivity and morphology of nanostructured polyaniline, synthesized by the chemical oxidative polymerization of aniline with cerium(IV) sulfate in aqueous solution without added acid, were studied as a function of oxidant/monomer initial mole ratio, reaction time and temperature. Polyaniline nanoparticles, exhibited mainly ordinary spherical shape with particle size of about 30–220 nm, were prepared by using Ce(IV)/aniline initial mole ratios in the range 2.0–2.5. Optimum reaction conditions for the synthesis of the most conductive nanostructured polyaniline with uniform particle size (30–80 nm) were found to be Ce(IV)/aniline initial mole ratio ~2.3, low initial reaction temperature ~2 °C, and relatively short reaction time (3 h). The early stages of aniline oxidation in water with one-electron oxidant Ce(IV) were theoretically studied by the AM1 semi-empirical quantum chemical method.

Introduction

Nanostructured conducting polyaniline (PANI) has attracted recently increasing attention from a wide area of scientific interests. PANI nanoparticles have the following advantages: firstly, the decrease in particle size can promote more effective doping, strenghten inter- or intrachain interactions and enhance the degree of cristallinity; secondly, PANI nanoparticles have some special electrical, optical and opto-electrical properties due to their smaller size; thirdly, with the decrease of PANI particle size, PANI dispersion medium become more stable and uniform, and helpful for producing uniform, transparent, conducting polymer thin film, thus overcoming the problem of processability [1–3]. Various supramolecular structures of the PANI were obtained, depending on the conditions of the reaction [4, 5]. In the case of aniline oxidation with ammonium peroxydisulfate (APS) in aqueous solutions it was found that the morphology of PANI depends on the acidity conditions during the reaction [4]. In solutions of sulfuric acid, granular PANI was produced; in solutions of acetic acid, PANI nanotubes were obtained. The evolution of polyaniline morphology during the course of aniline oxidation with APS in aqueous solutions, in the absence of any added acid, was also analyzed [5]. Although the conductivity of PANI thus prepared is rather low [5], $\sim 10^{-2}$ S cm^{-1}, the observed nanotubular morphology of the products makes such a system of substantial interest. The knowledge and understanding of the factors that control the nanostructured morphology of PANI present a challenge.

In this paper, we analize the influence of oxidant/monomer initial mole ratio, reaction time and temperature on the conductivity and morphology of nanostructured PANI, prepared by oxidation of aniline with cerium(IV) sulfate in aqueous solution without added acid.

Results and Discussion

Oxidation of aniline with cerium(IV) sulfate in water yields mixture of PANI hydrogensulfate (polaronic form) and PANI sulfate (bipolaronic form). Sulfuric acid and cerium(III) sulfate are byproducts, Fig. 1.

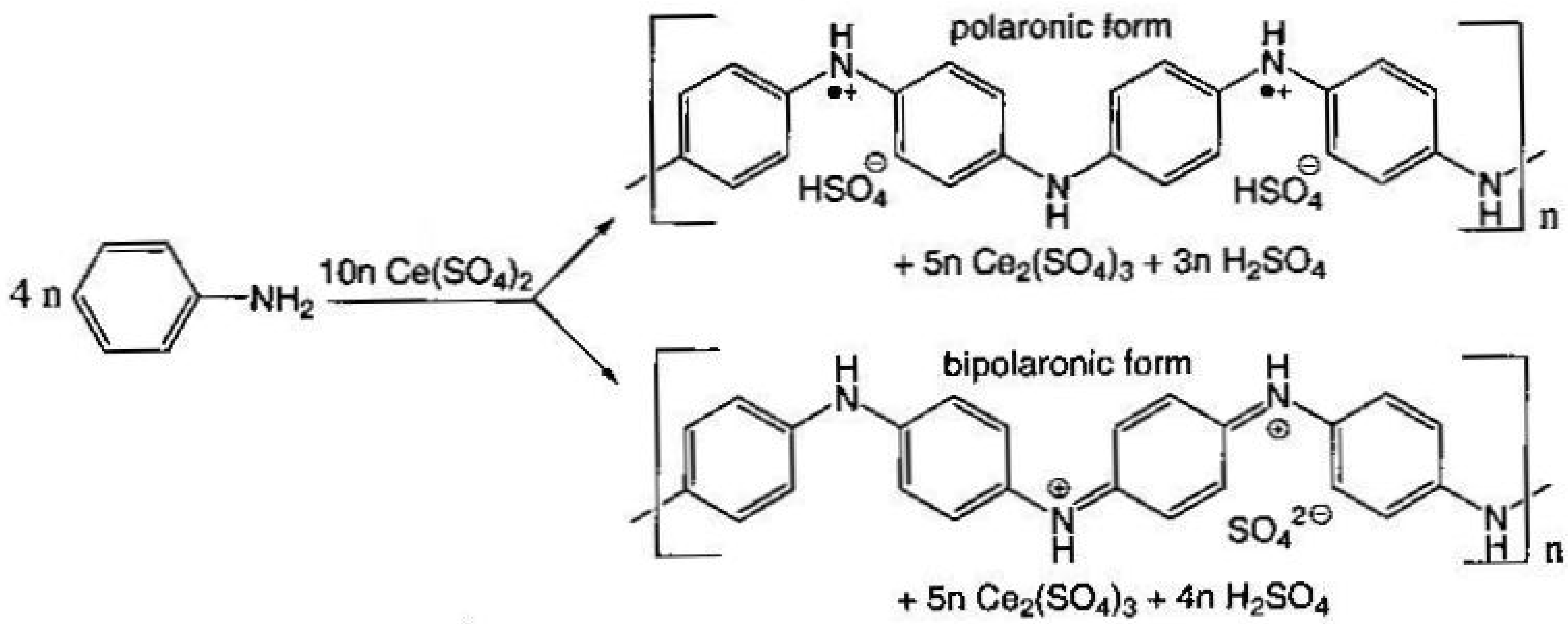

Fig. 1. Oxidation of aniline with cerium(IV) sulfate in water.

The conductivity of PANI thus prepared is ~10^{-3} S cm^{-1}. Conductivity of PANI doped by HCl, prepared by using different Ce^{4+}/aniline mole ratios (reaction time 24 h, room temperature), is ~10^{-2} S cm^{-1}, Table 1.

Table 1. Conductivity of PANI HCl.

Mole ratio Ce^{4+} / aniline	Conductivity (S cm^{-1})
2.0	0 028
2.1	0.022
2.2	0.031
2.3	0.036
2.4	0.026
2.5	0.023

It was found that the optimum mole ratio Ce^{4+}/aniline, producing the most conductive PANI, is 2.3. It is important to note that this mole ratio oxidant/monomer is slightly lower than theoretically expected (2.5). This can be explained by participation of dissolved oxygen in oxidation process. Decrease of the initial reaction temperature (room temperature to 2 °C), as well as decrease of reaction time (24 h to 3 h) induced increase of PANI conductivity.

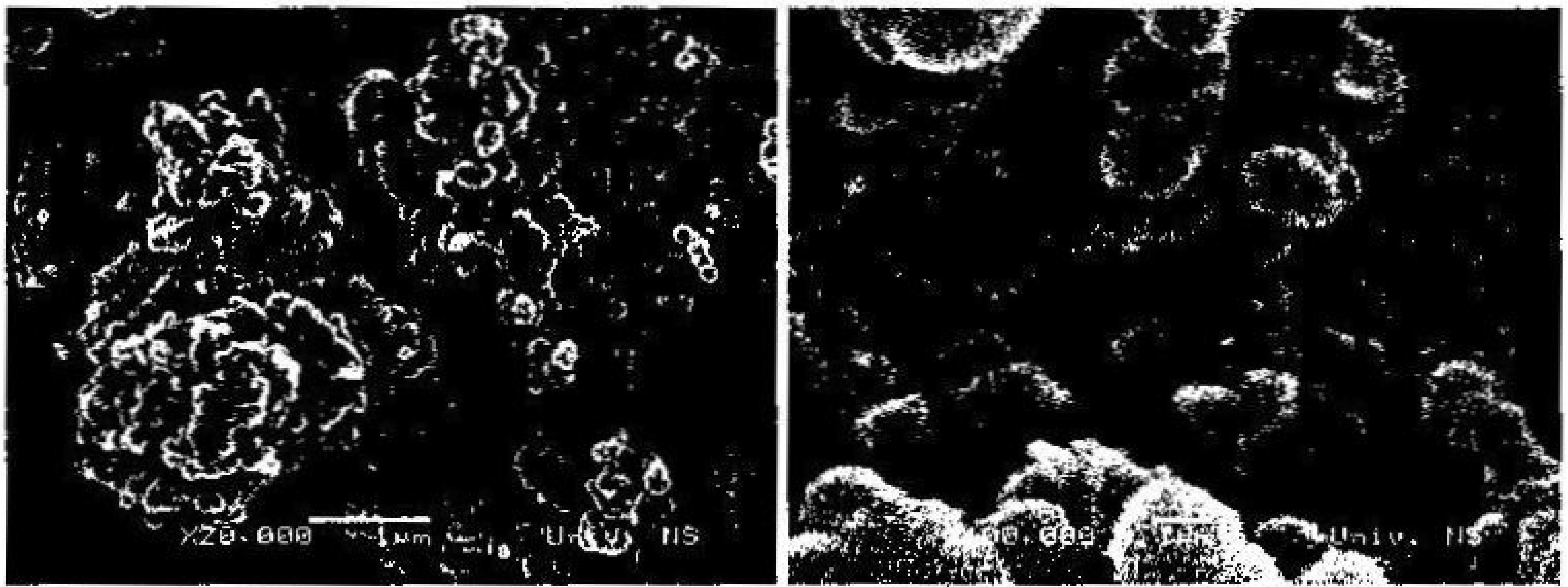

Fig. 2. SEM images of PANI doped with HCl ($[Ce^{4+}]/[aniline]=2.3$; RT; $t_{polym.}=3h$)

Scanning electron microscopy investigation of the morphology of undoped and doped PANI revealed formation of PANI nanoparticles, prevalently nanospheres with particle size 30–220 nm, in the whole range of studied experimental conditions, Fig. 2. The preparation of the smallest nanoparticles with the narrowest particle size distribution (30–80 nm) was achieved by using Ce(IV)/aniline initial mole ratio ~2.3, initial reaction temperature 2 °C, and reaction time 3 h.

Semi-empirical quantum chemical AM1 computations of the heat of formation and spin density of solvated reactive species and intermediates show prevalence of N–C4 aniline dimer units (Fig. 3).

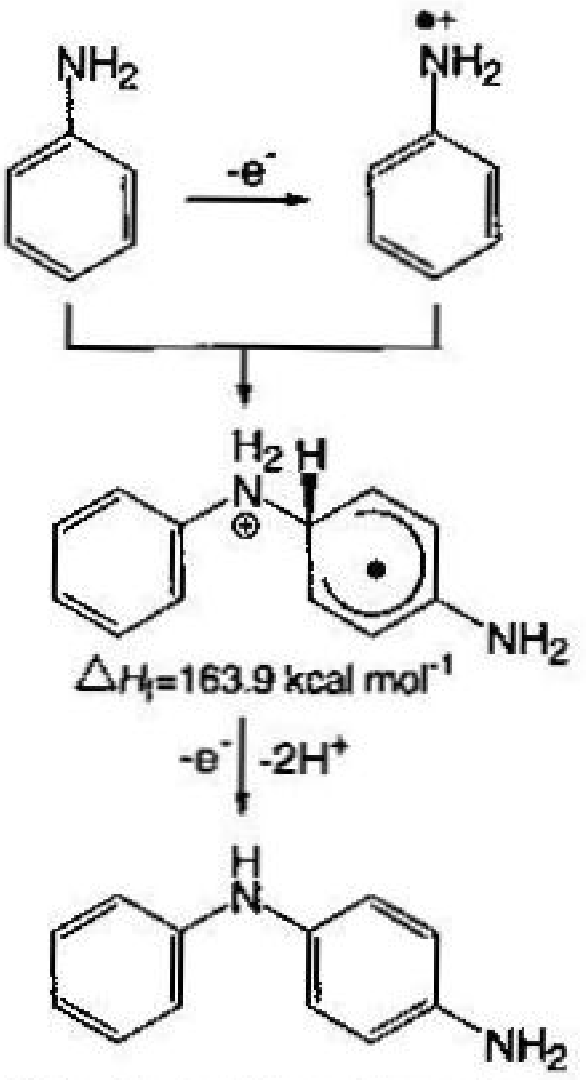

Fig. 3. Aniline dimerization mechanism

Conclusion

The use of cerium(IV) sulfate in the chemical oxidative polymerization of aniline in aqueous solution without added acid leads to the formation of PANI nanospheres. The conductivity and particle size of nanostructured PANI depend considerably on the initial Ce(IV)/aniline mole ratio, reaction temperature and time.

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