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ORIGINAL PAPER

Formation of nanostructured polyaniline by dopant-free oxidation of aniline in a water/isopropanol mixture

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Nanostructured polyaniline (PANI) was synthesised by the oxidation of aniline in a water/isopropanol (propan-2-ol, IPA) (50 vol. %) mixture, without added acid, using ammonium peroxydisulfate (APS) as an oxidant. Influence of the IPA co-solvent and the reaction time on the molecular structure, morphology and properties of synthesised PANI samples was studied by FTIR, Raman, and UV-VIS spectroscopies, scanning and transmission electron microscopies (SEM and TEM), and conductivity measurements. The course of the reaction was followed by monitoring changes in the temperature and acidity of the reaction medium. The results were compared with those obtained for PANI prepared in water without IPA under the same reaction conditions. The importance of the solvation effects, dielectric constant of the solvent, and the enthalpy of mixing of IPA with water on the course of the polymerisation reaction and on the properties of polymeric products in the water/IPA medium in comparison with those in water was pointed out.

Keywords: polyaniline, nanoribbons, solvent mixture, propan-2-ol, dopant-free polymerisation

Introduction

Simple and low-cost synthesis, reversible acid/base doping/dedoping chemistry, redox activity, tunable conductivity, and environmental stability rank polyaniline (PANI) high among the most studied conductive polymers. Increased interest in efficient and scalable production of PANI nanostructures has been recently shown due to their improved performance in many applications, e.g. sensors, catalysts, electron field emitters, field-effect transistors, supercapacitors, corrosion protection, data storage, actuators, membranes, solar and fuel cells, or rechargeable batteries (Ćirić-Marjanović, 2010). Numerous hard template (nanoporous, nanostructured seed, reactive) and soft template (oligomer-, polymer-, surfactant-, and amphiphilic acid-assisted), as well as template-free methods (not shaken–not stirred, aqueous/organic interfacial, rapid-mixing, dilute, and falling-pH polymerisations, etc.) were developed during the last two decades in order to synthesise 1-D PANI nanostructures (nanofibers, nanorods, nanotubes) (Ćirić-Marjanović, 2010). Similarly to the synthesis of granular PANI (Stejskal & Gilbert, 2002), most of these syntheses were performed in acidic media at pH < 2.

It has been revealed by Stejskal's group that simple room-temperature oxidation of aniline with APS in water, without any added acids, leads to the formation of PANI nanotubes/nanorods accompanied with nanosheets (Trchová et al., 2006; Konyushenko et al., 2006). This breakthrough finding, which opened new perspectives in the nanoscience and nanotechnology of PANI, was followed by numerous studies of this simple synthetic method (referred to as the dopant-free template-free falling-pH method) (Chiou et al., 2007; Ding et al., 2008; Laslau et al., 2009; Huang & Lin, 2009, 2010a, 2010b; Konyushenko et al., 2011; Rakić et al., 2011; Ćirić-Marjanović et al., 2009a, 2009b; Radoičić et al., 2010, 2012). Attention was paid to the influence of the APS/aniline mole ratio

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