

Nanostructured PANI-based materials for sensor and molecular electronics applications

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Emerging fields of printed and molecular electronics put new challenges for development of solution processable polymers with desirable electrical characteristics (high carrier mobility, stability of properties, etc.). In our presentation we report on the structure and sensor properties of several intelligent nanostructured conducting polymer composite systems based on polyaniline (PANI) as an active component. Our choice is based on PANI ability to vary its electronic properties in a broad range (from semiconducting to metallic) depending on its structural organization and the type and degree of doping. The latter is strongly tied to the very important ability PANI to reversibly change its protonation degree through reaction with basic or acidic environments without changes in the redox-state unlike most of other conducting polymers^[1]. PANI is, therefore, a well established environmentally friendly material, which can be used in electronics and sensor devices^[1-7]. The lack of mechanical stability of PANI can be surmounted via its blending with other polymers or by application of sub-micrometer polymer particles with core-shell architecture. We have demonstrated that the latter approach provides a versatile way of constructing quite robust nanostructured composites where electrically conductive percolation network can be finely controlled^[4]. This also allows combining of otherwise incompatible polymers, such as a polar ferroelectric polymer poly(vinylidene fluoride) (PVDF) which can be used as a core and electrically conductive or semiconductive shell (such as PANI). Nanostructured PANI systems are especially attractive for sensor applications, as they response with an enhanced magnitude of such signals and response rates to the environment changes due to their high surface area and the accessibility of their sensitive centers^[4,5]. Fig. 1 shows schematically internal structure of PANI-based active sensing layers prepared through two approaches: application of core-shell nanoparticles, or embedding of PANI nanofibers into polyurethane (PU) matrix.

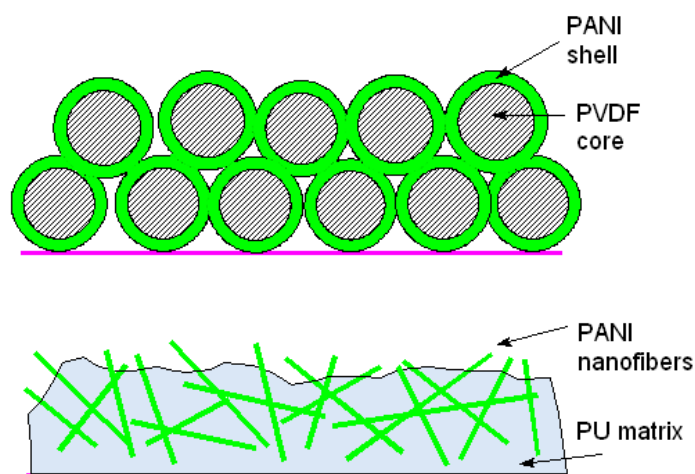


Fig. 1. Schematic representation of an active layer used for ppb range sensing of ammonia in case of core-shell approach (top) and nanofibers approach (bottom). In both cases the active layer has a percolation network of PANI and a developed surface with a high specific surface area available for NH_3 - PANI interaction.

High resolution helium ion microscopy (HIM) images (Fig. 2) demonstrate creation of a porous polymer film with a percolation network formed by PANI as a result of sintering of such core-shell particles. Fig. 3 demonstrates that such systems possess extremely high sensitivity to ammonia gas (in ppb range).

The mechanism of conductivity variation is based on the simple reversible interaction of emeraldine salt or base forms of PANI with compounds having basic or acid functions correspondingly. This response essentially depends also on the morphology of PANI and on degree of its doping [6]. In the second approach high aspect ratio PANI nanofibers (see Fig. 2) are fabricated through a well established protocol and then blended with PU to form the active layer [7].

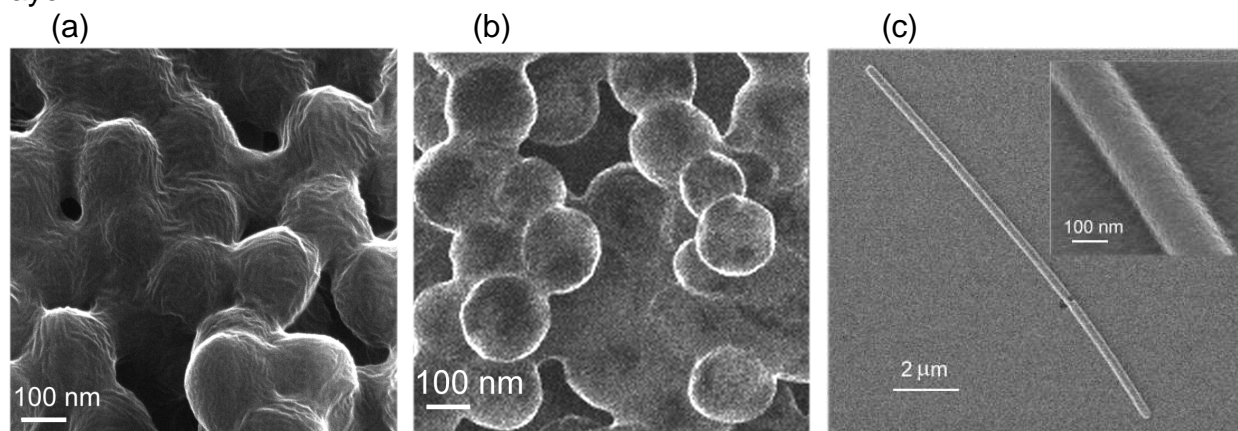


Fig. 2. HIM images of a sensing film based on PVDF-PANI core-shell particles (a); the same film after exposure to NH₃ vapors (b), and an individual PANI nanofibers 12 μm long (c). The inset shows higher magnification of the nanofiber.

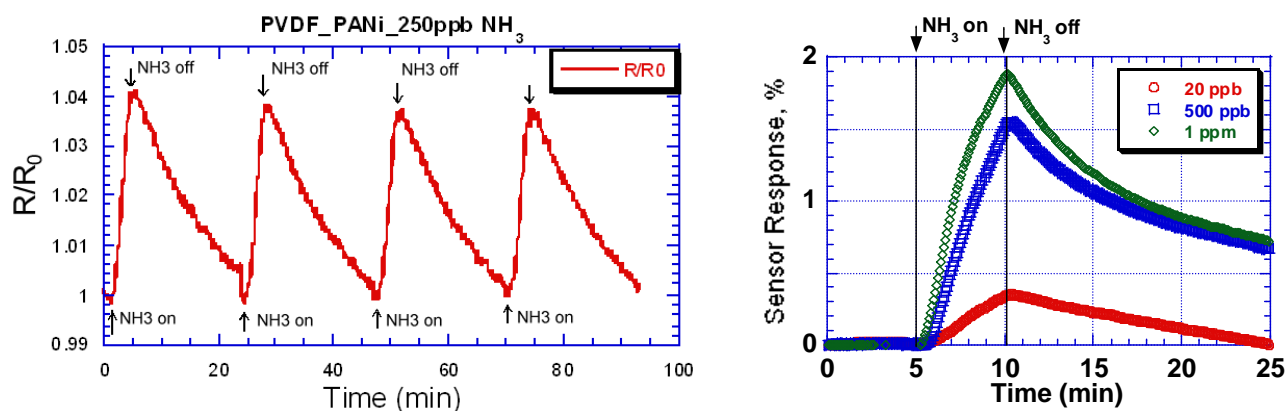


Fig. 3. Example of a PVDF-PANI core-shell based sensor response to 250 ppb ammonia exposure (left), and of a PANI(CSA doped)-PU nanocomposites film response to ppb range concentrations of ammonia (right).

Structure-properties relationships for semiconducting nanocomposites have been studied with atomic force microscopy, HIM, Raman spectroscopy, and surface conductivity characterization. We believe our approach can be extended to other polymer systems such as polythiophenes to create advanced polymer materials with tunable electrical properties for molecular electronics applications.

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