Proceeding Paper

Comparative Analysis of Structure, Synthesis, and Properties of Polyaniline and Polypyrrole: Insights into Conductive Polymer Variability [†]

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Abstract: Polypyrrole (PPy) and polyaniline (PANI) nanoparticles were synthesized using stabilizer—poly(vinyl alcohol) (PVA). The obtained nanostructures of conducting polymers were characterized using advanced analytical techniques such as scanning electron microscopy (SEM), dynamic light scattering (DLS), and ultraviolet-visible spectroscopy (UV-Vis). These comprehensive analyses provided valuable insights into the morphology, size distribution, and spectral characteristics of the nanostructures, contributing to a deeper understanding of their potential applications in materials science and nanotechnology.

Keywords: polyaniline; polypyrrole; synthesis; polymers; nanostructure

1. Introduction

In recent years, there has been a growing interest on conductive polymers (CPs) for applications in electrical devices, leading to the exciting development of the new category of advanced smart functional materials. These polymers possess a unique combination of excellent electrical conductivity and electroactivity, making them particularly appealing for cutting-edge technologies [1]. In broad terms, polymers can be described as substances consisting of extensive molecules created through the repetition of a basic building block known as monomers (where "poly" signifies many, and "mers" denotes units). Polymers fall into three main categories: natural, artificial, and partially synthetic [2]. CPs, sometimes referred to as synthetic metals, are categorized into four groups: composite, redox, ionic, and intrinsic. Intrinsic conducting polymers possess a conjugated π system within their backbone structure, and their electrical characteristics closely resemble those of metals. This conjugated π system enables electrons to traverse the molecular chain, granting the polymer electrical conductivity similar to that of metals. Intrinsic conducting polymers are lightweight, porous, and exhibit stability in ambient conditions [3]. The chemical polymerization of CPs offers the benefit of being adaptable to various substrates and can be scaled up more effortlessly when compared to electrochemical methods. Nonetheless, CPs obtained by chemical polymerization generally require additional adjustments after synthesis to achieve optimal electrochemical performance. Additionally, the conductivity of the synthesized polymers can range from insulating to semiconducting properties [4]. polypyrrole (PPy) and polyaniline (PANI) stand out among CPs due to their ability to effectively combine valuable properties [5,6]. PPy has impressive characteristics including ease of synthesis, structural adaptability, non-toxicity, exceptional conductivity, and strong redox capabilities. In turn, PANI has advantages such as ease of synthesis, and high environmental friendliness [7].

In this work, PANI and PPy nanostructures were synthesized using a polymeric stabilizer. The obtained polymers were characterized using different techniques. In order to gain a deeper understanding of structural features, scanning electron microscopy (SEM) was used to obtain high-resolution images of the nanostructures. Furthermore, the dynamic light scattering (DLS) technique was used to evaluate the particle size. In addition, UV-Vis spectroscopy has been used to study the optical properties and composition, providing valuable insights into the absorption and electronic transitions occurring in the polymer structures. This multifaceted approach enabled a comprehensive investigation of PANI and PPy nanostructures and their potential applications.

2. Methods

2.1. Materials Characterization

The morphology of the synthesized nanostructured polymers was analyzed using a SEM (SU-70; Hitachi, Tokyo, Japan). The absorbance spectra of PPy and PANI nanostructures were determined using a UV-Vis spectrometer (UV-1900i, Shimadzu, Japan). The measurements were performed in the wavelength range from 350 to 1000 nm. The hydrodynamic sizes were measured with the Zetasizer Nano ZS from Malvern (Herrenberg, Germany) equipped with a 633 nm He-Ne laser.

2.2. PANI Nanoparticles Synthesis

PANI nanoparticles (PANI NPs) were prepared using polymeric stabilizer—poly(vinyl alcohol) (PVA) following the protocol of Cho et al. [8]. Dispersion polymerization in water was carried out as follows: 1,09 g PVA (Sigma Aldrich, Steinheim, Germany) was slowly dissolved in 28 mL of deionized water. Then 0.46 mL of 37% HCl (Sigma-Aldrich, Steinheim, German) and 0.53 mL of aniline (Fluka, Neu-Ulm, Germany) were added to the solution and the reaction mixture was stirred continuously at 0 °C in an ice bath. Following this, 0.692 g of ammonium persulfate (Fluka, Neu-Ulm, Germany) was added to the solution. The light yellow solution gradually darkened within 30 min., turned emerald in color, and finally became dark green, which is the characteristic color of PANI emeraldine salt. The reaction mixture was stirred for 24 h at 0 °C. Further, the reaction solution was mixed 1:1 with acetone and centrifuged at a speed of 10,000 rpm for 10 min. Following this step, the solution was decanted and the precipitate was resuspended in a solution containing 20 mL of 0.1 M HCl and 20 mL of acetone (Carl Roth, Germany), and centrifuged again. This procedure was repeated 3 times. Finally, the sediments were collected and dried in a thermostat at 40 °C for 24 h.

2.3. PPy Nanoparticles Synthesis

To obtain PPy nanoparticles, a methodology identical to that of PANI was used. The amount of pyrrole monomer (Alfa Aesar, Kandel, Germany) required for the synthesis was accurately calculated to be 0.563 mL.

3. Results and Discussion

3.1. SEM Analysis

Following the polymerization process of both PANI and PPy nanoparticles by using PVA as a stabilizer, we prepared 1 mg/mL dispersions of each solution in deionized water. To accomplish this, the required quantity was added to deionized water and mixed in an ultrasonic bath for approximately 10 min (for PANI NPs) and 40 min (for PPy NPs). Samples for SEM analysis were prepared on silicon wafers.

The SEM images presented in Figure 1 clearly show the spherical shapes of nanoparticles in both PANI and PPI samples. Notably, when the stabilizer PVA was introduced, it caused distinctive effect on the nanoparticle distribution within the structures. In the case of PPy, the particles tend to forming denser clusters, while PANI NPs ehibits more individual particle structures. Futhermore, there is a noticeable variation

in nanoparticle size: the PANI NPs are 40.33 ± 2.95 nm in size, whereas PPy NPs are notably smaller at 17.83 ± 1.64 nm. These observations suggest a significant impact of PVA stabilizer on both the morphology and size of nanoparticles in these materials.
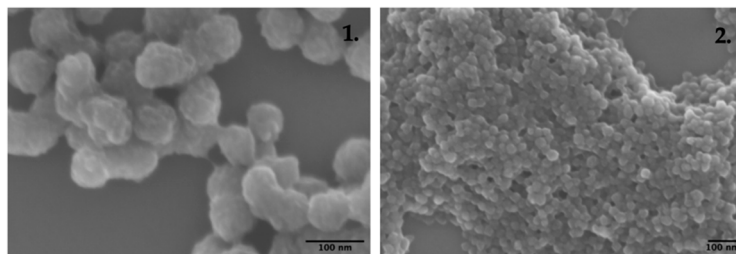

Figure 1. SEM images of (**1**) PANI and (**2**) PPy nanoparticles.

3.2. UV-Vis Analysis

Before using these polymers in subsequent research, colloidal aqueous solutions containing PANI or PPy NPs at a concentration of 1 mg/mL were prepared. After that, the prepared solutions were diluted 10 times and their UV-Vis spectra were recorded (Figure 2).
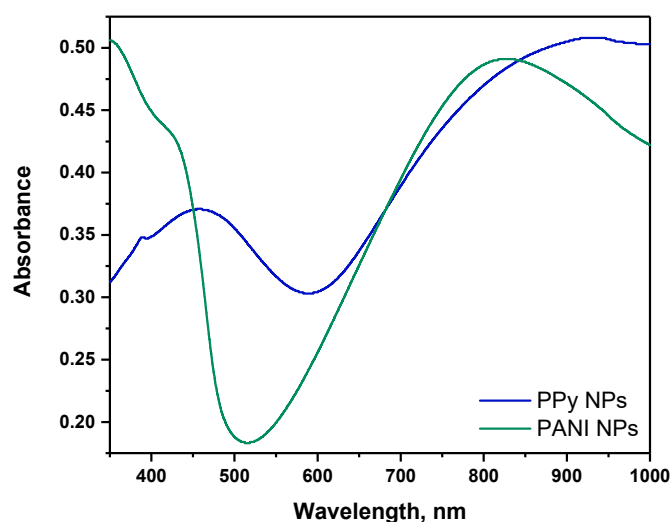

Figure 2. Absorbance spectra of (-) PANI and (-) PPy NPs solutions.

The UV-Vis absorption spectra of PANI NPs is illustrated in Figure 2, which shows the presence of two absorption peaks. Specifically, it exhibits a peak at 437 nm, representing the π-π^* transition centered on the benzenoid unit, and a wider peak at 824 nm, indicative of the π–polaron transition [9]. Similar to PANI NPs, the absorption spectra of PPy also exhibits the presence of two distinct absorption peaks. One of these absorption bands is located at approximately 471 nm, while the other is observed at around 900 nm. These observations collectively suggest that PPy nanoparticles are actively participating in the π–π^* transition and the bipolaron band [10,11].

3.3. DLS Analysis

Ultimately, the assessment of hydrodinamic size of the nanoparticles was conducted using DLS method. Both samples were prepared according to the methodology described earlier in this work.
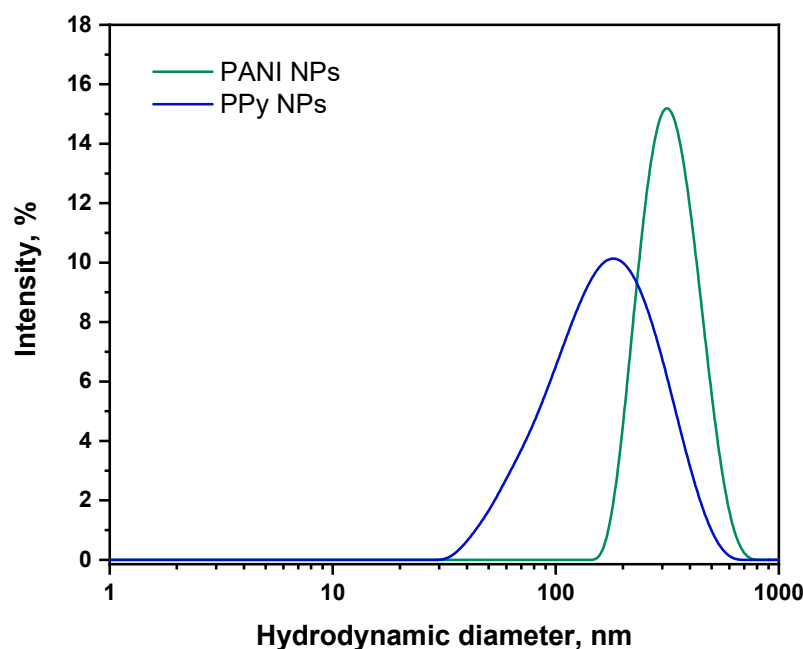
Figure 3. PANI and PPy NPs size distribution by dynamic light scattering (DLS).

The analysis revealed a hydrodynamic size of 295.3 nm for PANI NPs and 190.1 nm for PPy NPs. In addition, PANI and PPy nanoparticles were found to be stable in aqueous solution for a long time. The obtained hydrodynamic size of nanoparticles was significantly different in comparison with SEM results.

When assessing the hydrodynamic size of the synthesized polymers by the DLS method, disparate findings were obtained, which do not accurately represent the true dimensions of the nanostructures. The primary factor contributing to this variation lies in the fundamental measurement principle of DLS, which relies on the diffusion behavior of particles, while many other methods directly rely on the geometric dimensions of the particles [12].

4. Conclusions

Nano-sized PANI and PPy particles were synthesized in an aqueous environment, using the PVA as a polymeric stabilizer. The synthesized polymers nanoparticles that were synthesized exhibited a spherical morphology characterized by a fairly uniform size distribution. The size of PANI nanoparticles was 40.33 ± 2.95 nm, while PPy nanoparticles were 17.83 ± 1.64 nm in size. These research findings indicate that the particles we obtained are capable of forming consistently stable colloidal solutions, making them suitable for further investigations.

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