

Polypyrrole/Silver Nanocomposite: Synthesis, Characterization and Antibacterial Activity

Ghorbani, Mohsen*⁺

Babol Noshirvani University of Technology, P.O. Box 484, Babol, I.R. IRAN

Ehsani Amoli, Armin

Shomal University, P.O. Box 731, Amol, I.R. IRAN

Soleimani Lashkenari, Mohammad

*Faculty of Engineering Modern Technologies, Amol University of Special Modern Technologies,
Amol, I.R. IRAN*

ABSTRACT: Polypyrrole/silver (PPy/Ag)nanocomposite was synthesized by a chemical oxidative method. SEM and TEM analyses were performed for studying the morphology of the nanocomposite. It was shown that the obtained nanocomposite particles have a spherical structure with the high surface area to volume ratio that is the important factor in the biological application. The particle sizes of the PPy/Ag were 15–25 nm obtained by TEM. The antibacterial property was assessed by the disk diffusion method against gram-negative *Escherichia coli* and gram-positive *Staphylococcus aureus* bacteria. The antibacterial mechanism of action for PPy/Ag nanocomposite was discussed. PPy/Ag showed antibacterial activity against *S. aureus* (5 ± 0.5 mm) and *E. coli* (8 ± 0.5 mm). Based on satisfactory antibacterial properties of PPy/Ag nanocomposite, it could be considered as a suitable material in biomedical applications.

KEYWORDS Polypyrrole; Silver; Nanocomposite; Morphology; Antibacterial mechanism.

INTRODUCTION

Scientists have been interested in conducting polymers subject since they have great potential for technological applications to a wide variety of areas [1]. Among various conducting polymers, polypyrrole (PPy) because of its ease of synthesis, its relatively high environmental stability, and noticeable conductivity in comparison to the other conducting polymers have attracted much attention between scholars [2, 3].

The PPy can be utilized in various applications such as anticorrosion coating [4], drug delivery[5], batteries [6], heavy metals adsorbent [7,8] and fuel cells [9]. Polymeric antimicrobial agents have the advantages that they are nonvolatile, chemically stable, and find it difficult to permeate through the skin of man or animal and may enhance the efficiency of some existing antimicrobial agents and minimize the environmental

* To whom correspondence should be addressed.

+ E-mail: m.ghorbani@nit.ac.ir

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problems accompanying the residual toxicity of the agents in addition to prolonging their lifetime [10].

Several benefits of PPy such as the high surface area, small particle size, non-volatility, chemical stability and, the active functional group in the main polymer chain make it a good choice for use as an antibacterial agent [11]. In the other hand, poor mechanical properties and processability of PPy make it necessary to be improved. This can be achieved either by addition of side groups to the polymer backbone [12], grafting of polymers to a non-conducting polymer, forming copolymers of pyrrole[13], or by forming PPy composites or blends with some commercially available polymer that offers better mechanical and/or chemical properties [14]. The association of PPy with other materials in order to prepare composite which combines the properties of both materials is the promising way to obtain the particular requirements for different type of application [15]. Silver (Ag) has been one of the important metals for studying on the nanoscale, due to its extremely high electrical conductivity in bulk and its remarkable optical properties which depend on nanoparticles size and shape [16]. Ag particles have enormous applications in the biomedical, catalysis, optoelectronics, etc. areas [17, 18]. The preparation of polypyrrole/silver (PPy/Ag) composite has been of increasing interest due to unique optical and electrical characteristics of metal and conductive properties of the polymer [15]. In addition, it was shown that organic polymers are excellent hosts for trapping nanoparticles of metals, because of their ability to act as stabilizers or surface capping agents [19]. Several attempts have been made to investigate the effect of reaction conditions on properties and morphology of PPy/Ag composites [15, 20]. Marakova and co-workers studied the antibacterial and cytotoxicity of cotton fabric coated with PPy/Ag composite. Their analysis revealed sufficient antibacterial activity and low cytotoxicity of PPy/ag-coated samples.

The present work is aimed to in one hand utilized the synergetic effect of PPy and Ag, and on the other hand propose an antimicrobial nanocomposite with higher solubility and mechanical properties. PPy/Ag nanocomposite was prepared in the aqueous solution using FeCl_3 as an oxidant in the presence of silver nanoparticles as the additive, and hydroxypropyl cellulose (HPC) as a surfactant. The morphology of

PPy/Ag nanocomposite was characterized by SEM and TEM. The biological activity of PPy/Ag was explored against Gram-negative bacteria; *E. coli* and Gram-positive bacteria; *S. aureus* by means of disk diffusion method. It was tried that the article discusses the mechanism of the antimicrobial performance of PPy/Ag in both schematic and description.

EXPERIMENTAL SECTION

Instrumentation

The morphology, structure and particle size of the PPy/Ag nanoparticles were investigated using a transmission electron microscope (TEM; Zeiss EM10C, Germany, operating at 80 KV) and scanning electron microscope (SEM; KYKY EM-3200, China). TEM samples were prepared by casting one drop of a dilute particle suspension onto a copper grid with a carbon support membrane.

Reagents

Materials used in this work were pyrrole ($d = 0.97 \text{ g/mL}$), silver nanoparticle (Ag, %99.99), ferric chloride (FeCl_3), hydroxypropyl cellulose (HPC, $M_w = 10^6$) from Merck. All reagents were used as received without further purification unless stated otherwise. Distilled deionized water was used throughout this work. The pyrrole monomer was purified by simple distillation.

Bacteria

The Gram-negative bacteria; *E. coli* (PTCC 1398) and Gram-positive bacteria; *S. aureus* (ATCC 25923), provided by the Babol University of Medical Sciences, was used as a test bacterium in the experiments on the antibacterial activity of PPy/Ag. Microorganisms were incubated at 37°C for 24 h on a nutrient agar plate before use.

Preparation of polypyrrole nanocomposite

For the preparation of PPy/Ag nanocomposite, 5.4 g FeCl_3 was added to 100 mL of water and then a uniform solution was resulted by using a magnetic mixer. Then 0.4 g of HPC and 0.1 g Ag nanoparticle were added to the solution and 1 mL of freshly distilled pyrrole monomer was injected to stirred the solution. The reaction was carried out at room temperature for 5 hours. Consequently, the product was filtered and in order to separate

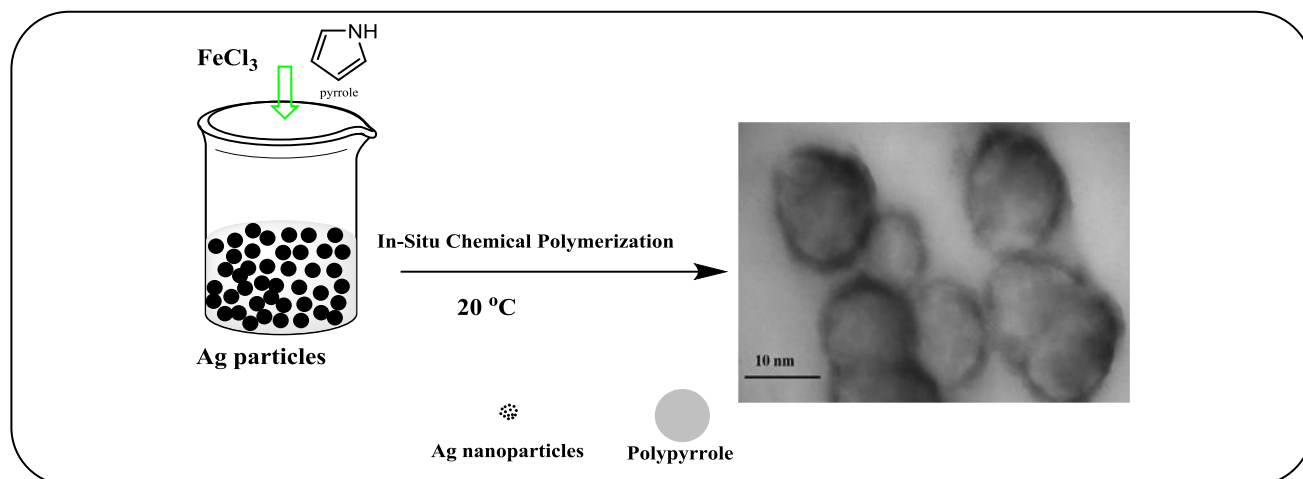


Fig. 1: Schematic representations of formation mechanisms of PPy/Ag nanocomposite.

the oligomers and impurities, the product was washed several times with deionized water. It was then dried at the temperature of about 60 °C in the oven 24 h. The synthesis procedure of the PPy/Ag nanocomposite is illustrated in Fig. 1.

Disk diffusion technique

The antibacterial properties were measured by the disk technique against Gram-negative bacteria *E. coli* and Gram-positive bacteria; *S. aureus*. For the disk diffusion technique, sterile filter paper disks with the diameter of 15 mm that were saturated with PPy/Ag suspension was put on the center of agar plates which had 200 μ L inoculums fairly well-distributed. The inhibition zone was measured after 24 h incubation at 37°C. Area of the zone of inhibition is used as a criterion to ascertain the biocidal activity. According to this criterion, 20 mm zone of inhibition represents significant activity while 10–12 mm inhibition activity is good, 7–9 mm is low, and an inhibition zone below 7 mm represent non-significant activity [21].

RESULTS AND DISCUSSION

The morphology of PPy/Ag nanocomposite was studied using SEM and TEM. In Fig. 2 morphology of the synthesized PPy/Ag is shown. As was anticipated, PPy shows uniformly dispersed spherical particle morphology and the surface of PPy is covered with uniformly dispersed Ag particle were average diameters of PPy particles are 15–25 nm. Adsorption or electrostatic interaction between Ag and PPy particles is the main reason for the deposition on PPy [22].

Spherical morphology provides the high surface area to volume ratio that is the important factor in different biological application because can contribute to their specific functions even at low concentration [23, 24].

PPy/Ag actively inhibited the growth of *S. aureus* and *coli* microbes and therefore tested positive for its antimicrobial activity. The pictures displayed in Fig. 3 indicate that after 24 h of incubation, the zones of inhibition for the PPy/Ag versus two microorganisms are significantly outlined (5 – 8 mm; the inhibition zone diameter does not include the diameter of a sample). In Fig. 3 white, hazy areas indicate bacterial growth, whereas the more transparent circles surrounding the PPy/Ag, in the agar, indicate bacterial-free regions, i.e. zones of inhibition. PPy/Ag showed antibacterial activity against *S. aureus* (5 ± 0.5 mm) and *E. coli* (8 ± 0.5 mm). One reason for the effective performance of PPy/Ag nanostructures as an antibacterial component is because of its nanostructure where the majority of molecules in the PPy/Ag nanostructure reside at the surface, which maximizes the contact of PPy/Ag to the target functional groups in microorganisms [25].

Bactericidal mechanism

Generally, the antibacterial mechanism of action falls within one of four mechanisms, inhibition of enzymes involved in cell wall biosynthesis, inhibition of nucleic acid synthesis, inhibition of protein synthesis and disruption of membrane structure [26]. It is generally accepted that the main bactericidal mechanism of action of the polymeric biocides involves adsorption to the cell

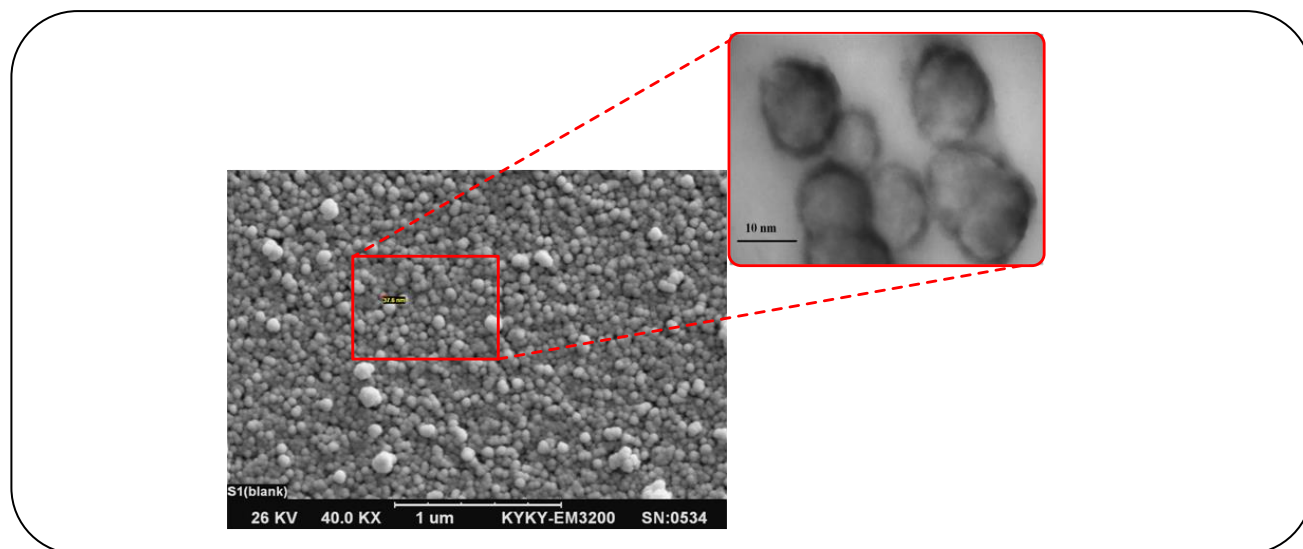


Fig. 2: SEM and TEM of PPy/Ag nanocomposite.

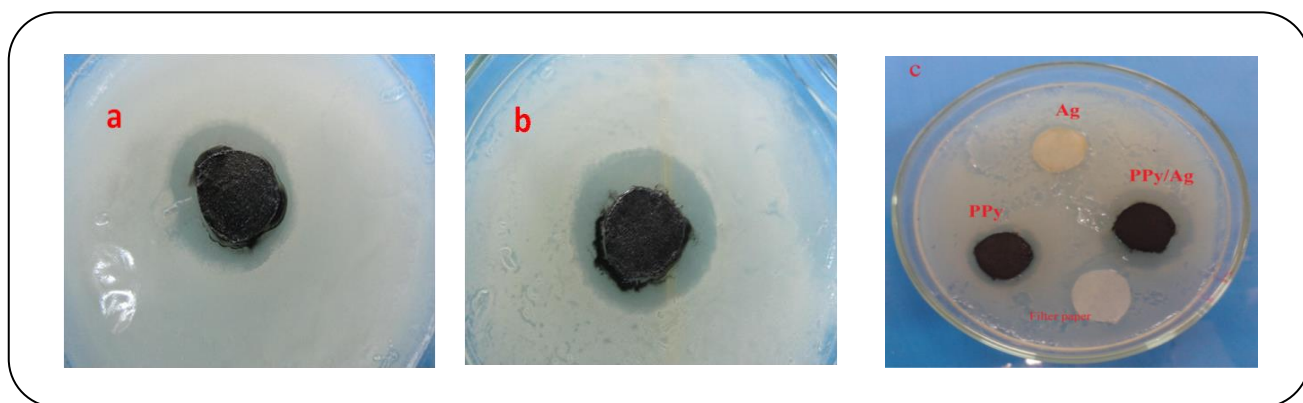


Fig. 3: Inhibition zones of PPy/Ag against (a) *S. aureus* and (b) *E. coli* and (c) filter paper and PPy control sample against *E. coli*.

wall and/or cytoplasmic membranes and inhibition of metabolic reactions alongside cell wall membrane disruption [27]. In this regard, the antibacterial effect of PPy/Ag nanocomposite could be explained by the “phospholipid sponge effect” hypothesis [28]. According to this hypothesis, the biocidal action is triggered by the interaction between the negatively charged phospholipids in the microorganism cellular membranes and the positively charged surface of PPy/Ag nanocomposite. Mechanisms of antibacterial action of PPy/Ag nanocomposite are depicted in Fig.4. As Fig.4 shows that, in step 1 PPy/Ag nanocomposite via electrostatic contact, made direct binding to cell wall phosphate-containing components and subsequently at step 2, leads to disruption of the microorganism cell wall membrane and leakage of critical cell contents and cell death.

CONCLUSIONS

In this paper, we reported the synthesis of PPy/Ag by chemical polymerization of pyrrole in the presence of FeCl_3 as an oxidizing agent. The product was characterized in terms of morphology and antibacterial performance. The results of SEM and TEM measurements indicated that the PPy/Ag nanocomposite was successfully prepared. Also, the results show that the morphology of the particles is spherical and the surface of PPy is covered with uniformly dispersed Ag particles. The particle sizes of the PPy/Ag were 15–25 nm obtained by TEM. PPy/Ag showed antibacterial activity against *S. aureus* (5 ± 0.5 mm) and *E. coli* (8 ± 0.5 mm). Spherical morphology of PPy/Ag increase surface area of polymer and lead to significant enhancement in antibacterial activity against *S. aureus* and *E. coli*. It is the hypothesis that PPy/Ag

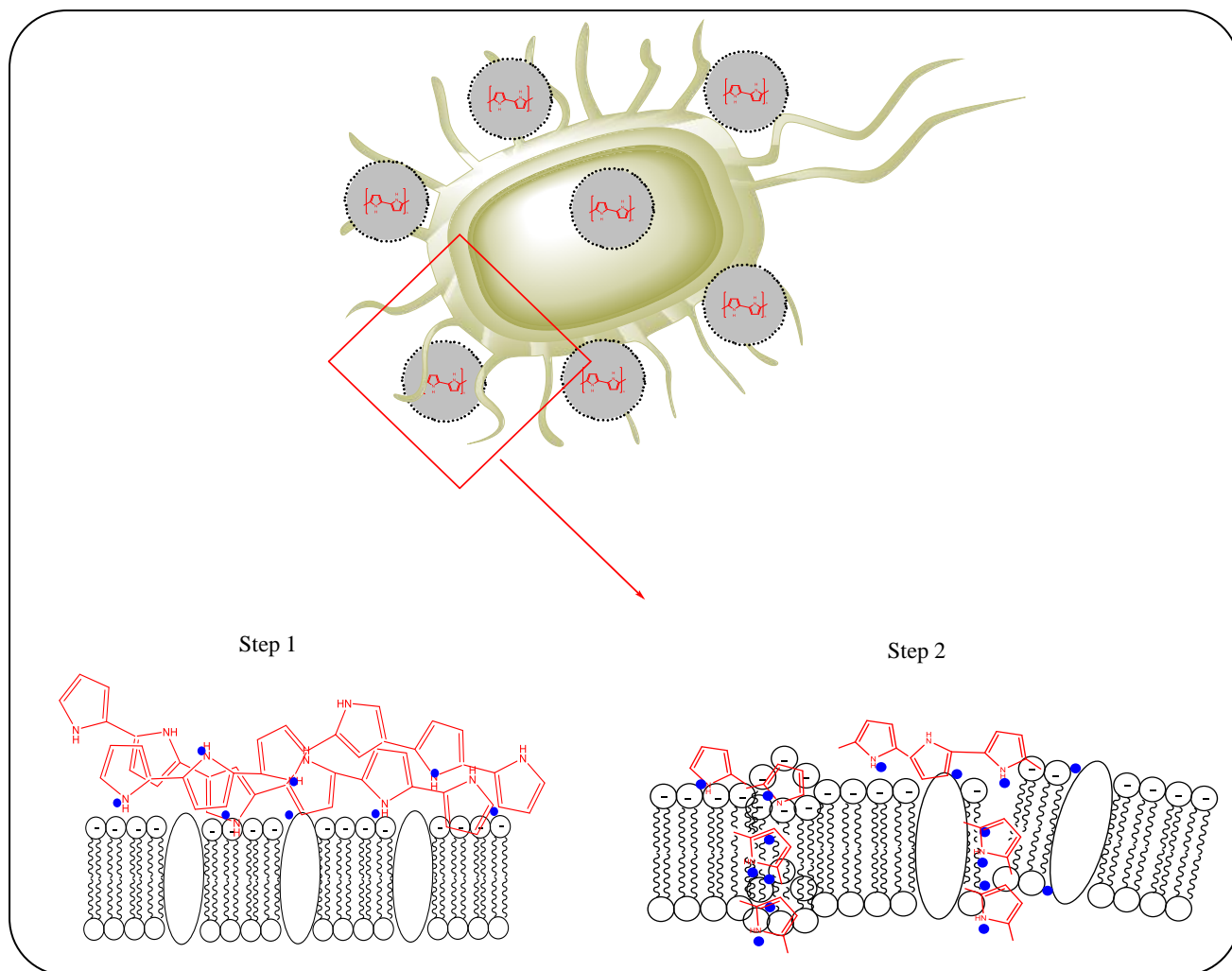


Fig. 4: Mechanisms of antibacterial action of PPY/Ag nanocomposite.

nanocomposite via electrostatic contact made direct binding to cell wall phosphate-containing components and subsequently leads to disruption of the microorganism cell wall membrane and leakage of critical cell contents and cell death.

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