



# A novel, rapid synthetic protocol for controllable sizes, conductivities and monomer units of soluble polypyrrole



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## ABSTRACT

We report a facile synthesis of polypyrrole spheres with controllable sizes, monomer units and conductivities using sodium nitrite and nitric acid in presence of the anionic surfactant sodium tetradecyl sulfate. The rapid synthesis of polypyrrole spheres was accomplished without employing any explicit oxidizing agents. The characterization of polypyrrole (PPy) is carried out using FTIR, XRD, SEM, TEM and TGA while the molecular weight is estimated from the MALDI TOF analysis. The precise tuning of various physicochemical properties is accomplished by altering the concentrations of sodium nitrite and is attributed to the *in situ* generation of NO<sub>2</sub>. The size of the PPy spheres varies from 45 nm to 350 nm depending upon the concentration of NaNO<sub>2</sub>. The dynamic light scattering studies provide mechanistic insights into the role of sodium nitrite in altering the pyrrole-incorporated micellar size of the surfactant, leading to different diameters of the PPy spheres. The surfactant-induced solubility of PPy is rationalized with the help of the X-ray diffraction patterns. The solution of PPy in dimethylsulfoxide has a remarkable ability of selectively detecting Cu<sup>2+</sup> and Hg<sup>2+</sup> among a host of other bimetallic ions, as inferred from colorimetry and UV–Visible absorption spectroscopy.

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## 1. Introduction

Conducting polymers having metal like conductivity and polymeric properties render themselves as potential candidates for a wide range of applications in sensors [1,2], electrochromic devices [3], batteries [4], supercapacitors [5], optical devices [6], energy storage [7], etc. Conducting polymers are insulators in their neutral states and can be converted into conductive states by doping [8] with conductivities spanning a range of 10<sup>-3</sup> to 10<sup>4</sup> S cm<sup>-1</sup>. This doping can be achieved by chemical or electrochemical oxidations, wherein the positive charges are acquired by the polymer backbone and to maintain electroneutrality, the oppositely charged counter anions enter the polymer matrix. This leads to impressive alterations in optical as well as physico-chemical properties. Several conducting polymers viz polypyrrole (PPy), polyaniline, polythiophene, polyindole, polyethylenedioxy thiophene have been widely employed during the past few decades [9–14]. Among these conducting polymers, PPy has attracted great interest due to its ease of preparation, wide conductivity range (10<sup>-2</sup> to 10<sup>4</sup> S cm<sup>-1</sup>), satisfactory environmental stability and biocompatibility. PPy has been employed in sensors [15,16], batteries [17], supercapacitors [18], electrochromic devices [19], etc. In order to enhance the performance in various applications, PPy nanostructures in conjunction with simpler synthetic strategies are required. PPy nanomaterials provide large surface areas as well as

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unique properties which facilitate the interaction of PPy with the species of interest, thereby rendering them as suitable materials in diverse contexts.

The chemical polymerization of pyrrole can be accomplished using dispersive polymerization [20], interfacial polymerization [21,22], seeding techniques [23,24], emulsion polymerization [25,26], etc. Surfactant-assisted emulsion techniques offer facile routes for synthesizing PPy whereby interesting optical, electrical and morphological properties can be achieved in conjunction with easy removal of templates. Further, the surfactants enable tuning of the morphologies and dimensions of the polymers via micelle formation through interactions between the reactants and solvent molecules [27]. Depending upon the nature of the surfactants, the morphologies of PPy vary from nanospheres, nanotubes to nanofibers [27–29]. The nanofibers and nanospheres of PPy have been synthesized using the cationic surfactant Cetyltrimethylammonium bromide (CTAB) which influences the solubility and conductivity [28,30]. Indeed, the anionic surfactants are also interesting since they act both as surfactants and counterions. Thus, diverse morphologies of PPy can be synthesized using sodium dodecyl sulfate, dodecylbenzenesulphonic acid, azobenzenesulphonic acid, etc. [31,32]. The chemical polymerization process also offers the simplest method of tuning the conductivities by doping with strong acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> or HClO<sub>4</sub> [33,34]. However, the formation of PPy requires in general, a time duration ranging from 6 to 12 h due to the initially sluggish oxidation of pyrrole monomers. Thus simple, robust and rapid synthetic protocols for PPy with tunable physicochemical properties are especially challenging.

Here we report a novel methodology for the synthesis of polypyrrole (PPy) nanomaterials with controllable sizes, monomer units and conductivities. The synthesis is carried out with sodium nitrite in acidic medium (HNO<sub>3</sub>) in contrast to the customarily used oxidizing agents for polymerization. Since surfactants often yield interesting morphological and spectral features, PPy is synthesized using a new anionic surfactant sodium tetradecyl sulfate (STS). We demonstrate that the sizes, monomer units and conductivities of PPy can be altered by solely varying the concentration of NaNO<sub>2</sub>. Further, PPy prepared in the presence of STS is soluble in various solvents viz dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), dimethyl acetamide (DMA), etc. The origin of the solubility is rationalized using the XRD data. We also establish that the PPy solution is capable of selectively detecting Cu<sup>2+</sup> and Hg<sup>2+</sup> ions among various bimetallic ions. For quantitative estimation of these ions, the UV–Vis spectroscopy has been employed.

## 2. Experimental section

### 2.1. Chemicals

Pyrrole (SRL chemicals India) was distilled at 140 °C under nitrogen atmosphere at reduced pressure and stored in the refrigerator. Sodium nitrite (NaNO<sub>2</sub>), nitric acid (HNO<sub>3</sub>), potassium chloride (KCl), dimethyl sulphoxide (DMSO) cupric sulfate (CuSO<sub>4</sub>) and mercuric sulfate (HgSO<sub>4</sub>) (SRL chemicals India) were employed without further purification. Sodium tetradecyl sulfate [CH<sub>3</sub>(CH<sub>2</sub>)<sub>13</sub>OSO<sub>3</sub>Na] procured from Sigma Aldrich was used as received. All experiments were performed using triply distilled water.

### 2.2. Synthesis of polypyrrole

In a typical synthesis, 0.031 g of STS was added to 20 mL of triple distilled water in a 100 mL beaker and stirred using a mechanical stirrer for five minutes. Subsequently, 0.77 g of distilled pyrrole and 60 μL of 12 M HNO<sub>3</sub> were added and then sonicated for 10 min in order to obtain a clear solution, followed by the drop wise addition of 20 mL of 0.25 M solution of NaNO<sub>2</sub> with continuous stirring. The instantaneous appearance of a black precipitate due to the addition of NaNO<sub>2</sub> indicates the formation of polypyrrole. The entire reaction was carried out at a temperature of 30 ± 1 °C. After five minutes, the precipitate was filtered using a Whatman 42 filter paper and washed repeatedly with distilled water so as to remove all the soluble oligomers and other side products. The black precipitate was then dried in an oven at 50 °C for four hours. The same procedure was also employed for synthesizing PPy in the absence of the surfactant STS. The PPy synthesized by adopting the above procedure using the aforementioned composition in presence and absence of surfactant are designated as WSPPy and WOSPPy respectively.

The synthesis of PPy was carried out in the presence and absence of the anionic surfactant STS using identical concentrations of pyrrole and other chemicals viz. NaNO<sub>2</sub>, HNO<sub>3</sub> in order to study the differences in their properties. For comprehending the effect of NaNO<sub>2</sub>, different compositions of pyrrole and NaNO<sub>2</sub> were employed by altering the NaNO<sub>2</sub> concentrations. Since our objective is to analyze the surfactant-induced polymerization, different PPy samples were synthesized by altering the pyrrole: NaNO<sub>2</sub> concentration in the range of 1: 2/3, 1: 4/3, 1: 5/3, 1: 8/3 using the concentration of STS and HNO<sub>3</sub> as 0.00125 M and 0.018 M respectively. These different compositions were made by keeping a fixed concentration of pyrrole (as 0.075 M) while NaNO<sub>2</sub> concentrations were varied from 0.05 M to 0.20 M. However, the concentrations of STS and HNO<sub>3</sub> were kept constant in general. The PPy prepared in presence of STS using the above-mentioned different composition ratios of pyrrole and NaNO<sub>2</sub> are denoted as WSPPy 1, WSPPy 2, WSPPy 3 and WSPPy 4.

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