Characterization of Stable Aqueous Dispersions of Polypyrrole Nanospheres Synthesized Using Ozone Oxidation

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Conducting Polymers (CP) such as polyaniline (PANI) and polypyrrole (Ppy) have been synthesized and characterized extensively during the past few years, owing to their promising applications in several fields including corrosion inhibition, capacitors, artificial muscles, solar cells, polymer light emitting diodes, and energy storage devices.[1] Nanostructures of conducting polymers (CPN) further enhance electrical, optical and mechanical properties of CPs. Stable dispersion of CPNs is desirable if the properties are to be utilized to its fullest potential, however, it is challenging to maintain CPNs in stabled dispersions due to increased Van der Waals attraction forces due to increased surface area.

The stable dispersions of CPNs have conventionally been achieved using colloidal dispersants such as polyvinyl pyrrolidone (PVP) and polyvinyl acetate (PVA). However, colloidal stabilizers might modify properties of CPNs by incorporating its own properties; while increasing the cost of the synthesis. Therefore, synthesis of stable dispersions of CPNs without using external stabilizers is of scientific interest. We have previously reported synthesis of stable aqueous dispersions of PPY and PANI nanospheres using ozone oxidation, in a one-step one-pot synthesis, without using external stabilizers.[2] It is worth mentioning that the PPY and PANI nanospheres obtained in the synthesis exhibit uniform spherical morphology as well as narrow particle size distribution.

Use of ozone as an oxidant for the synthesis of CPNs present unique challenges as well as several experimental opportunities, due to pH and temperature dependence of reaction of ozone with water. Not only ozone but also reactive radicals produced from the reactions of ozone and water take part in oxidation of pyrrole to PPY. In this work, PPY nanospheres synthesized using ozone oxidation has been characterized using various characterization techniques. The effect of ozone concentration on the size and morphology of the nanospheres is studied using electron microscopy. To study the roll of water as a solvent in the synthesis, water was replaced systematically with methanol.

Table 1: Reaction Summary

Ozone Concentration Experiments		**Methanol Concentration Experiments**	
Reaction	Concentration of ozone	Reaction	Water/Methanol Ratio (V/V)
R-1	17.31%	R-6	100 : 00
R-2	15.75%	R-7	90 : 10
R-3	14.38%	R-8	80 : 20
R-4	13.47%	R-9	70 : 30
R-5	13%	R-10	60 : 40

In a typical experiment, 0.17 M pyrrole solution was prepared in 18 MΩ Millipore water. Ozone was bubbled through 100 mL pyrrole solution for 60 seconds. Excess ozone was removed from the flask using air stream. Finally, the reaction was allowed to rest for four days before characterizing the samples. Table 1 lists the reactions that were performed to study effect of ozone concentration and effect of methanol on the morphology and electrochemical activity of the PPY nanospheres

Analysis of PPY nanospheres using scanning electron microscopy (SEM) suggests that with decrease in ozone concentration particle size as well as particle size distribution of nanospheres increased (Figure 2: top). Replacement of water with methanol similarly resulted in a larger particle diameter as well as larger particle size distribution (Figure 2: bottom).

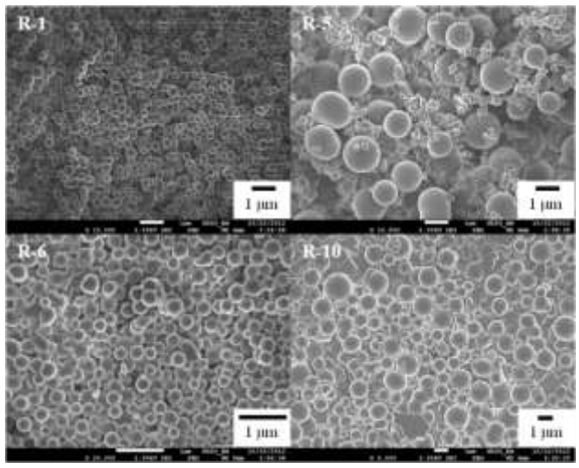

Figure 2: SEM images of ozone concentration (top) reactions Left (R-1) and Right (R-5). SEM images of methanol concentration (bottom) reactions left (R-6) and right (R-10) (Note: Scale bars reproduced)

Electrochemical activity of PPY nanospheres (Figure 1) was characterized using Cyclic Voltammetry (CV). CV was performed on PPY nanospheres using 1.5 M hydrochloric acid solution as an electrolyte at a scan rate of 100 mV/sec. The potential was applied against Ag/AgCl reference electrode. The oxidation peak was observed at approximately at 145 mV while reduction peak was observed at approximately at -40 mV. The nanospheres were further characterized using X-ray photoelectron spectroscopy (XPS), dynamic light scattering (DLS), and UV VIS spectroscopy.

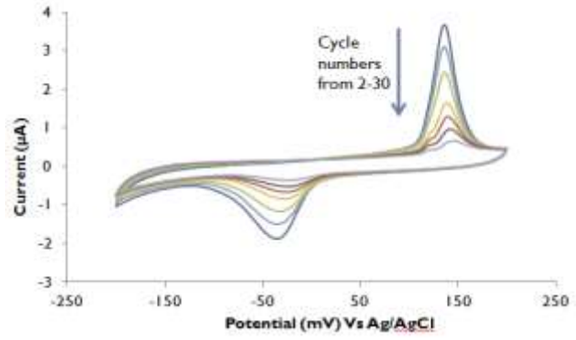

Figure 1: Cyclic voltammetry curves of PPY nanospheres

References:

1. Inzelt, G., Applications of Conducting Polymers. *Conducting Polymers* 2012, 245-293.
2. Vetter, C. A.; Suryawanshi, A.; Lamb, J. R.; Law, B.; Gelling, V. J., Novel Synthesis of Stable Polypyrrole Nanospheres Using Ozone. *Langmuir* 2011, 27, 13719-13728.