Synthesis of One-Dimensional Tetraaniline Nanorods via Interfacial Polymerization Method

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Abstract: ***One dimensional Tetraaniline nanorods have been synthesized by interfacial polymerization method using N-phenyl-1, 4-phenylediamine as monomer (NPPD), ammonium persulphate (APS) as an oxidant in toluene/water biphasic medium. As synthesized Tetraaniline nanostructures have been characterized by a range of spectroscopic as well as microscopic techniques such as UV-Visible, FTIR, XRD and SEM. The spectroscopic results indicated that formation of Tetraaniline nanostructures. The SEM images clearly reveals the morphology of as prepared Tetraaniline were critically depends on molar ratios of monomer to oxidant.***

Keywords: One dimensional nanostructures, Interfacial polymerization, Tetraaniline and Nanorods

1. Introduction

Since the discovery of intrinsic conducting polymers (ICPs) significant efforts have been carried out on conducting polymers. Among the all ICPs, Polyaniline (PANI), its derivatives and oligomers have attracted attention due to their unique electro-chemical, redox properties, environmental stability [1-3] and their technological applications such as batteries [4], electromagnetic shielding devices [5], anticorrosion coatings [6] and sensors [7]. PANI can be synthesized through oxidative polymerizaiton [8], emulsion [9], inverse emulsion polymerization [10], self-assembly methods [11]. Recent past, PANI nanostructures such as nanorods, nanofibers, nanoflowers and nanorods etc. have been extensively investigated for so many applications such as sensors in chemical and biological sectors [12-13] due to their low dimensionality and high surface to volume ratios. PANI Nanostructues have been synthesized by various approaches such as soft, hard templates [14, 15], interfacial polymerization [16], electrochemical polymerization [17], electro-spinning [18] methods. However it is very difficult to remove the soft and hard templates in template assisted synthesis of PANI nanostructures. Moreover the removal of hard template can destroy the PANI nanostructures. More recently, interfacial polymerization method has emerged as potential technique for preparation of PANI nanostructures such as rods, wires and flowers etc.[19]. In this interfacial polymerization, the morphology of PANI nanostructures can be tuned by the reaction parameters such composition of organic/aqueous phases and molar ratios of monomer to oxidant [20].

Though numerous studies on PANI nanostructures, less attention was paid on oligomers of PANI such as Tetraaniline (TAN), Hexaaniline and Octaaniline etc. The oligomers of PANI have similar properties and structures and thus they have regarded as model compounds for PANI. More recently, TAN has emerged as a potential candidate for technological applications due to its similar structure and unique chemical and electrochemical properties. In this paper, we report the synthesis of TAN nanorods using N-phenyl-1, 4-phenylediamine (NPPD) as a monomer and ammonium persulphate (APS) as an oxidizing agent in toluene and water as the reaction medium via interfacial polymerization method. The effect of molar ratio of NPPD to APS on morphology was investigated.

2. Experimental

2.1. Materials

N-phenyl-1, 4-phenylediamine (NPPD) and acetone was purchased from Aldrich and used without further purification. Ammonium persulphate (APS), Toluene and Hydrochloric acid (HCl) were obtained from Merck Chemicals, India and used as received. Throughout the synthetic processes Milli-Q water with resistance greater than 18 MΩ was used. All the reagents were analytical grade and used without any further purification.

2.2. Synthesis of Tetraaniline (TAN) nanorods

In typical synthesis process, 0.093 g of NPPD was dissolved in 50 ml of toluene. 0.114 g of APS was dissolved in 50 ml of Milli-Q water and then 5 ml of 1M HCl was added to aqueous APS solution. Finally acidified aqueous APS solution was added to the NPPD solution and then the reaction was allowed to proceed at room temperature. After 30 minutes the reaction mixture was changes into light green color at the interface of toluene-water and gradually the entire aqueous phase was turned into green color which indicates formation of TAN. The reaction was further preceded for 5 hours. The aqueous phase then filtered and washed several times periodically with acetone, water and finally dried under vacuum at room temperature. The similar procedure was adopted for synthesis of TAN by varying the molar ratio of monomer to oxidant as 1: 0.125, 1: 0.25, 1: 0.5 and 1: 1.

2.3. Characterization

The absorption spectra were obtained using a Perkin-Elmer double beam LS-50 UV-Visible spectrophotometer. FTIR spectra were recorded over the range of 400-4000 cm^{-1} with Perkin Elmer SPECTRUM 1000 FTIR spectrophotometer. Phase identification was carried out with powder x-ray diffraction analysis (XRD - Siemens AXS D5005 X-ray diffractometer with Cu-Kα radiation). Morphology of TAN was investigated by scanning electron microscopy (SEM-JEOL JSM 6610LV).

3. Results and Discussion

In the interfacial polymerization method, NPPD is completely dissolves in toluene and forms brown color solution. When NPPD was oxidized by APS, initiation of polymerization occurs and forms TAN, then entire organic phase becomes colorless and if any other monomers left in solution it remains in original color. The exact growth mechanism of formation of nanorods is yet to be not known but there are some reports which suggest hypothetical growth mechanism [21, 22]. In general formation of nanorods occurs via two ways. In the first only nanorods were observed due to the homogeneous nucleation of TAN. The formed nanorods acts as nucleation sites for further reacting monomers. In the second further polymerization proceeds, preferential growth on previously formed nanorods by heterogeneous nucleation which results irregular shape of TAN in micro-size. The formed TAN nanorods at the interface of the two solutions can enters into the aqueous phase [23] thereby avoid further polymerization and produces only nanorods.

UV-Visible spectrum (**Figure 1**) of TAN shows that two characteristic peaks were raised at 290 and 600 nm. The former arises due to $\pi \rightarrow \pi$ * transitions, while latter are due to the excitonic transition from benzenoid rings to the quinoid ring [24] of TAN chain. For 1:1, 1: 0.5 and 1: 0.125 ratios the first peak was obtained at 293 nm and for 1: 0.25 ratio the peak was raised at 296 nm. The second peal at 600 nm was obtained for 1:1, 1: 0.5 and 1: 0.25 ratios and 620 nm for 1: 0.125 ratios.

Figure 2 depicts the FTIR spectrum of TAN. The peak at 3458 cm-^{1} is attributed to N-H stretching vibration of aromatic amine, while the peak at 3020 cm^{-1} is due to the aromatic CH stretching vibration of TAN. The peak at 1595 cm^{-1} can be ascribed to C=N stretching vibration in a quinoid ring. The peaks at1493 cm-1 and 1304 cm^{-1} corresponds C-C stretching vibrations in a benzenoid ring and quinonoid ring [25] while peak at 1321 cm^{-1} is due to C-N stretching of benzene ring. The peak at 832 cm^{-1} is attributed to out-plane blending of C-H of 1-4 disubstituted aromatic rings [26]

The powder XRD patterns of TAN were presented in **Figure 3**. XRD pattern clearly shows the peaks at 14.6 ^{o}, 20.7 ^{o} and 27.7 ^{o} which correspond to the amorphous nature of TAN [27]. The relative phase can be indexed as (011), (020) and (200).

SEM images of TAN prepared at different molar ratios of monomer to oxidant were shown in **Figure 4**. SEM images clearly reveal that the morphology of TAN was critically dependent on the molar ratios of monomer to oxidant. The TAN nanorods were observed for 1:1 molar ratio of monomer to oxidant. However fibrillar like morphology were obtained for other molar ratios (1: 0.125, 1: 0.25 and 1: 0.5).

4. Conclusions

TAN nanorods have been successfully synthesized through interfacial polymerization method. UV-Visible and FTIR results confirm that successful formation of TAN. The three characteristic peaks of XRD of TAN at 14.6 ^{o}, 20.7 ^{o} and 27.7 ^{o} reveal the amorphous nature of TAN. SEM images of TAN clearly indicated that the morphology of TAN is dependent on molar ratios monomer to oxidant. TAN nanorods were for 1:1 molar ratio of monomer to oxidant.

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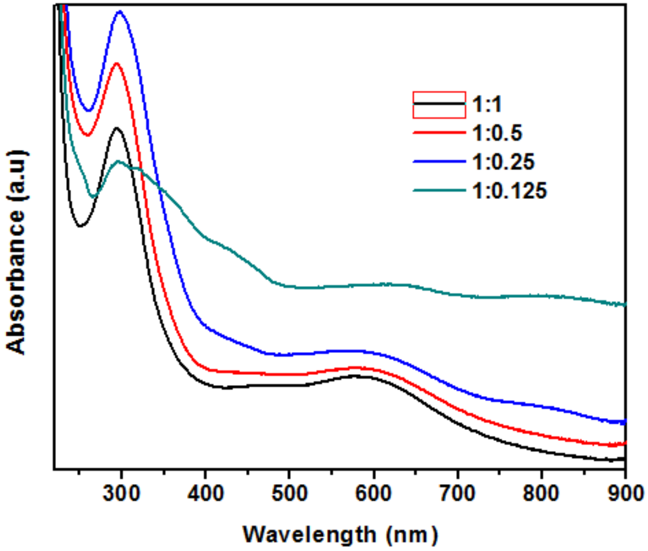


Figure 1: UV-Visible spectra of TAN prepared at various molar ratios of NPPD to APS.

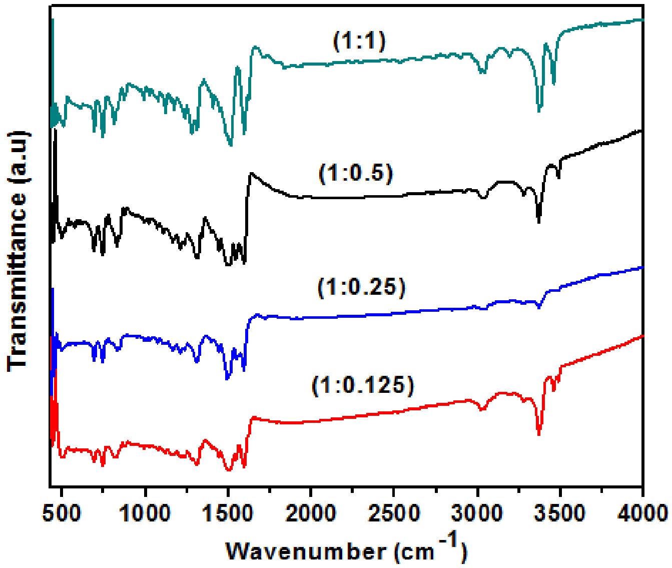


Figure 2: FTIR spectra of TANI prepared at different molar ratios of NPPD to APS

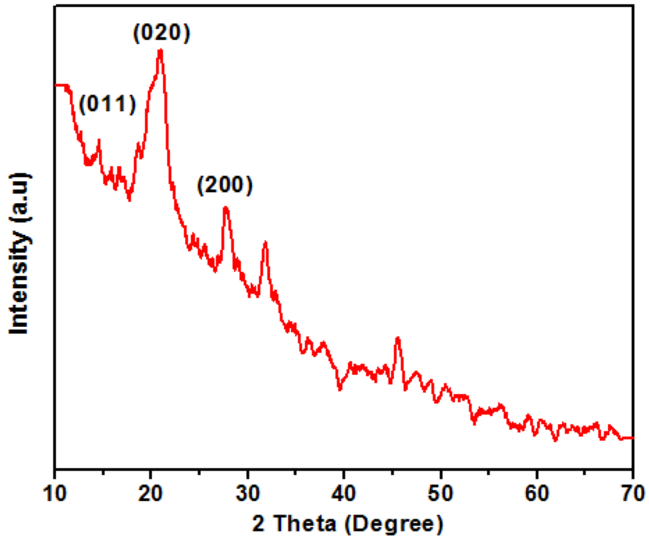
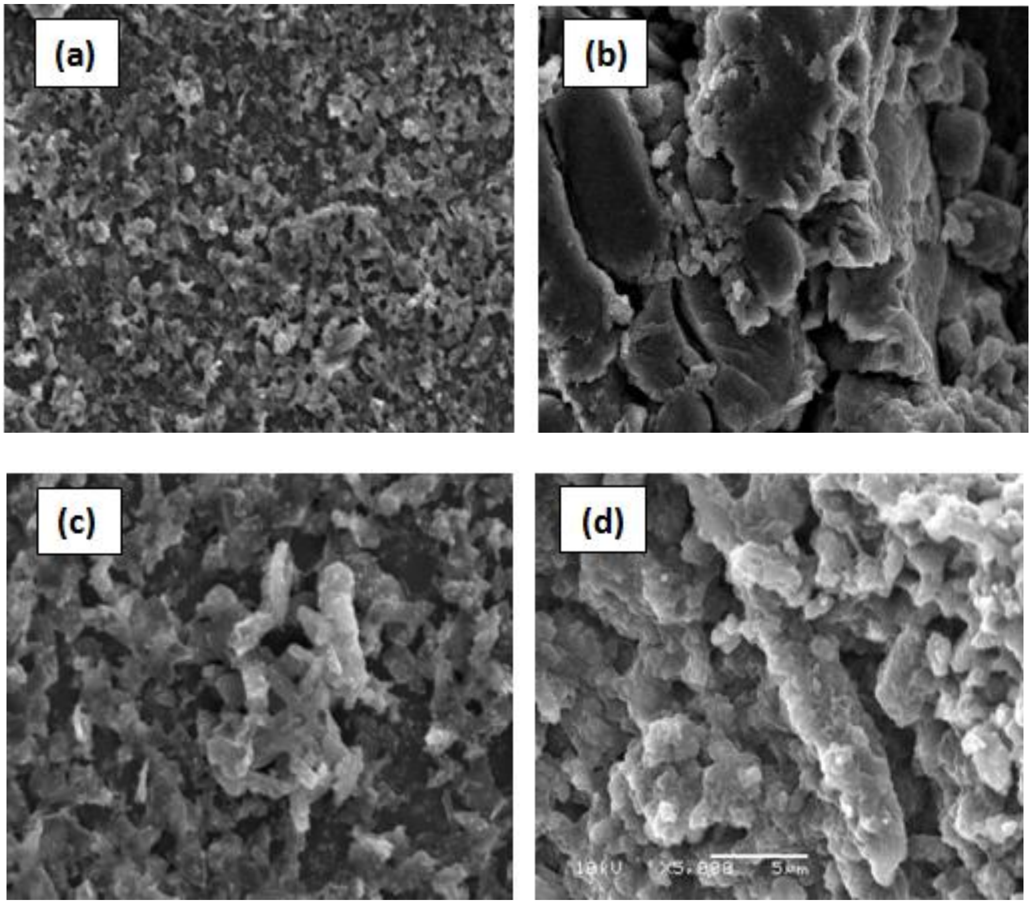


Figure 3: XRD of TAN prepared at 1:1 molar ratio of NPPD to APS.



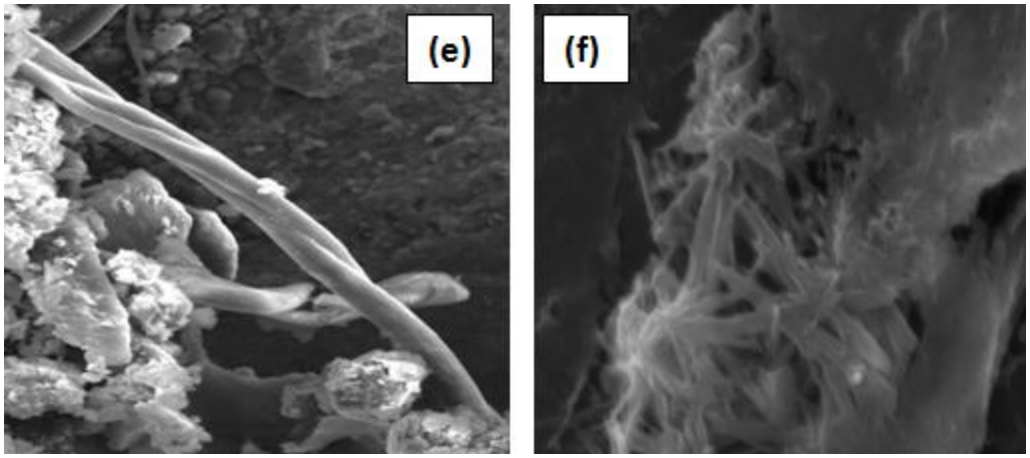


Figure 4: SEM images of TAN prepared at (a) 1:0.125, (b) 1:0.25, (c) and (d) 1:0.5, (e) and (f) 1:1 molar ratios of NPPD to APS.