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Notes

Novel method of fabrication of doped polyaniline nanostructures

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Micro and nanostructures of doped polyaniline are grown directly on a ground glass surface. An *in situ* vapor phase chemical oxidative polymerization, directed by the oxidant which has been pre - deposited on the ground glass surface, is used to obtain the micro/nano structures. The morphology of these structures is studied using optical microscopy and field emission scanning electron microscopy. Formation of different types of one-dimensional nanostructures like tubules, fibers, wires and even ribbon-like structures is indicated. The structures obtained have a wide range of size distribution and also different geometries. Infrared spectroscopic characterization of the obtained polyaniline nano/microstructures also indicates the presence of well-ordered doped polyaniline chains. The present work reports a novel, convenient and economical technique for obtaining polyaniline nanostructures and has high technological importance.

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Over the last decade, extensive research has been conducted on synthesis of one-dimensional nanostructures (nanotubes/nanowires/nanorods) of various inorganic and organic materials[1-4]. Organic conjugated polymers, in particular, are being widely synthesized in nanodimensions because of their unique optical and electronic properties. These nanoarchitectures have shown unusual physical properties because of their low dimensionality and high interactive surface area. Many synthetic strategies have been reported and reviewed for fabricating one-dimensional nanostructures in desired geometries[5]. These include template synthesis[5], reprecipitation[6], microemulsion[7], and evaporation[8]. Vapour phase method for synthesizing nanotubes/nanowires without the use of template has received less attention[4].

Tubular structures of polyaniline have shown enhanced conductivity due to presence of a larger ratio of oriented polyaniline chains in small diameter and large surface area[9]. The polyaniline nanostructures have shown a high degree of self-organization (doped as well as undoped state), resulting in increased conductivity[9]. Hence, there is a growing need for obtaining polyaniline nanostructures. Synthesis of polyaniline based nanostructures has been widely explored and extensively reviewed[10-13]. Since altering the synthetic method influences the electrical/electrochemical properties of polyaniline nanostructures, search for an improved method is still an area of interest. Oxidative polymerization at the organic-aqueous interface has recently been reported for synthesizing nanofibres of polyaniline[13]. Template synthesis within the void spaces of nanoporous membranes has been commonly adopted to obtain polyaniline nanotubes of desired lengths and diameters[14]. This method suffers the drawback of being expensive and tedious due to post synthesis treatment. Search for a convenient and economical method is thus needed in order to meet the technical applications. Therefore, it was thought worthwhile to explore a synthetic strategy that can be used to grow polyaniline nano/microtubules conveniently and directly on a commonly available and applied substrate. In the present study, we report a novel, generic technique in which nucleation and growth of polyaniline tubular/fibrillar structures in micro/nano dimensions occurs rapidly on a ground glass surface.

Experimental

Glass slides of dimension, $25\ \mathrm{mm} \times 75\ \mathrm{mm}$ for optical microscopy and $8\ \mathrm{mm} \times 8\ \mathrm{mm}$ for scanning electron microscopy, were ground for 10 min on one surface using carborundum powder having grain size 125 μm. The ground surface of the slides was coated with a solution of ammonium persulphate using a dip-coating technique (10-12 cycles). In order to optimize the oxidant-monomer vapour ratio required for obtaining best possible nano/microstructures of polyaniline, the slides were coated using ammonium persulphate solutions of concentrations, 2%, 4%, 6%, 8% and 10%. The slides were then air dried for a few minutes and used as substrates subsequently.

Aniline monomer was freshly distilled under reduced pressure prior to the reaction. *In situ* vapor phase polymerization reaction was performed directly on the coated slides in a closed glass chamber. A glass vial containing a solution of monomer in 2*M* HCl in the ratio 1:4 was placed inside the chamber and the slide was placed at a distance of ~ 3 cm from the vial containing monomer. The chamber was heated untill the aniline started vaporizing and the glass slide was exposed to the aniline vapors for ~20 minutes. The slide was removed from the chamber and a series of such slides was prepared. Characterization of doped polyaniline micro/nanostructures obtained as above was performed using optical microscope (Olympus BX 60, eyepiece magnifications, 20X and 50X) and field emission scanning electron microscope (LEO 440, 3.5 resolution in SEI mode, 5.5 nm BEI mode).

IR characterization

Doped polyaniline nano/microstructures were also grown on KBr substrates coated with methanolic suspension of ammonium persulphate. FTIR spectrum of the same was collected in the range 400-4000 cm^{-1} on Bio-Rad 175 C spectrophotometer. Hundred and twenty eight scans were taken at a resolution of 4 cm^{-1}, using air as background. The raw spectrum was subjected to smoothening using Savitzky Golay at 11 points and a multiple point baseline correction.

Results and discussion

A few typical optical microscopic images of doped polyaniline micro/nanotubules obtained in the process using substrates precoated with different concentration of oxidant, are depicted in Fig. 1(a-f). The slide with 2% solution shows the formation of small and fine needle like structures (Fig. 1a), which appear more defined and longer with tube/fiber like shape in the slide with 4% oxidant solution (Fig. 1b). The structures also seem to be nucleating from some central core, most likely solid particles of the oxidant. Micrograph collected at higher magnification from a different part of the same slide depicts image of a smooth walled individual fiber (Fig. 1c). The slide coated with 6% oxidant also renders defined tubular structures but with enhanced diameter (Fig. 1d). Further increase in oxidant concentration to 8% and 10% leads to formation of distorted structures depicted in Fig. 1e and Fig. 1f respectively. The images reveal micro-tubule exhibiting wide channels and an almost bamboo-like morphology. It emerges from the study of the micrographs that a 4% oxidant solution coating, renders well-defined and smooth one-dimensional structures in nano/micro dimensions.

In order to study the morphology and to estimate the size of the structures so obtained the micrographs of structures grown on 4% oxidant coated slide were collected using high-resolution scanning electron microscope. Figure 2, a typical SEM image of as-synthesized polyaniline nanostructures scanned at a lower magnification (3KX) confirms the formation of one-dimensional nanostructures with geometrical configuration of mostly tubular/fibrillar type, growing in different directions but mostly parallel to the etched glass surface. The structures show a broad range of size distributions. The image reveals nanostructures with lengths in the range of around 2-15 micrometers and the diameters in the range of 70-100 nanometers. The tubules/fibers are more or less straight and have nearly uniform diameter along the length. The surfaces also appear to be clean and smooth. It is clearly indicated that the nanostructures tend to agglomerate in a sort of network rather than growing in bundles. This agglomeration network may be attributed to the fact that oxidant is deposited all over the ground surface. It can be observed from the micrographs that most of the tubular/fibrillar structures are attached to an edge of a groove formed as a result of etching. Further enhancing the magnification to 5KX has revealed some interesting images shown in Fig. 3(a-c). Existence of a few coiled/ribbon like structures in nanodimensions (width ~ 100-200 nm) is also observed (Fig. 3b), although the tubular/fibrous shapes are still apparently the preferred geometries (Fig. 3c). The flat, ribbon like geometrical configuration observed here is different from cylindrical nanostructures observed earlier[15].

As indicated by the micrographs the polyaniline nanostructures grown by above method are obtained in different shapes and sizes, and the density of the structures is not too high. It may be suggested here that the monomer vapor-oxidant ratio available at the site of reaction, temperature and the time of exposure appear to be the dominant processing factors in controlling the density and morphology of nanostructures obtained. A growth mechanism may however be speculated upon for the formation of these structures. It may be possible that when the monomer vapor comes in contact with the oxidant

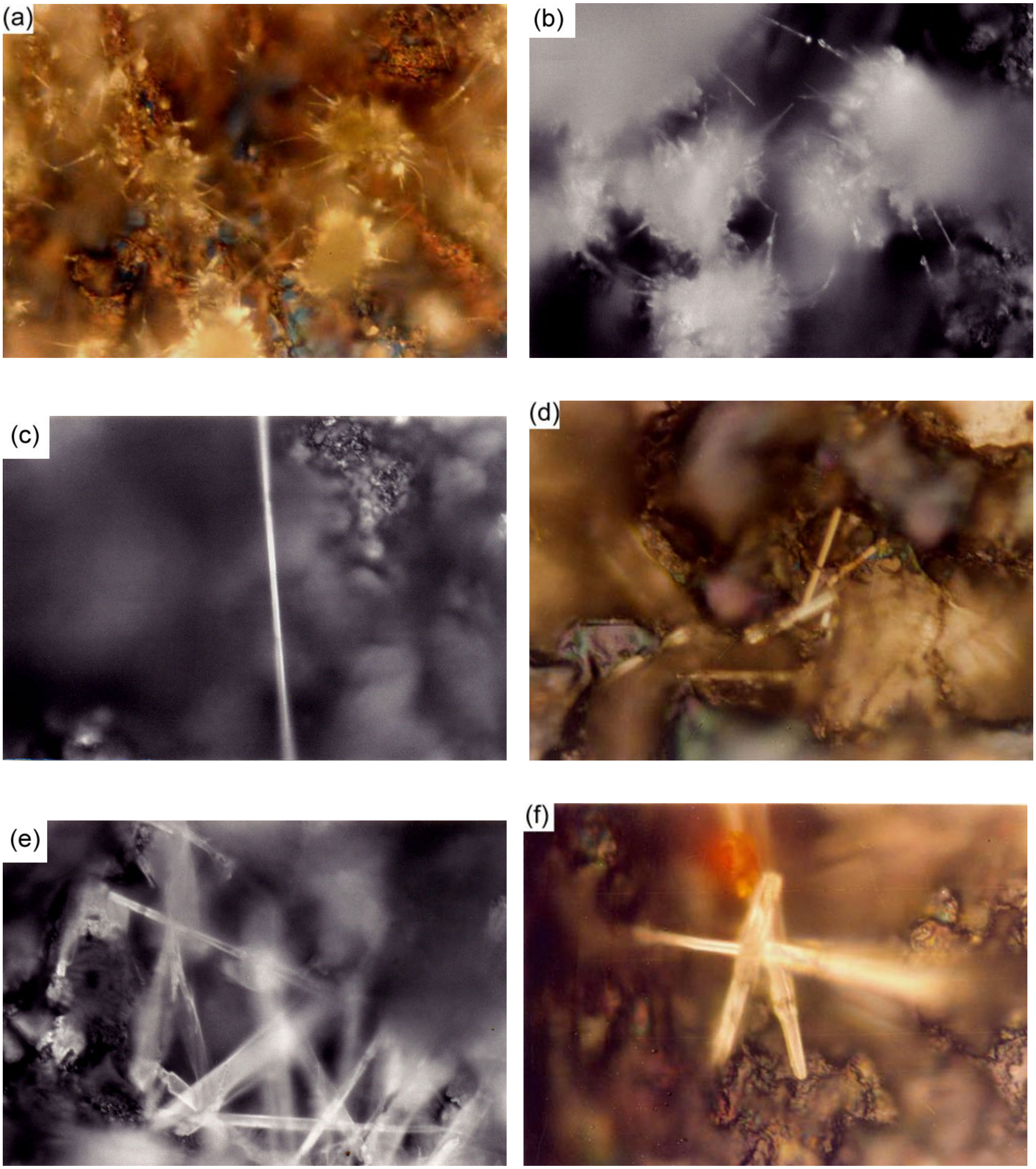

Fig. 1 — Optical microscopic images of polyaniline nano/microstructures obtained on slide with: (a) 2% oxidant; (b) 4% oxidant; (c) 4% oxidant and higher magnification; (d) 6% oxidant; (e) 8% oxidant, and (f) 10% oxidant.

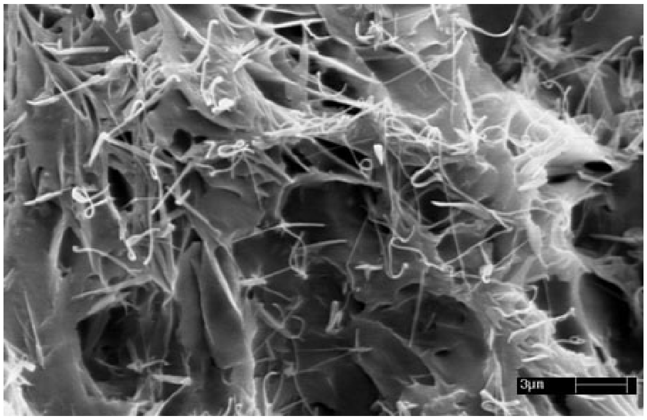

Fig. 2 — A low magnification SEM image (3KX) showing formation of polyaniline nanostructures.

deposited on the etched surface, polymerization starts and nucleates the formation of one-dimensional structures, which tend to grow in scattered fashion all over the surface.

Figure 4 shows the mid infrared spectrum of the nanostructures grown on a KBr substrate using the said technique. All the bands, characterized previously to doped form of polyaniline are present[16]. Sharp, well-resolved bands in the IR spectrum reflect well-defined orientation of molecules in the nano/microstructures so obtained. Broad band at ~ 2924 cm^{-1}, usually characteristic of conducting form of polyaniline, appears well resolved, indicating the possibility of enhanced conductivity of fabricated structures. Also, the peak at ~ 1243 cm^{-1} corresponding to protonated form of polyaniline also

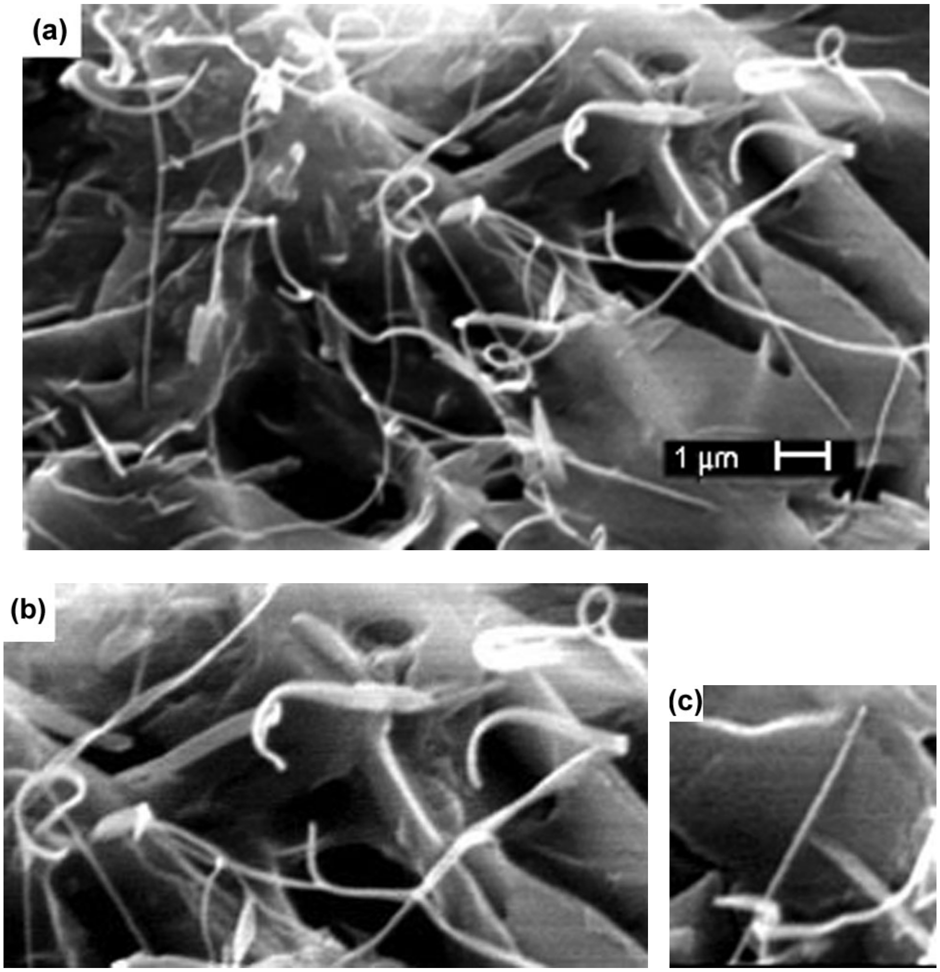

Fig. 3 — (a) A higher magnification (5KX) SEM image revealing different geometries of synthesized polyaniline nanostructures; (b) A part of SEM image showing ribbon like nanostructure, and, (c) A part of SEM image showing a single nanofiber.

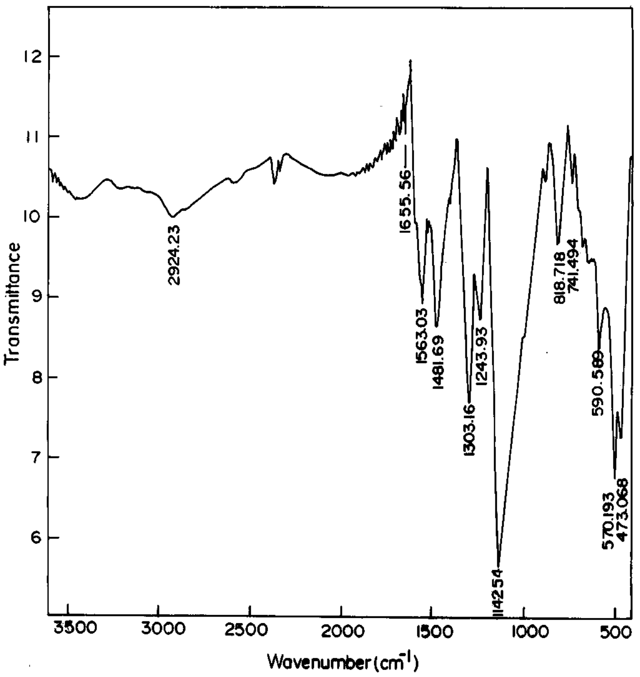

Fig. 4 — FTIR spectrum of polyaniline nano/micro structures in the range 480-3520 cm^{-1}.

appears sharp and well resolved[17] confirming the well protonated state. Well defined absorption at ~3400 cm^{-1}, usually marked as hydrogen bonding peak between interchain NH and NH groups, reflects organization of polyaniline chains in well ordered fashion within the nano/microstructures formed[18]. Similar hydrogen bonding peaks have been observed in polyaniline films consisting of well organized chains[19]. The grown nanostructures appear to be in ~50% oxidation state, as is revealed by comparing the relative integrated absorbance of 1563 to 1470 cm^{-1} peak[20]. No additional changes like oxidation producing carbonyl groups have been observed during growth of nano/microstructures.

By the above method, we have successfully grown one-dimensional micro/nanostructures of doped polyaniline on ground glass surface using an *in situ* oxidative polymerization reaction without the support of host templates. The yield of nanostructures obtained is not as high as in the case of template method where it is controlled by density of nanopores available per unit area but the method has other definite advantages. The method represents a novel, simple and low cost route for synthesis of one-dimensional organic nanomaterials, which are expected to exhibit very interesting physical properties. The method can be of general use for customized synthesis of nanomaterials on potential surfaces. The method, however, does not allow the control of size, shape and orientation and needs further refinement to become a general route for controlled morphological synthesis of polyaniline nanostructures.

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