

MORPHOLOGY EVOLUTION OF POLYANILINE MICROSTRUCTURES IN TOLUENE AND THEIR SURFACE PROPERTIES

Tao Wen¹, Jia-Hua Shi¹, Minrui Zhang², Chorong-Haur Sow², Hardy Sze On Chan¹

¹Department of Chemistry, ²Department of Physics, National University of Singapore, 3 Science Drive 3, Singapore 117542

Abstract

Polyaniline (PANI) morphology evolution in non-polar media has been observed. Various structures, including 1D open-ended microtubes, 2D novel solid microplates and 3D solid microspheres were controllably synthesized in the same reaction system. The structures obtained were sensitive to oxidant concentration and molar ratio of monomer to oxidant. In diluted reaction solutions, solid microplates were mainly produced at the reactor wall/solution interfaces due to adsorption polymerization; while other structures were mainly obtained from solution by employing various reverse micelles as polymerization templates. Studies on the effect of reaction temperature, mechanical stirring and additional acid were also carried out. PANI films prepared from microspheres exhibit novel intrinsic hydrophobic properties.

Introduction

Conducting polymer nanostructures, such as one-dimensional (1D) nanofibers, nanotubes, nanorods, nanoneedles and nanowhiskers, and three-dimensional (3D) microspheres, have been intensively studied. Two-dimensional (2D) nanoflakes, nanosheets and nanodisks have only been recently reported. These structures and their oriented arrays have high potential for applications in sensors micro-electronics.

Template-free growth is a promising way to produce polymer nanostructures in bulk quantities without the need to remove templates. However, the preparation of polymer micro- or nano- structures with controlled morphologies and dimensions is still a challenge. Here we demonstrate for the first time that controllable morphology evolution of various micro- and nano-structures could be realized in non-polar solvent. The main attribute of our technique is that it is much simpler as those discussed previously.

Experimental

1 mmol of aniline (An) and 2.5 mL of 12 mM HAuCl₄/TOAC/toluene solution were dissolved in 250 ml toluene. The solution was thoroughly mixed for several minutes. The reaction was then carried out at room temperature for 12 h. The resulting precipitate was centrifuged and washed with distilled water and ethanol several times to remove residual surfactants and reactants.

The morphology of the samples was studied using a JOEL SEM and TEM. PANI films for evaluation of surface properties were prepared by spin-coating from ethanol solution. Effect of [Aniline] to [HAuCl₄], reaction temperature and stirring on the morphology of the product will be discussed.

Results and Discussion

Figure 1 shows the different morphologies obtained by varying the chloroauric acid concentration. Microtubes were produced at high [HAuCl₄]. Spheres, plates and tubes were formed at intermediate [HAuCl₄]. At low [HAuCl₄], almost pure

plates were found on the glass wall of the reactor while small spheres were formed in solution.

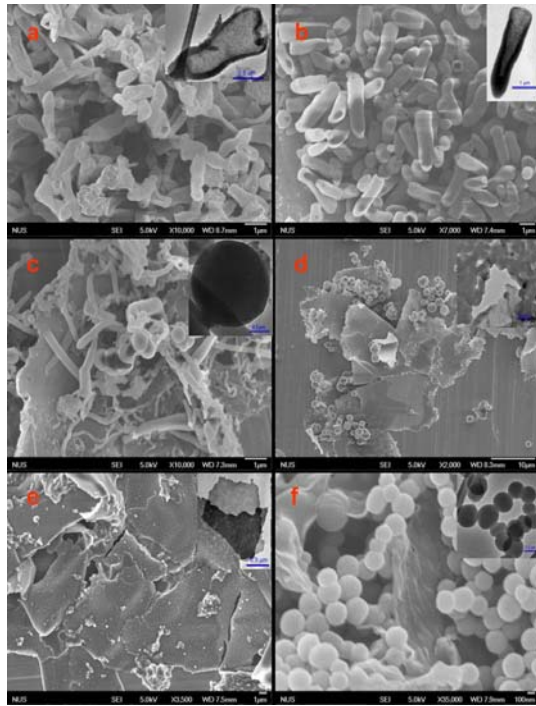


Fig. 1 SEM images with TEM insets of the PANI structures at different $[HAuCl_4]$ with fixed $[Aniline]/[HAuCl_4]$ at 33. (a) 12mM; (b) 6mM; (c) 3mM; (d) 0.57mM; (e) 0.12mM on reactor wall; (f) 0.12mM in solution

Contact angle measurements were carried out to investigate the surface properties of the films prepared from the different PANI microstructures. The results are presented in Fig 2.

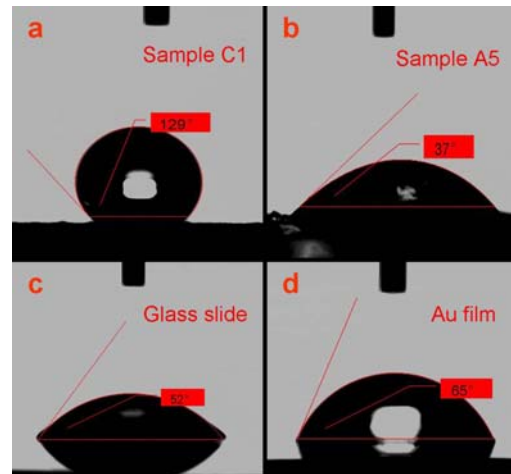


Fig. 2 Contact angle measurement (a) Films cast form mainly spheres, (b) Film cast form mainly plates (c) Glass slide (d) Au film

Conclusions

Various PANI microstructures were controllably prepared by adjusting chloroauric acid concentration and other reaction conditions in a simple one-pot synthesis. These include 1-D open-ended microtubes, 2-D solid microplates and 3-D microspheres. FTIR and UV-vis studies show the PANI products were predominantly in the emeraldine form.

Most of the PANI films show hydrophilic properties except for the film prepared from microspheres.