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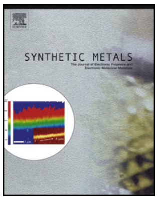

Novel strategy to prepare polyaniline—Modified SiO_2/TiO_2 composite particles

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ABSTRACT

The most commonly used method to deposit polyaniline on TiO_2 particles begins with the adsorption of surfactants on TiO_2 particles followed by deposition of polyaniline. To avoid the use of surfactants, we propose a novel strategy that employs SiO_2 nanoparticles during deposition of polyaniline on TiO_2 particles. Thus, polyaniline/SiO_2/TiO_2 composite particles were successfully prepared during chemical oxidative polymerisation of aniline in a weakly acidic aqueous medium. Polymerisation of aniline in the presence of TiO_2 and SiO_2 was initiated at $pH = 3.5$ by ammonium peroxydisulphate. Prior to polymerisation, dispersed phases exhibited negative electrophoretic mobility after addition of SiO_2 particles into the dispersion of TiO_2 particles at $pH = 3.5$. pH measurements conducted during preparation implied that polymerisation was not altered by TiO_2 and SiO_2 particles. The electrophoretic mobility was modified due to deposition of the polyaniline onto TiO_2 and SiO_2 particles. The electrophoretic mobility of the composite particles was negative when the amount of TiO_2 and SiO_2 was high. It gradually turned to positive with increasing proportion of polyaniline to TiO_2 and SiO_2 in the composite. Particle size measurements and scanning electron microscopy studies showed that agglomeration of the particles occurred during polymerisation. Agglomerate size did not depend on the concentrations of TiO_2 and SiO_2. Infrared spectroscopy studies indicated that emeraldine salt form of polyaniline was obtained during preparation of the composite particles.

1. Introduction

In the last several decades, conducting polymers have received considerable attention because of their wide potential in diverse applications including: gas sensors [1], biosensors [2,3], tissue engineering [4], drug release systems [5,6], corrosion protection [7,8], electronic diodes [9], capacitors [10], transistors [11], electrochromic displays [12], rechargeable batteries [13,14]. In particular, a growing interest has been shown in preparation of composite structures by coating a conducting polymer on micro or nanosized particles. Among all conducting polymers, polyaniline has been frequently studied due to easy synthesis procedures, low cost, high conductivity, and good environmental and thermal stability [15]. Also, there is a growing interest in preparation of composite structures by coating polyaniline onto micro and nanosized particles. Such composites have a promising potential in sensor, charge storage, electrochromic, photocatalytic, photovoltaic applications and for protecting metals from corrosion [15,16]. Various preparation routes including non-aqueous processes have been reported for the synthesis of the composite structures [17,18]. Most common preparation method has been in situ deposition of polyaniline onto particles during chemical oxidative polymerisation of aniline in a strongly acidic aqueous media. In this method, deposition of polyaniline on solid surfaces is facilitated by adsorption of the hydrophobic aniline oligomers onto particles during polymerisation of aniline and subsequent growth of the oligomers to polymers. As a result of this process, coarse granules of polyaniline and polyaniline coated particles are collected as precipitate. It has been proposed that growth, coarsening and morphology of polyaniline nucleates can be controlled by tuning the polymerisation conditions such as acidity, aniline to oxidant mole ratio and dilution of reactant concentrations [18–20]. Aqueous synthesis of polyaniline in a neutral or weakly acidic medium and in the presence of inorganic particles has been reported several times [21–24]. Although extensive morphological characterisation of the composite particles has been reported, the properties regarding their size, their tendency to agglomerate and their electrophoretic mobility have remained scarce [24,25]. In fact, these properties are crucial for the processability of the composite particles during various fabrication practices.

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Preparation of polyaniline coated TiO_2 particles in acidic aqueous media has been reported in several studies [26–32]. As a matter of fact, deposition of a continuous polyaniline coating on TiO_2 particles is unlikely to occur in acidic media because of the repulsive electrostatic interactions and the hydrophilicity [19,33]. Therefore, Kim et al. [31] have proposed that deposition of polyaniline on TiO_2 surface can be enhanced by introducing negative charges onto the surface of TiO_2 particles to facilitate the adsorption of aniline. Li et al. [27] have suggested that deposition of polyaniline on TiO_2 surface is induced by an anionic surfactant (sodium lauryl benzene sulfonate) which assisted adsorption of aniline onto TiO_2 surface. Also, Luo et al. [34] have shown that polyaniline preferentially grows on hydrophilic SiO_2 microparticles rather than underlying carbon electrode surface during electropolymerization. This has been advocated by adsorption of aniline monomers on the SiO_2 particles [23,34]. It has been proposed that aniline may adsorb on negatively charged surfaces due to its polycationic nature in acidic media [19,35,36].

It is of great interest to develop an environmentally friendly process which does not include a non-aqueous solvent, free of surfactant and efficient in a weakly acidic medium. Therefore, in this study, physicochemical and morphological properties of the composite particles obtained by aqueous synthesis of polyaniline in the presence of SiO_2/TiO_2 raspberry-like particles were investigated for the first time. Since adsorption of aniline polycations on positively charged TiO_2 is difficult in acidic media, enhanced deposition of polyaniline has been achieved by covering TiO_2 particles with SiO_2 nanoparticles. Polymerisation of aniline was initiated at pH = 3.5 by ammonium peroxydisulphate (APS). Properties of the prepared composite particles were evaluated by varying the amount of TiO_2 and SiO_2 content. Characterisation studies of the polymer/SiO_2/TiO_2 composites were carried out by electrophoretic mobility, particle size measurements, scanning electron microscopy (SEM) and attenuated total reflection Fourier transform infrared spectroscopy (ATR–FTIR).

2. Materials and methods

2.1. Materials

Commercially available TiO_2 powder (Aeroxide P25, Evonik Degussa GmbH) having a specific surface area of $50 \pm 15\,m^2/g$ (reported by the supplier) was used for preparation of the composites. It was reported that TiO_2 powder comprises agglomerates and solid aggregates of nanoparticles (26 nm) [37]. SiO_2 (Bindzil 30/220, EKA Chemicals AB) was received as an aqueous sol of nanoparticles. SiO_2 sol contained 30% SiO_2 by weight. The specific surface area and average size of the SiO_2 particles were $220\,m^2/g$ and 7 nm, respectively. Aniline (Sigma–Aldrich) and APS (Prolabo) were used as received. Analytical grade HCl (Merck) and NaOH (Merck) were used to adjust pH.

2.2. Preparation of the composites

An aqueous solution was prepared from deionised water that was adjusted to pH 3.5. This solution was used for the following experimental procedures. SiO_2/TiO_2 dispersion was prepared by mixing SiO_2 sol with TiO_2 powder in 50 mL of the aqueous solution. Dispersion was treated by ultrasonic irradiation (Elma Transsonic 420) for 5 min and homogenised by magnetic stirring for 30 min. Aqueous solution of aniline (0.390 mL) was prepared in 25 mL deionised water at pH = 3.5 before it was added to the SiO_2/TiO_2 dispersion. Dispersion was stirred for another 30 min after aniline was added. Finally, 0.490 g APS was dissolved in 25 mL of the aqueous solution and was added to the dispersion. The reaction mixture was stirred for 5 h at room temperature. During the synthesis of the composites, pH of the reaction mixture was measured for different time intervals with a pH meter (Mettler Toledo). Polyaniline/SiO_2/TiO_2 composite particles were then cleaned by 3 successive centrifugation, washing and redispersion in deionized water (pH 3.5). Several batches of the composite particles were prepared by changing the amount of TiO_2 powder and SiO_2 sol. Aniline and APS content was kept constant for all of the batches. Polymerisation of aniline with APS was also performed in TiO_2 dispersion without adding any SiO_2 sol. As a comparison, pristine polyaniline was prepared under the same conditions. A summary of the synthesis parameters and the names assigned to different batches are presented in Table 1.

2.3. Characterisation

Dilute aqueous dispersions of TiO_2 and SiO_2/TiO_2 particles, pristine polyaniline and polyaniline/SiO_2/TiO_2 composite particles were sonicated in deionised water (pH = 3.5) for 15 min. The electrophoretic mobilities were measured with a microelectrophoresis cell (Mark II, Rank Brothers) without using any background electrolyte. With this latter apparatus, only particles having a size higher than about 200 nm can be observed for measurement. So silica nanoparticles which may not be adsorbed on TiO_2 particles are not taken into account. Size (hydrodynamic diameter) distributions of the dispersions were evaluated by using the dynamic light scattering technique (Malvern Zetasizer 3000 HSa). Electrophoretic mobility and hydrodynamic diameter measurements were also conducted on the samples (TiO_2, SiO_2/TiO_2 and PANI–TS1) dispersed in 1 mM aqueous NaCl solution at pH = 3.5 (Malvern Zetasizer Nano ZS). The morphology of the composite particles was studied by using a high resolution SEM (Quanta 450 W, FEI) with electron beam energy of 10 keV. SEM characterisation was conducted on the silicon wafers coated by composite particles drop casted from dilute aqueous dispersions. Powder samples were prepared by drying the SiO_2/TiO_2 and the polyaniline/SiO_2/TiO_2 particles at 60 °C and then used for ATR–FTIR (Vertex 70 FT Bruker) analysis. FTIR spectra were recorded between 600 and $4000\,cm^{-1}$ at ambient temperature.

3. Results and discussion

Formation of the composite particles (Scheme 1) was monitored by measuring electrophoretic mobility and size of the particles after each step of the process. Prior to polymerisation, the effect of SiO_2 sol on the electrophoretic mobility of TiO_2 was evaluated by changing the SiO_2 amount in the SiO_2/TiO_2 dispersion. The

Table 1
Synthesis parameters of the polyaniline and the composites.

Sample	Particles	Aniline content (g)	APS content (g)	TiO_2 content (g)	SiO_2 content (g)
PANI	–	0.398	0.490	0	0
PANI–T	TiO_2	0.398	0.490	1.0	0
PANI–TS1	TiO_2 and SiO_2	0.398	0.490	0.1	0.045
PANI–TS2	TiO_2 and SiO_2	0.398	0.490	0.3	0.135
PANI–TS3	TiO_2 and SiO_2	0.398	0.490	0.5	0.225
PANI–TS4	TiO_2 and SiO_2	0.398	0.490	1.0	0.450