



## Preparation and characterization of fly ashes and polyaniline core/shell microspheres

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### ABSTRACT

To modify the surface of fly ashes (FAs), conductive polyaniline (PANI) layer were chemically grafted on the surface of the self-assembled monolayer (SAM) coated FA particles, resulting in SAM-FAs/PANI composites. The surface functionalization of FAs with amino groups was found to play an important role in the formation of the well-defined core/shell structure. The composites possess good conductivity, average specific capacitance and good magnetic properties at room temperature. Moreover, the conductivity stability and thermal stability of SAM-FAs/PANI composites were clearly improved. The resulting composites were characterized by using wide-angle X-ray diffraction analysis, Fourier transform IR spectroscopy, UV–vis spectroscopy, thermogravimetric analysis, and scanning electron microscopy.

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### 1. Introduction

Conductive polymers (CPs) remain a subject of intense investigation in many research groups worldwide as a result of the discovery of conducting polymers and their doping over the full range from insulators to metals [1,2]. Among the CPs and their composites investigated, polyaniline (PANI) is one of the most extensively studied. The promise of polymer electronics depends in part on the development of stable conductive materials that can be inexpensively processed [3,4]. Therefore stability is an extremely important factor especially for materials applied under harsh circumstances. Two shortcomings of PANI are its limited room temperature conductivity and high temperature dependence of conductivity. Conductivities at room and high temperatures are important properties of a conducting polymer for most commercial applications such as conducting coatings, electronic circuits, and electromagnetic interference shielding materials [5,6].

Fly ashes (FAs) consist of quartz as crystalline phases and some quantity of glassy phase. A portion of the inorganic constituents is comprised of spheroidal and spherical particles (dense, vesicular, mixed,) and their agglomerates [7–9]. FAs are the major combustion residues (normally 60–88%) produced during the combustion of pulverized coal in thermoelectric power stations. The large numbers of coal fired power plants worldwide dispose huge quantity of FAs causing serious environmental problems. Due to environmental regulations, new ways of utilizing FAs have to be explored in order to safeguard the environment and provide useful ways for disposal [8–10].

On the other hand, FAs are an inactive inorganic host without any redox character, so their polymerization can be controlled and their magnetic properties permit their used as an admixture for electromagnetic interference shielding and enhanced chemical resistance. In the present work, we use  $\gamma$ -aminopropyltriethoxysilane (APTES) to form a self-assembled monolayer (SAM) on the surface of FA particles (mainly a silica surface) which allows a further surface oxidative graft polymerization to form a dense PANI layer. Besides, this method applied to the FAs/PANI composites has not been reported. Moreover, our experiments were revealed that the presence of SAM-FAs improved the conductivity stability and thermal stability of the composites. Conductivity, average specific capacitance and magnetic properties were also improved at room temperature for certain contents of SAM-FAs in SAM-FAs/PANI composites.

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## 2. Experimental section

### 2.1. Materials

Aniline monomer (purity 99.5%, Tianjin Baishi Chemical Industry Co. Ltd, Tianjin, China) was vacuum distilled prior to its use.  $\gamma$ -Aminopropyltriethoxysilane (APTES) was obtained from Nanjing Aocheng Chemical Co. Ltd; Toluene, ammonium persulfate (APS), hydrochloric acid (HCl), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), dimethyl formamide (DMF), sodium bicarbonate and absolute ethanol were purchased from Tianjin Baishi Chemical Industry Co. Ltd. All chemicals were of analytical grade and used without further purification. Samples of fresh FAs samples were obtained from Datang Gansu Power Generation Co. Ltd in China.

### 2.2. Preparation of SAM-FAs/PANI composites

Our approach to prepare SAM-FAs/PANI composites consisted of two major steps [11–14]. As shown in Fig. 1, the first step was to prepare particles of SAM-coated FAs (SAM-FAs), and the second step was grafting PANI onto them. In the first step, 40 g neat-FA particles were first dispersed into 400 mL of  $1 \text{ mol L}^{-1}$  HCl aqueous solution, and the mixture was stirring for 8.5 h at  $80^\circ\text{C}$  to get a particle surface with high coverage of Si–OH groups. The particles were collected on a paper filter using a filtration funnel, washed repeatedly with  $\text{NaHCO}_3$  aqueous solution and distilled water until the filtrate was neutral, followed by a drying at  $80^\circ\text{C}$  in vacuo. Then, the particles were dispersed into a toluene solution of APTES ( $1.05 \text{ mol L}^{-1}$ ) while stirring for 8.5 h at  $80^\circ\text{C}$ . Then the unreacted APTES was extracted with absolute ethanol in a Soxhlet apparatus, and the SAM-coated FA particles were finally dried at  $60^\circ\text{C}$  in vacuo.

In the second step, 1 mL distilled aniline was added to 89 mL of  $1 \text{ mol L}^{-1}$  HCl aqueous solution, and then SAM-FA particles (between 0.05 g for 7.46 wt% and 3 g for 86.01 wt%) were dispersed in the reaction mixture under a nitrogen atmosphere with ultrasonic vibrations for 15 min. After that, 10 mL of APS solution ( $0.11 \text{ mol L}^{-1}$ ) were added dropwise to the solution within 15 min while stirring so as to start the polymerization. The mixture was allowed to polymerize under a nitrogen atmosphere for another 9 h at  $0\text{--}5^\circ\text{C}$ , then SAM-FAs/PANI particles were collected on a filter paper using a filtration funnel, and washed repeatedly with distilled water until the filtrate was neutral to ensure that the excess acid was removed. The water washes were followed by washing with ethanol several times. At last SAM-FAs/PANI composites were obtained which were dried at  $25^\circ\text{C}$  in vacuo.

### 2.3. Preparation of neat-FAs/PANI composites

As a control, neat-FAs/PANI composites were also prepared by using chemical oxidative polymerization of aniline in the presence of as-received FAs particles without HCl pretreatment and SAM coating, the resultant composite particles were referred to as neat-FAs/PANI composites.

### 2.4. Characterization techniques

The composite was pressed in a manual hydraulic press in vacuo at 8 tons into a pellet of 13 mm diameter and about 1.5 mm thickness. Pellet conductivity measurements were carried out at room temperature using a four-probe device (SDY-4 Resistivity Measuring Instrument, Guangzhou Semiconductor Material Academy, Guangzhou, China). The temperature dependence of conductivity was determined by WDJ-1 Temperature Change Resistance Measuring Instrument (Institute of Chemistry the Chinese Academy of Sciences, Beijing, China). The magnetic measurements at room tem-

perature were performed using a Lakeshore 7400 Series vibrating sample magnetometer (VSM) system. Charge–discharge tests were performed at a constant current density ( $5 \text{ mA cm}^{-2}$ ), with cut-off voltages ranging from  $-0.20$  to  $0.70 \text{ V}$ . The electrolyte was  $1 \text{ M H}_2\text{SO}_4$  solution. The experiments were carried out using a beaker-type electrochemical cell, in which a platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrodes. The electrode performances were all measured on the CHI660C electrochemical work station at room temperature ( $25^\circ\text{C}$ ).

The FTIR measurements (Impact 400, Nicolet, Waltham, MA) were carried out using the KBr pellet method. Electronic absorption spectra of SAM-FAs/PANI and PANI were recorded in DMF solvent in the wavelength range of  $290\text{--}800 \text{ nm}$  at room temperature using the Lambda 35 UV–vis spectrophotometer (PerkinElmer, USA). The TA Instrument 2050 thermogravimetric analyzer was used for TGA; heating rate was  $10^\circ\text{C}/\text{min}$  from  $45$  to  $550^\circ\text{C}$  in the air. The X-ray diffraction (XRD) patterns were recorded in the range of  $2\theta = 2\text{--}65^\circ$  by step scanning with the XRD-6000 (Shimadzu, Japan). Nickel-filter  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) was used with a generator voltage of  $40 \text{ kV}$  and a current of  $30 \text{ mA}$ . A field emission scanning electron microscope (FE-SEM, Hitachi High-Technologies CO. S-4300 model) was used to get SEM images. Elemental analysis of C, N, and H was carried out using the Elementar Vario EL instrument.

## 3. Results and discussion

### 3.1. Elemental analysis

The untreated APTES was completely removed with absolute ethanol in the Soxhlet apparatus. As confirmed by the elemental analysis results in Table 1, the FAs showed the higher relative contents of nitrogen and carbon in SAM-FAs with respect to neat-FAs which was indicative of the participation of APTES to form the SAM on the surface of the FA particles as shown in Fig. 1. In this preparation approach, APTES was selected as a coupling agent and SAM was formed when it reacted with surface  $-\text{OH}$  groups on the HCl-treated FA particles [11,14].

### 3.2. Microstructure characterization

As shown in Fig. 2a and b, we found that the neat-FAs particles formed a cluster or agglomerate among themselves, due to strong polarity of the hydroxyl groups on the FA surfaces [11]. Specifically, the SAM-FAs had a well-dispersed nature and spherical shape compared with neat-FAs. Therefore the PANI coating of SAM-FA particles provided better dispersion.

SEM images were obtained to characterize the shape of the SAM-FAs/PANI composites. Fig. 2c–e depict typical SEM images of SAM-FAs/PANI microspheres, they indicated that the core/shell products were well dispersed with spherical morphology. Compared with the smooth spherical morphology of SAM-FAs (Fig. 2b), the cluster and transparent shagginess of PANI were coated onto the surfaces of the SAM-FAs, and well-defined core/shell structured SAM-FAs/PANI composites were obtained.

The SEM images of Fig. 2c–f showed some differences in surfaces of the neat-FAs/PANI and SAM-FAs/PANI particles. Fig. 2c–e

**Table 1**  
Results of elemental analysis for FAs.

	Elemental analysis (wt%)		
	N	C	H
Neat-FAs	0.245	7.679	0.532
SAM-FAs	0.361	9.125	0.435

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