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Potential E-ink from polypyrrole complex nanospheres

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ABSTRACT

A novel E-ink was easily synthesized by redox polymerization from pyrrole and tungstophosphoric acid. The resultant nanospheres were uniformly sized, nonconductive and highly charged. By controlling the reactant concentrations, temperature and time, the sphere sizes were finely tuned below 250 nm. Analyzed by Fourier-transformed infrared spectrum, Thermogravimetric analysis and X-Ray diffraction, the spheres were revealed as layer-by-layer complex structure of nonconductive polypyrrole and $PW_{12}O_{40}^{4-}$. This structure provides a zeta potential as high as −51 mV, allowing potential application in electrophoretic display of high resolution and high response rate.

1. Introduction

Electrophoretic display has attracted significant interest of researchers, due to its low-eyestrain reflective mechanism and near-zero-power operation [1,2]. To improve its resolution and response rate, size and charge density of electrophoretic particles (E-inks) are essential characteristics [3,4]. So far, the syntheses of charged particles are limited in dispersion polymerization of vinyl monomers and sol–gel formation of inorganic particles, during which various charge control agents (CCA′s) and colorants are involved [5–8]. These CCA′s and colorants have to be carefully selected with desired properties to match the specific E-ink system. And they are often wasted in synthesis due to the limited encapsulation yield. Here, we present a much simpler and more convenient preparation of electrophoretic nanospheres using only pyrrole and tungstophosphoric acid.

Polypyrrole (PPy) is one of the most extensively studied conductive polymers, which conductivity can be tuned by various oxidants [9]. A number of studies have been devoted to the preparation of PPy colloids, because of their easy handleness. Since the pioneering work of Bjorklund and Liedberg in 1986, who obtained PPy particles in the aqueous solution of methyl cellulose, many organic surfactants and inorganic stabilizers were exploited to prepare stable PPy colloids [10–13]. However, the study on PPy colloid synthesis is still limited in development of conductive materials. Nonconductive PPy spheres of special ink applications have not been reported. Here, we report a uniform, highly charged and nonconductive PPy nanosphere complexed with a polyoxometalate (POM) cluster.

POMs are early-transition metal oxygen anion clusters, among which tungstophosphoric acid (HPW, $H_3PW_{12}O_{40}$) is the most often choice [14]. Keggin-type HPW molecule has a spheric cage-like structure, and is a super acid and oxidizer. The molecule size of HPW is 11–12 Å, and its hydrolysis results in a rarely large anion [15]. During redox reaction of HPW, its keggin-type structure does not change. In this work, HPW was employed to oxidize pyrrole into PPy, to complex with PPy in molecule scale and produce highly charged nanospheres. The nonconductive spheres were finely controlled in size, supporting an E-ink application in electrophoretic display.

2. Experimental

Pyrrole (Py, M=67) and tungstophosphoric acid (HPW, $H_3PW_{12}O_{40}$, M=2898) were purchased from Aldrich Co. (Hong Kong) and used as received. Polychlorotrifluoroethylene (DP 4–10) dielectric suspending fluid was purchased from Halocarbon Product Co. (New Jersey, USA). A typical synthesis of nanosphere was described as follows. At room temperature (25 °C), 0.5 mL Py was added into 20 mL aqueous solution containing 0.46 g HPW (pH=1.8) under vigorous stirring (mole ratio Py: HPW=45: 1, providing abundant Py since HPW is more expensive). This stirring continued for 5 days without heating. The resultant inky colloid was vacuum-filtered through a PTFE membrane (Whatman Co., Maidstone, UK) and washed with water and methanol to remove unreacted monomer and impurities.

Particle size and surface charge were measured on Malvern Zetasizer 3000HSA. The morphology of products was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) on JEOL JSM-6335Fand JEOL JEM-2010, respectively. Samples for SEM were coated by gold sputtering before observation. For TEM samples, Cu grid with holey carbon was used

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to collect colloidal spheres. Fourier-transformed infrared (FTIR) spectrum was recorded on a Perkin Elmer System 2000 with powder samples pressed into KBr tablet. Thermogravimetric analysis (TGA) was performed using a METTLER TOLEDO TGA/DSC 1 from 30 to 700 °C with a heating rate of 10 °C/min under air atmosphere (one sample of 10 mg was tested). X-Ray diffraction (XRD) pattern was recorded on a Rigaku SmartLab diffractometer using Cu Kα radiation (α=1.54 Å) at 45 kV and 200 mA (powders were filled into a sample holder and tested). The electrical conductivity of the colloid spheres was measured by a standard four-probe technique (Jandel RM3000 meter with CYL probe, Bridge Technology, USA) at room temperature with discs of diameter 1.6 cm prepared by pressing the collected particles at 300 bar for 3 min.

3. Results and discussions

During a typical synthesis, the oily Py was quickly dissolved into HPW solution because of its protonation by the strong acid. Then the solution gradually changed from light yellow to inky black, due to the oxidative polymerization of Py into PPy with HPW as oxidizer that was reduced into $PW_{12}O_{40}^{4-}$ [16]. After 5 days reaction, the collected colloidal particles were dried and observed by SEM, giving monodisperse diameters around 220 nm (Fig. 1c). Samples were also taken periodically during the reaction, and spin-coated on silica wafers for SEM observation. Two samples were shown in Fig. 1a and b: spheres of 120 nm at 19 h and 180 nm at 75 h. Clearly, through the whole reaction period, nanospheres always have smooth surface and nearly monodisperse size that increases with reaction time. Therefore, spheres of desired small size can be easily obtained by controlling the reaction time. After 5 days, a yield of 0.53 g powders was obtained, indicating conversion rates of 91% and 24% for HPW and Py based on the sphere composition as shown later. Typically, the nanosphere growth curves from two recipe were presented in Fig. 2a. Their growth rates decreased with the consumption of Py and HPW in the solution. Notably, this slow growth is attributed to the low redox potential of $PW_{12}O_{40}^{3-}/PW_{12}O_{40}^{4-}$ (0.22 V) [16]. In comparison, the common used redox pair Fe^{3+}/Fe^{2+} has a higher potential of 0.77 V, and oxidizes Py more quickly into PPy[17]. However, the common oxidant $FeCl_3$ cannot directly provide a stable nonconductive PPy colloid. From the HPW recipe, a higher growth rate can be obtained by increasing concentration and temperature of the reaction mixture, as experimentally observed.

In FTIR spectra of the collected PPy-HPW colloid spheres (Fig. 2b), characteristic absorption peaks of PPy and $PW_{12}O_{40}^{4-}$, 1200 and 810 cm^{-1}, were clearly observed, approving the coexistance of PPy and $PW_{12}O_{40}^{4-}$ [18,19]. In comparison to normal PPy spectrum in literature, the Py ring antisymmetric and symmetric streching absorptions upshifted from 1535 to 1547 cm^{-1} and from 1445 to 1460 cm^{-1}, respectively [18]. While the HPW terminal W=O stretching absorption downshifted from 986 to 979 cm^{-1} [19]. These changes indicated the complexation interaction between Py ring and the $PW_{12}O_{40}^{4-}$ W=O groups. Estimating from the high intensity of peak 1547 cm^{-1} and low intensity of peak 1460 cm^{-1}, this PPy product's conductivity should be very low, if it is conductive [17]. It may contain highly cross-linked structure, resulting in very short conjugate length.

The collected nanospheres were also observed by TEM. In a typical TEM image (Fig. 1d), homogeneous dark spheres in uniform size (d=220 nm) are clearly observed. This uniform solid appearance of spheres indicates a homogeneous distribution of $PW_{12}O_{40}^{4-}$ anions in the spheres. There is not any notable phase separation, supporting the molecularly complexation between protonized PPy block and $PW_{12}O_{40}^{4-}$. Their mole ratio in solid spheres can be evaluated by TGA. TGA curve of the collected nanospheres was shown in Fig. 2c. The weight loss below 250 °C was resulted from the elimination of adsorbed and combined H_2O from the

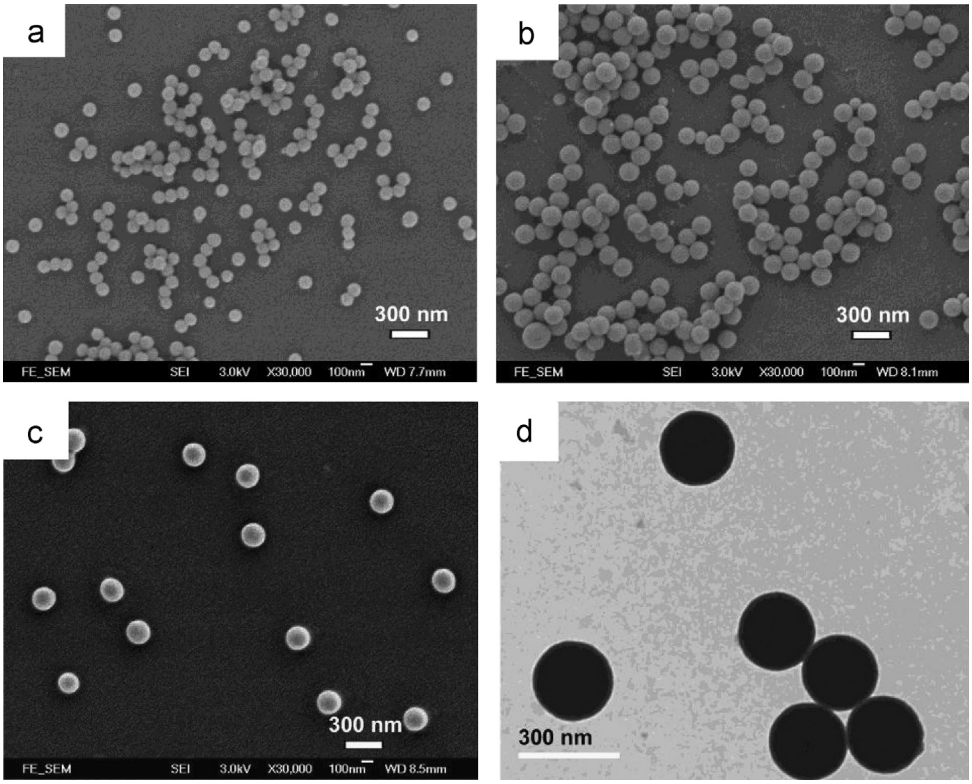

Fig. 1. SEM images of PPy complex nanospheres from recipe Py/HPW/H_2O=0.5/0.46/20 (in weight ratio) at various time periods: (a) 19 h; (b) 75 h; (c) 120 h, and (d) TEM image of the same spheres at 120 h.