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.

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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 ($\alpha = 1.54$ 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
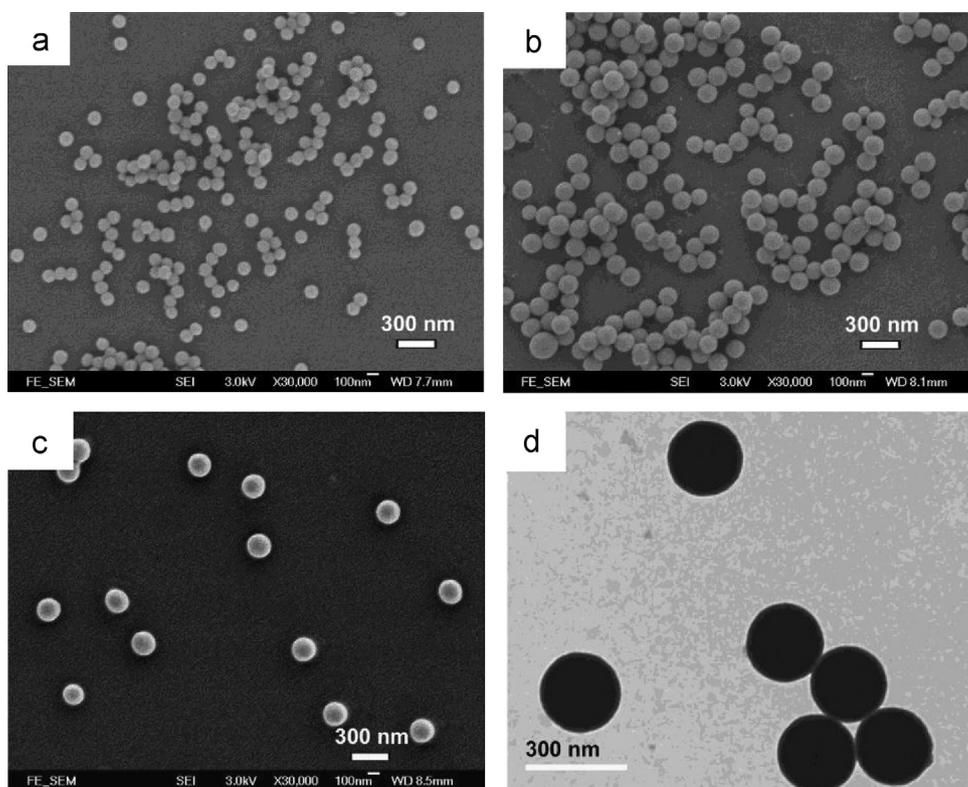

Fig. 1. SEM images of PPy complex nanospheres from recipe Py/HPW/H_2O=0.5/0.46/20 (in weight ratio) at various time periods: (a) 19 h; (b) 75 h; (c) 120 h, and (d) TEM image of the same spheres at 120 h.

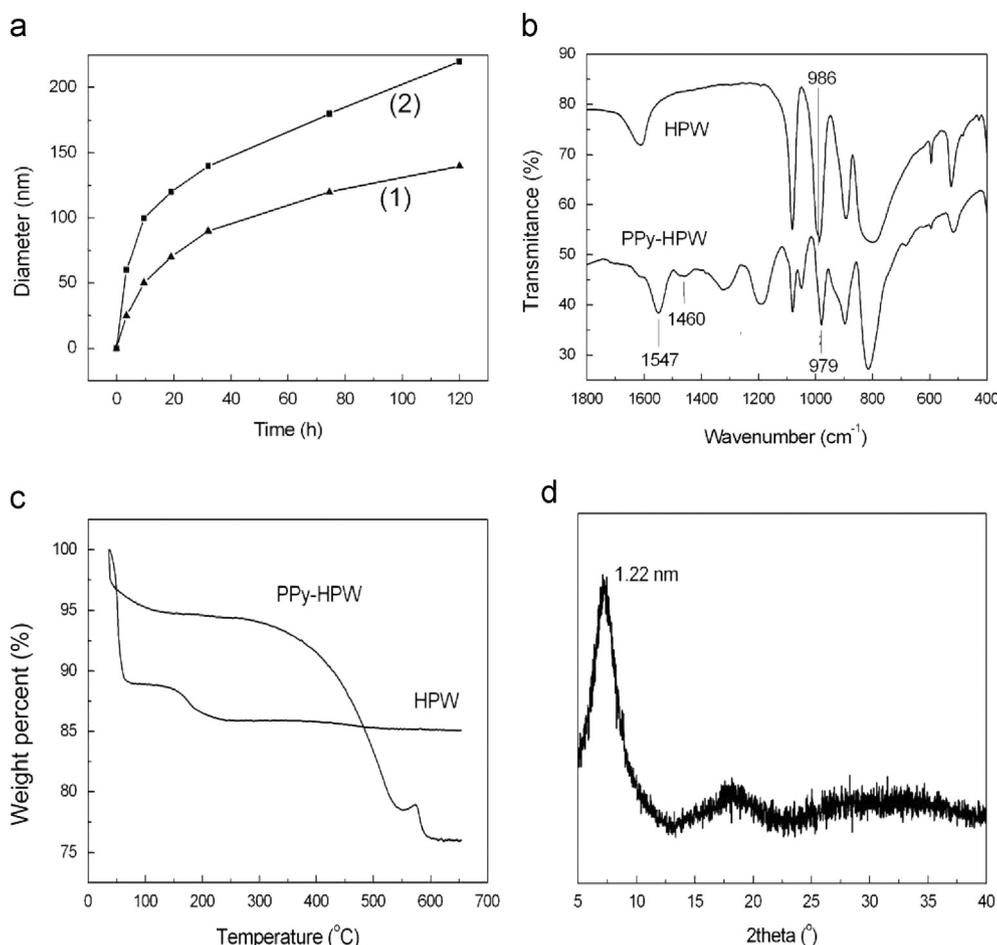Fig. 2. (a) Nanosphere growth curve from two recipe: (1)- Py/HPW/H$_2$O=0.5/0.046/20; (2)- Py/HPW/H$_2$O=0.5/0.46/20. (b) FTIR spectra of pure HPW and as prepared 220 nm complex sphere. (c) TG curves of pure HPW and as prepared 220 nm complex sphere. (d) XRD pattern of as-prepared 220 nm complex sphere.
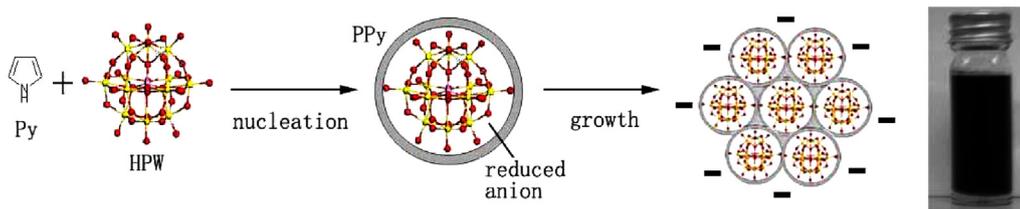

Fig. 3. Schematic illustration of nanosphere growth through layer-by-layer deposition of PPy and PW$_{12}$O$_{40}$$^{4-}$ (inset image—the inky colloid).

samples. Pure HPW kept constant weight in the 250–650 °C range, while PPy-HPW complex nanospheres lost nearly 20 wt% in the same temperature range. This weight loss was attributed to oxidative decomposition of PPy within the complex spheres. Therefore, the mole ratio of Py unit to PW$_{12}$O$_{40}$$^{4-}$ was estimated at about 11:1 in the nanospheres, and each 3 Py units may carry a positive charge to match the anions. Considering the large size of dopant anion, this hybrid sphere is hardly conductive. After measuring with the normal four-probe technique, the hybrid nanospheres were experimentally confirmed as a nonconductive material.

Based on this TGA result of composition and the above TEM observation, the spheres are supposed to be formed by the layer-by-layer deposition of cationic PPy blocks and anionic POM clusters, as illustrated in Fig. 3. In the whole process, the POM cluster acted as oxidizer, doping anion and charge control agent. The above assumption was supported by further XRD analysis of

the collected spheres. As shown in Fig. 2d, a prominent diffraction peak at a low angle around 7° indicated an evident period distance of 1.2 nm, corresponding well with the PW$_{12}$O$_{40}$$^{4-}$ cluster size. The spheres of different sizes gave the similar XRD patterns that are not shown here. Therefore, the nanospheres were composed of periodically distributed PPy blocks and PW$_{12}$O$_{40}$$^{4-}$ clusters.

When the collected complex spheres were redispersed into polychlorotrifluoroethylene by ultrasonication (Bronsonic 2510-MT at 100w and 42 kHz), a stable inky colloid was obtained. Measured by the Malvern Zetasizer 3000HSA, this colloid gave a highly negative Zeta potential $\zeta=-51$ mV and a narrow distribution of size around $D_n=220$ nm ($D_v/D_n=1.06$), which agree well with the above morphology observation and structure analyses. The electrophoretic mobility (μ) was calculated by the conversion of the ζ-potential with the Smoluchowski relation, $\zeta=\mu\eta/\varepsilon$, where η (2.0 cP) and ε (2.6) are the viscosity and dielectric constant of the suspending fluid, respectively

[3]. The nonconductive complex sphere gave a high mobility of -6.63×10^{-5} cm^2/V s, which promises an E-ink application in electrophoretic display.

4. Conclusions

In summary, highly charged uniform nanospheres were prepared from Py and HPW mixture without additional CCA's or colorants. This method allowed fine control over the size of the PPy-HPW complex nanospheres. TEM, FTIR and XRD characterizations revealed a uniform molecular complex of PPy block and $PW_{12}O_{40}^{4-}$ anions, and supported a layer-by-layer complexation mechanism. Based on their small size and high charge density, these nonconductive hybrid nanospheres have potential applications as E-ink in electrophoretic display.

Acknowledgment

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