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Conducting polymeric nanoparticles synthesized in reverse micelles and their gas sensitivity based on quartz crystal microbalance

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Abstract

Conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) nanoparticles were prepared by reverse micelle method, which could be well dispersed in water or alcoholic solvent with ultrasonic treatment. The formation and doped state of PEDOT nanoparticles were confirmed by UV–vis–near IR absorption spectrum, X-ray photoelectron spectroscopy (XPS) and FT-IR spectrum. The nanoparticles with the size of ca. 20–40 nm were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Compare to electrical conductivity of conventional PEDOT particles (ca. 0.5 S/cm), the as-prepared palletized nanoparticles have higher conductivity (ca. 10.2 S/cm) and the conductivity varies with the doped and de-doped states of PEDOT. As for sensing property, it has been found that QCM device coated with nanoparticles shows faster response and recovery to 20 ppm ammonia gas (ca. 50 s) than that of conventional PEDOT particles. The PEDOT nanoparticle covered device exhibits almost linear relation to lower NH_3 gas concentration and shows a saturate tendency of gas sensitivity with the increase of gas concentration over 500 ppm. The mechanisms of electrical conductivity and gas sensitivity of PEDOT nanoparticles were also discussed.

Keywords: Reverse micelles; Nanoparticles; PEDOT

1. Introduction

Conducting polymer nanostructure has been a subject of growing interest in recent years for their promising application in microelectronics, sensor, solar cell, etc. [1–4]. As for sensing application, conducting polymer nanostructures including nano-rod, nanoparticle, nano-tube have a larger surface area than their conventional bulk counterparts. Therefore, they have the capability of offering amplified sensitivity and real-time response as a result of enhanced interaction between conducting polymer and analyte [5–9].

In recent years, nano-micelle polymerization method to prepare conducting polymer nanoparticles has attracted more attention [10–16]. The one-dimensional (1D) water–oil interface or nanometer size 'water pool' formed by surfactant provides nanometer space for the polymerization of monomers, which results in the formation of polymer nanostructure in water or oil phase. Therefore, a high level of control could be exerted on the geometric characteristics of conducting polymer structure through various synthetic conditions, and some kind of conducting polymer nanostructure, such as PPY and PANI, has been successfully prepared using this method [17,18]. These materials are expected to exhibit excellent sensing properties and to have potential application for gas sensor and microelectronics. However, most of the previous reports focused on the preparation and characterization of these nanoparticles and a few have been performed for device application on the development of electrical and sensor systems.

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As a promising conductive polymer, PEDOT is suitable for sensor application due to its high conductivity, environmental stability and sensitivity for the detection of ammonia, nitrogen dioxide and other organic toxic vapors [19–21]. Jeong et al. prepared PEDOT nanoparticles by using DBSA as micelle template and investigated the electrical performance of the nanoparticles [22]. So far, a few works have been studied on the preparation of PEDOT nanoparticles by reverse micelle polymerization method and investigated the gas sensitivity of this promising material based on quartz crystal microbalance (QCM), which is highly sensitive to mass change $\sim 1\ \mathrm{ng/cm^2}$ and has been widely used as sensing device. Thus, the combination of PEDOT nanoparticles and QCM may show promising application for the fabrication of novel gas sensor. In this work, with the formation of reverse ionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) micelle in oil solvent, one-dimension (1D) water–oil interface compartmentalized by reverse micelles were constructed, and the interfacial polymerization of EDOT was fulfilled at nanometric scale. The obtained PEDOT nanoparticles were characterized by UV–vis–near IR spectrum, FT-IR spectrum, SEM, TEM and XPS techniques, and the electrical conductivity was characterized by four-point probe technique. Gas sensitive property of the nanoparticles deposited on QCM surface was investigated. The conductive and gas sensitivity mechanisms of PEDOT nanoparticles were also analyzed.

2. Experimental

2.1. Materials and chemicals

3,4-Ethylene dioxythiophene (EDOT) was purchased from Bayer AG. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and other chemical reagents were purchased from Aldrich and used as-received.

2.2. Preparation of PEDOT nanoparticles

Reverse micelle dispersion was prepared by introducing 5.2 g of AOT into 30 ml isooctane and stirred simultaneously, and then 0.55 ml of aqueous $FeCl_3$ solution (12.4 M) was introduced into the AOT/isooctane solvent mixture in order to form oxidization spot at the micelle interface. Then, 0.4 g of EDOT monomer was added into the mixed solution and the color was changed from yellow to black, indicating the polymerization of EDOT monomer. After the polymerization reaction of EDOT proceeded for 12 h, the resulting product was washed with ethanol to remove AOT and residual reagent. This identical washing process was carried out at least three times. Then the obtained PEDOT nanoparticle powder was kept in vacuum oven at 60 °C for 4 h. The conventional PEDOT particles were prepared by oil–water interfacial polymerization method.

2.3. Measurements

UV–vis–NIR spectra were recorded with a DT-1000CE spectrometer. FT-IR spectrum was characterized with a WGH-30 analysis instrument (Tianjin, China). Surface morphology of the nanoparticles was investigated by using scanning electron microscopy (SEM) model S-2400 from Hitachi and transmission electron microscopy (TEM) model JMC-200E from NEC. X-ray photoelectron spectrum (XPS) was performed with a Scienta ESCA200 spectrometer with monochromatized Al Kα radiation ($h\nu = 1486$ eV).

The obtained PEDOT nanoparticles were compressed into pellets with ~0.05 cm thickness and then tested by four-point probe method. For gas sensitive test, QCM used in this study was 8 MHz AT-cut quartz crystal (Au sputtered electrode on Ti layer with an area of $0.25\ \mathrm{cm^2}$). The nanoparticles (1.1 wt.%) and conventional particles (0.8 wt.%) were first dispersed in ethanol by ultrasonic dispersion and 0.05 ml of the solution containing particles was dropped onto QCM and the particles deposited device was dried to remove residual solvent. The film thickness of the particles was measured with spectroscopic ellipsometer (SENTECH SE850, Germany). The sensitivity measurement was carried out in a homemade chamber with a volume of 2.5 l and NH_3 gas with various concentrations was continuously introduced into the airtight cell. The frequency shift of QCM device was *in situ* monitored by frequency counter (Iwatsu Co.). All of the measurements were performed at ambient temperature.

3. Results and discussion

3.1. Characterization of PEDOT nanoparticles

The AOT can form stable reverse micelle without other assistant surfactant. The stable ‘water pool’ and interface of oil–water formed by AOT enabled efficient place for the polymerization of EDOT monomer. The morphology of PEDOT particles (not dispersed) prepared in reverse micelles solution of AOT after 12 h reaction is shown in Fig. 1(a) (the inset is the TEM image of dispersed nanoparticles). The synthesized PEDOT in AOT reverse micelle solution appeared to be particle shape and the size varies from 20 to 40 nm, which is much smaller than conventional PEDOT particles prepared by conventional oil–water interface polymerization method (shown in Fig. 1(b)). In AOT reverse micelle phase, the anionic head-groups of AOT extract iron cations from aqueous $FeCl_3$ solution by an electrostatic attraction, and thus the iron cations can be adsorbed to the anionic head-groups of AOT. Iron cations act as the oxidizing agent for the chemical oxidation polymerization of EDOT monomers, and AOT reverse micelle containing water channels in their polar cores. Accordingly, one-dimensional water–oil interface compartmentalized by reverse micelle was constructed, and all prerequisites for carrying out interfacial polymerization were fulfilled at nanometer scale. The obtained PEDOT particles prepared by reverse micelles method can disperse very well in water or alcoholic solvent under ultrasonic treatment.

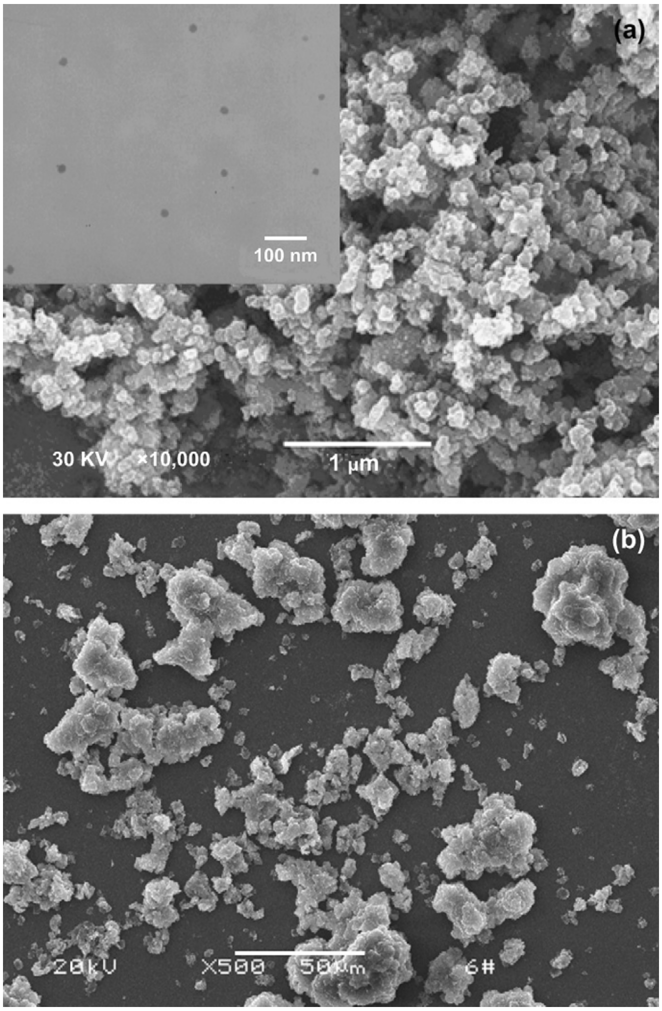

Fig. 1. SEM and TEM images of PEDOT particles prepared by (a) reverse micelle method and (b) conventional method.

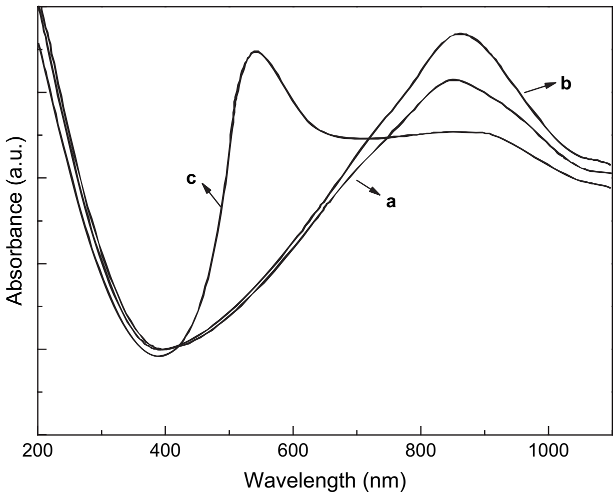

Fig. 2. UV–vis–NIR spectra of PEDOT nanoparticles (a) as-prepared, (b) after treated with HCl for 20 min and (c) after treated with ammonia for 20 min.

Whereas, the nanoparticles prepared by Jeong et al. in aqueous DBSA solutions could only disperse in alcoholic solution by mechanical stirring [22], which indicates that the PEDOT nanoparticles prepared in reverse micelles exhibit higher dispersion characteristics in solution and uniform nanoparticles' films can be obtained simultaneously. It also needs to mention that ultrasonic treatment is more efficient to disperse the PEDOT nanoparticles than mechanical stirring. When an additional exterior vibrating force from ultrasonic treatment is applied to conducting polymer solutions, dramatic reduction in viscosity occurs [27], so the oscillation leads to more uniform PEDOT nanoparticles. On the other hand, vibrating force can also separate superfluous surfactant (AOT) from PEDOT nanoparticles, which adsorbed on nanoparticles during synthetic process.

With the proceeding of polymerization reaction, the mixed solution color changes from red to black after introducing EDOT monomer into solution corresponding to the polymerization of EDOT at reverse micelle interface. Fig. 2 displays ultraviolet–visible–near IR (UV–vis–NIR) spectra of PEDOT nanoparticles. It shows an absorption peak at 880 nm, corresponding to the polarons and bipolarons in PEDOT due to partial doping of PEDOT by Cl^- during polymerization process. After this as-prepared particle was treated by HCl gas, the enhancement of adsorption intensity at 880 nm was observed. This indicates that PEDOT is further doped by Cl^- and more Cl^- ions insert into the PEDOT backbone. A new absorption peak at 550 nm appears after this particle was exposed to NH_3 gas and absorption intensity at 880 nm decreased. The 550 nm peak originates from the $\pi \rightarrow \pi^*$ electronic transition in de-doping PEDOT, which is responsible for the reductive state of PEDOT caused by NH_3 gas treatment.

FT-IR spectra (shown in Fig. 3(a)) also confirmed the formation of PEDOT particles as evidenced by the presence of the peaks at 1507 and 1322 cm^{-1} (C–C or C=C stretching of thiophene ring), 1189, 1073, and 1044 cm^{-1} (C–O–C bond stretching in ethylene oxide group), and 983, 825, and 688 cm^{-1} (C–S bond stretching in the thiophene ring). The absorption peak at 1640 cm^{-1} (noted by arrow) is in agreement with the report of Groenend et al. as the indication of

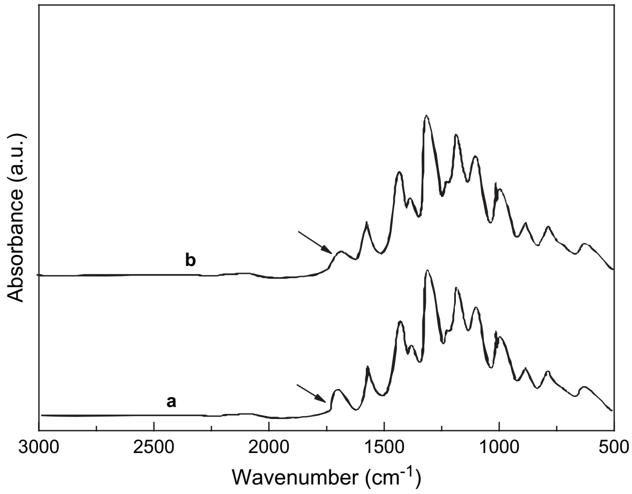

Fig. 3. FT-IR spectra of doped and de-doped PEDOT nanoparticles.

doping level of the polymer observed in FT-IR spectra [6]. This means the PEDOT particles prepared by reverse micelle method have been doped after polymerizing reaction. Furthermore, after treated by ammonia the adsorption peak at 1640 cm^{-1} decreases and shifts to lower wave-number position (shown in Fig. 3(b)), which is ascribed to the reductive state of PEDOT particle.

In order to analyze the atomic composition of PEDOT nanoparticle, XPS characterization was employed. The S(2p) spectrum of the particle is shown in Fig. 4(a). The binding energy exhibits a double intensity peak locating at 168.9 and 172.5 eV, respectively, which can be attributed to different sulfur atoms in different chemical environments. The former corresponds to the sulfur atoms in PEDOT itself and the latter is assigned to the sulfur atoms doped by Cl^- counter-ions. Moreover, further doping of PEDOT by HCl was utilized and confirmed by XPS investigation after the as-prepared PEDOT particles were exposed to HCl gas as shown in Fig. 4(b). It can be seen that, comparing to Fig. 4(a), the peak at 172.5 eV originating from the doping of Cl^- to backbone has been enhanced, which indicates that more Cl^- have been incorporated into PEDOT backbone.

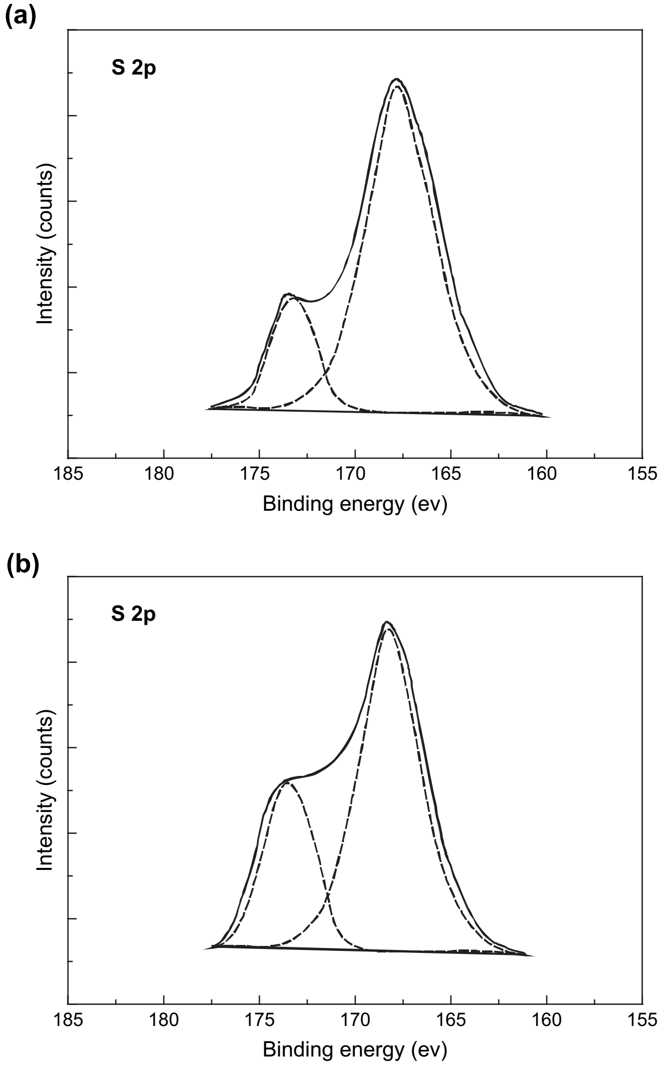

Fig. 4. S(2p) XPS spectra of PEDOT nanoparticles (a) as-prepared and (b) after treated with HCl.

3.2. Conductive property

The electrical conductivity of palletized PEDOT particles prepared by reverse micelle method and conventional PEDOT particles obtained from oil–water chemical reaction was studied by four-point probe technique, and the results are shown in Table 1. The as-prepared PEDOT particles prepared from reverse micelle solution show higher conductivity than conventional particles, and this conductivity is on the same order of the result obtained from Jeong et al. [22]. The conductivity definition of conducting polymer was firstly described by He and indicated that this conducting mechanism is different from that for metal conductors especially in nano-scale [23]. Otherwise, nano-effect, which has been demonstrated for unusual strength, high surface energy, surface reactivity, high thermal and electric conductivities, may play key role in the exhibited properties of nanomaterials. Wan et al. studied the properties of electrospun nanofibers in detail and confirmed that the nano-effect contributes to the unusual properties of this nanomaterials. The conducting polymer nanoparticles can be considered as artificial atoms and this special structure may present nano-effect or quantum-like property. Therefore, the remarkable electrical ability in conducting polymer nanoparticles may result from this nano-effect phenomenon, and the conductivity enhancement arises when the size of particles are reduced below certain critical size, and which leads to higher electric conductivity than conventional ones [24–26]. After this as-prepared PEDOT nanoparticles exposed to hydrochloric acid vapor for 20 min, conductivity increased from 10.2 to 60.5 S/cm, and then decreased to 0.28 S/cm after the particles were treated with ammonia ($NH_3\cdot H_2O$) for 20 min. This phenomenon is due to the reversible doping/de-doping of PEDOT. When the PEDOT nanoparticles were exposed to HCl vapor, negative charged counter-ions (Cl^-) were incorporated into polymer backbone and the emergence of polarons or bipolarons resulted in the enhancement of conductivity. In contrast, the introduction of NH_3 into PEDOT particles led to the formation of a neutral polymer backbone and a decrease in charge carriers, resulting in a decrease of conductivity [5]. We also found that the increase of conductivity is less than the decrease after the particles were treated with HCl and NH_3 gases, respectively, and

Table 1
Electrical conductivity of PEDOT nanoparticles and conventional PEDOT particles

PEDOT particles	As-prepared	Treated by HCl (20 min)	Treated by ammonia (20 min)
Nanoparticles	10.2	60.5	0.28
Conventional particles	0.5	6.4	$\sim 10^{-3}$

this may be due to the as-prepared PEDOT nanoparticles partly doped by Cl^- during polymerization.

3.3. Gas sensing performance of nanoparticles

As conjugated conductive polymer materials, PEDOT shows promising application for gas sensor and the nanometer size PEDOT particles will show more valuable potential as gas sensing material due to their larger surface-to-volume ratio. In order to evaluate the sensor performance of PEDOT nanoparticles and conventional particles, the solution of two different particles was dropped on the surface of QCM device, which is simple in sensing principle and more precision for adsorbed analyte, and tested in gas chamber after the thorough dryness of solution. The real-time frequency shift was recorded by frequency counter. The normalized frequency shift could be described as Eq. (1)

$$\Delta f = -2.3 \times 10 f_0^2 \left(\Delta m / A_{\mathrm{QCM}}\right) \tag{1}$$

where Δf (MHz) is the fundamental frequency of unloaded piezoelectric crystal, Δm (g) is the mass loading on the surface of crystal and A_{QCM} (cm^2) is the effective area of electrodes.

Fig. 5 shows the sensitivity of PEDOT nanoparticles and conventional PEDOT particles to a constant concentration of NH_3 gas. The film thicknesses of nanoparticles and conventional particles characterized by ellipsometer were 567 and 553 nm, respectively. The response time of QCM is defined as the time it takes to reach 80% of the steady-state, and the recovery time is defined as the time required to recover 80% of the steady-state. It can be seen that the response and recovery times of nanoparticles deposited on QCM is ca. 50 s to 20 ppm NH_3 gas, which is faster than conventional PEDOT particles deposited on QCM. This may be due to the larger surface-to-volume ratio of PEDOT nanoparticles than conventional particles resulting in faster adsorption and desorption of NH_3 on PEDOT surface. It also has been found that, comparing to conventional PEDOT particles, the nanoparticles exhibit excellent recovery performance with the frequency almost restoring to its initial value. The full recovery of conventional PEDOT particles deposited on QCM is not obtained even after device treated in oven at 50 °C during 2 h. However, the PEDOT nanoparticles deposited on QCM exhibit excellent recovery performance even at room temperature.

Interestingly, it has been found that by introducing toluene-*p*-sulfonic acid into mixed reverse micelle solution during polymerizing reaction, the sensing performance of the particles can be dramatically improved. As shown in Fig. 6, by introducing toluene-*p*-sulfonic acid into mixed reverse micelle solution, the obtained PEDOT nanoparticles show higher sensing performance to NH_3 gas. The reason to cause this phenomenon is unclear currently, and SEM investigation about particle size shows there is no distinct difference in particle size. The film thicknesses for conventional and nanometric PEDOT particles are almost at the same value as 720 and 727 nm, respectively, which clarifies that the particle size and film thickness have no effect on the difference of sensing performance. However, by introducing toluene-*p*-sulfonic acid into the synthetic reaction of EDOT, the obtained nanoparticles exhibit better dispersing performance in solution and onto substrate, which was confirmed by SEM investigation. We postulated that introduced toluene-*p*-sulfonic acid may improve the dispersing performance of nanoparticles and prevent the nanoparticles from aggregation, which leads to the formation of uniform conducting polymer sensitive layer on QCM surface for higher gas sensing property.

The PEDOT nanoparticle response as a function of different gas concentrations is shown in Fig. 7(a). It can be seen that the frequency shift of PEDOT nanoparticles increases with the increasing gas concentration. This indicates that more ammonia molecules adsorbed on the particles at higher ammonia concentration. The relationship between frequency

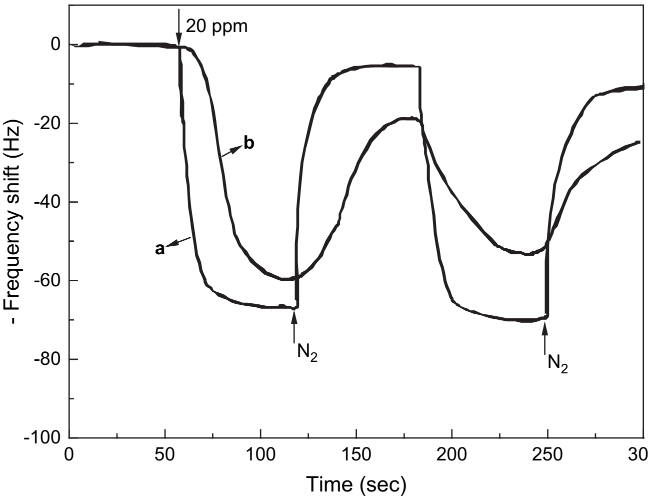

Fig. 5. Typical response of PEDOT particles to NH_3 gas (20 ppm) (a) nanoparticles and (b) conventional particles.

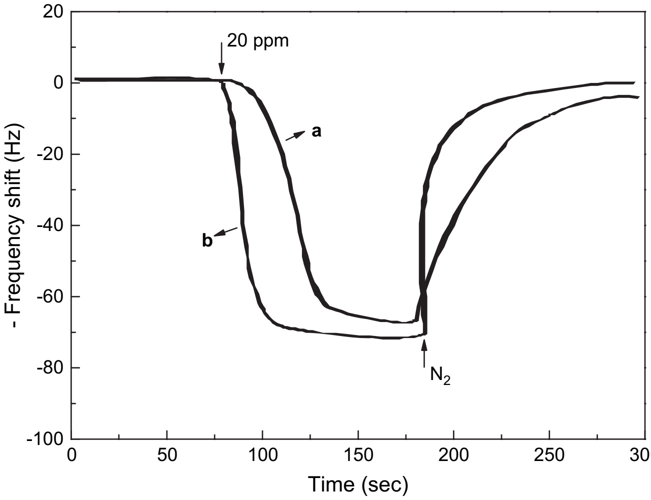

Fig. 6. Response of PEDOT nanoparticles obtained from different synthetic processes to NH_3 gas (20 ppm) (a) without acid introduced into solution during synthesis and (b) toluene-*p*-sulfonic acid introduced into solution during synthesis process.

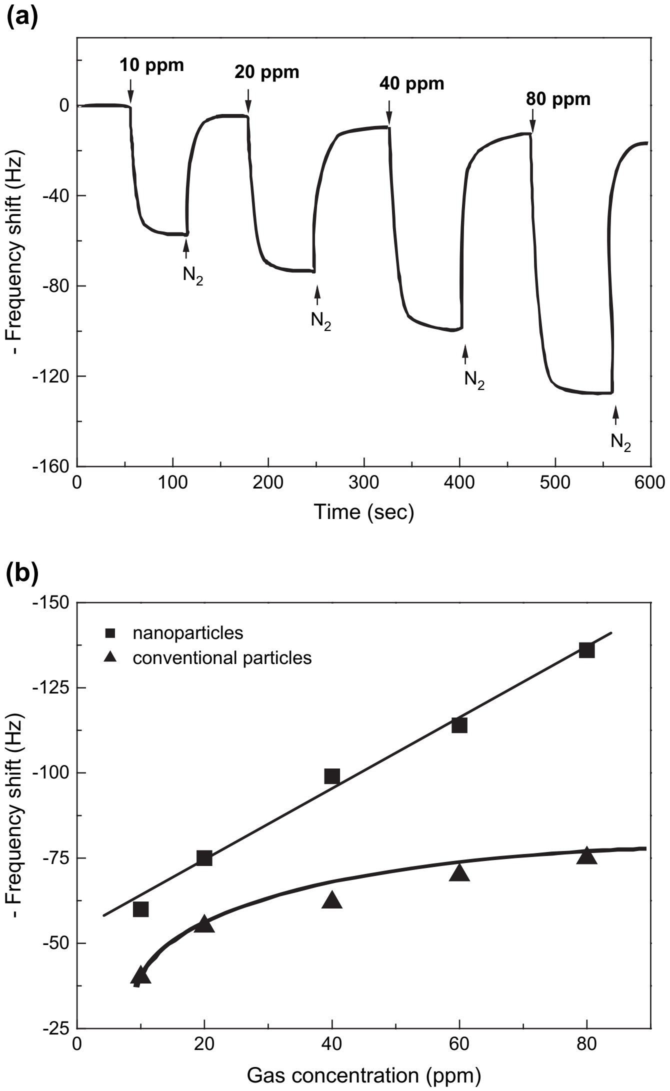

Fig. 7. (a) Reversible and reproducible response of PEDOT nanoparticles to various NH_3 concentration and (b) frequency shift versus gas concentration characteristic of two different particles.

shift and NH_3 concentration derived from Fig. 7(a) is plotted in Fig. 7(b). It was found that with the enhancement of gas concentration, the frequency shift increases and has almost linear response to gas concentration. Fig. 7(b) also shows frequency shift versus gas concentration of conventional larger PEDOT nanoparticles. It can be seen that the frequency shift tends to saturate even after 40 ppm, which indicates lower sensitivity of conventional PEDOT particles to NH_3 gas. Further correlation between frequency shift and gas concentration of PEDOT nanoparticles is illustrated in Fig. 8. It shows that the frequency shift continues to increase when gas concentration increases, but the slope of curve decreases, which indicates that the sensitivity of sensor tended to saturate with the enhanced concentration.

Low adhesion is a common problem for combination of nanoparticles and QCM to fabricate high performance gas sensor and it also occurred in this work. In our experiment, the adhesion of PEDOT nanoparticles to QCM surface was not so high by dropping solution on to QCM surface, which may be caused by weak interaction force between nanoparticles and QCM surface. Still now, this problem was not solved effectively. But, we are trying some supplementary methods, such as surface modification of QCM and PEDOT nanoparticles, which can form stable chemical bond between QCM and nanoparticle, to improve adhesion ability of PEDOT nanoparticle on QCM.

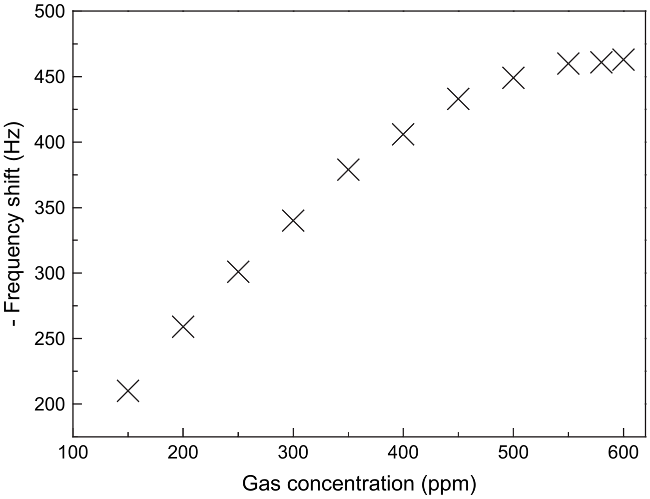

Fig. 8. Frequency shift of QCM as a function of gas concentration.

4. Conclusions

In this work, conducting polymeric PEDOT nanoparticles have been prepared by reverse micelle synthetic method. The formed PEDOT particles exhibited size ranging from 40 to 60 nm. The PEDOT nanoparticles were characterized by UV–vis–NIR spectrum, FT-IR and XPS techniques. The nanoparticles displayed higher conductivity than conventional PEDOT particles and showed excellent doping/de-doping characteristics. Quartz crystal microbalance technique was utilized to investigate the PEDOT nanoparticles sensing performance. PEDOT nanoparticles exhibited higher sensitivity to NH_3 gas than common particles, and linear behavior of NH_3 sensitivity was observed with the increasing of gas concentration. The frequency shift continues to increase with the increase of gas concentration to higher value, but the slope of the curve decreases, indicating the sensitivity of sensor tended to saturate with the increasing concentration. These PEDOT nanoparticles prepared by reverse micelle method show promising application for high quality and conducting polymer-based gas sensors and further investigation about its gas sensing performance to other organic gases and adhesion problem is in progress.

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