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On the use of dispersed nanoparticles modified with single layer β-cyclodextrin as chiral selecor to enhance enantioseparation of clenbuterol with capillary electrophoresis

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Abstract

A new strategy for chiral separation by capillary electrophoresis employing modified-nanoparticles as chiral selector is described for clenbuterol analysis. Nanoparticles modified with β-cyclodextrin (β-CD) form a large surface area platform to serve as a pseudostationary chiral phase, which can be applied for the enhancement of the enantioseparation. The application of four kinds of nanoparticles was investigated (multi-walled nanotubes (MWNTs), polystyrene (PS), TiO_2 and Al_2O_3) modified with single layer β-CD as chiral selector in the enantioseparation of clenbuterol by capillary electrophoresis (CE). Successful clenbuterol enantioseparation could be achieved with the β-CD-modified MWNTs as chiral selector. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) confirmed the β-CD modification of the nanoparticles. The effects of nanoparticles, surfactant, chiral selector (β-CD) and run buffer were studied in relation to the enantiomeric separation of clenbuterol. This study opens attractive perspectives for the use of modified nanoparticles for chiral separational purposes in CE.

Keywords: Modified-nanoparticles; β-CD; High performance capillary electrophoresis; Clenbuterol; Surfactant; Enantioseparation

1. Introduction

Nanomaterials have attracted extensive attention in various fields of physics, biology, and chemistry [1–5]. Physicists and chemists are intrigued by the gradual transition of the nanomaterials' properties from molecule-like to solid-state-like properties by a change of one single variable, i.e., the particle size. This property features practical and future applications for nonlinear optics and electronics [6]. There has been some research devoted to the application of nanoparticles for separational purposes with capillary electrophoresis (CE). Neiman and Grushka used gold nanoparticles to enhance CE separation [6]. Viberg et al. used polymer nanoparticles as pseudostationary phase in capillary electrochromatography (CEC) with electrospray ionization mass spectrometry detection [7]. Li and coworkers incorporated single-wall carbon nanotubes (SWNTs) into an organic polymer monolithic stationary phase for μ-HPLC and CEC [8]. The electrophoretic behaviour of γ-Fe_2O_3 nanoparticles has also been investigated by capillary zone electrophoresis [9]. To the best of our knowledge, there have been reported no prior efforts to use nanoparticles for achieving CE enantioseparation.

The major difficulty for achieving enantiometric separation by using nanoparticles is the lack of a chiral group on the surface of nanomaterials. As reported by several papers, an interaction between solutes and chiral selector is necessary to achieve enantiometric separation [10]. A three-point rule for successful enantiomeric separations was proposed, which stated three types of interactions must occur between the solute and the chiral selector [11]. One of the interactions must depend on the steric

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geometry of the solute. Both other types of interactions may include electrostatic, dipole–dipole, hydrophobic, attractive and repulsive interactions, and hydrogen bonding [10]. Thus, it is difficult to use nanoparticles in the application of chiral separations employing CE because of the limited characteristics of the nanoparticles' surface.

Chemical modification of the nanoparticles surface plays an important role to improve separation in CE [12–19]. Wang et al. reported on the utility and versatility of used carboxylic single-walled carbon nanotubes (c-SWNT) in CE. The distinct changes in the electrophoretic parameters occur at a critical concentration of c-SWNT in the run buffer [12]. Yang et al. used gold nanoparticles-modified etched capillaries for open-tube CEC [13]. Huang et al. modified the gold nanoparticles (GNPs) with poly(ethylene oxide) (PEO) in CE separation [14]. Luong et al. reported the electrophoretic separation of aniline derivatives by using silica capillaries coated with acid-treated SWNTs [15]. Huber and co-workers, as well as Rodríguez and Colón used derived polymer-based nanoparticles to coat fused silica capillaries for use in CE [16–18]. Neiman et al. used organic modified silica sol-mediated CE [19]. Unfortunately, no attempt was made by these authors to achieve chiral separation based on modified nanoparticles.

β-Cyclodextrin (β-CD) is a frequently used chiral selector in CE separations, bearing a hydrophobic inner cavity and a hydrophilic outer surface [10]. β-CD could be used in the modification of GNPs [20]. Star et al. reported that CD wrapped itself helically around SWNTs through sonication, leading to the solubility of SWNTs in aqueous solution [21]. This result would suggest a possibility to extend the modification of nanoparticles with single layer β-CD for enantiomeric separations. In order to demonstrate the enantioseparation with modified nanoparticles, four kinds of nanoparticles, including MWNTs, polystyrene, TiO_2 and Al_2O_3 modified with β-CD on the surface were prepared. These nanoparticles were used as a pseudostationary phase for CE separation. Clenbuterol was used as model solute. It is well known that clenbuterol is an important drug with potent β2-adrenoceptor stimulating properties and is used for the treatment of pulmonary disease. Enantiomeric separation of clenbuterol is interesting in pharmaceutical studies because the β2-agonistic as well as the β1-antagonistic effect of clenbuterol resides in the (−)-isomer. In contrast, the (+)-isomer does not seem to contribute to the pharmacological effects [22].

The aim of the present paper is to demonstrate the application of β-CD-modified nanoparticles as chiral selector in CE separations. During enantioseparation, large surface area platforms with β-CD organofunctional groups can serve as a pseudostationary chiral phase. Comparing with the comparable amount of β-CD as chiral selector alone, the distinct improvement of separation efficiency of clenbuterol can be concluded by applying modified-nanoparticles. We compared four kinds of β-CD-modified nanoparticles upon the separation of clenbuterol enantiomers using CE, with stabilization by surfactants in the run buffer. As will be shown, the use of MWNTs nanoparticles modified by single layer β-CD may successfully provide the enantioseparation of clenbuterol, because this nanomaterial forms a network in the run buffer on the basis of the unique tubule structure. The modification of β-CD on the surface of nanoparticles was characterized by using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The present study shows the great potential to separate chiral compounds based on CE with chemically modified nanoparticles as pseudostationary chiral-phase.

2. Experimental

2.1. Chemicals and reagents

The MWNTs, PS, TiO_2 and Al_2O_3 nanoparticles were gifts from the Department of Materials, Tsinghua University. The transmission electron microscope (TEM) images of the four kinds of purified nanoparticles are shown in Fig. 1, and were obtained with a Hitachi H-800 transmission electron microscope, the accelerating voltage of the electron beam installed at 200 kV.

Racemic clenbuterol (a bronchodilator) was provided by the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, PR China). Phosphoric acid (85%, w/w) was purchased from Beijing Chemical Plant (Beijing, PR China). Triton X-100 (TX100), sodium dodecylbenzenesulfonate (NaDDBS), sodium dodecyl sulfate (SDS) and β-CD were purchased from Sino-American Biofec (Beijing, PR China). All chemicals for the buffer solutions were of analytical grade.

Clenbuterol was diluted to 100 mg L^{-1} by the run buffer solution after dissolution in 0.2 mL methanol. The run buffer was composed of 5 mM β-CD in 50 mM phosphate buffer, made by

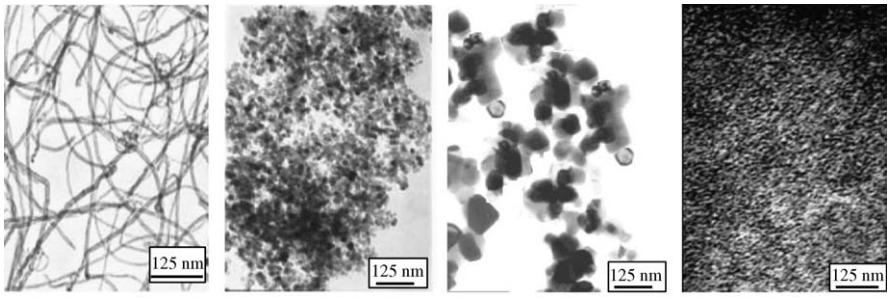

Fig. 1. TEM images of four kinds of nanoparticles: (a) MWNTs; (b) polystyrene; (c) TiO_2; (d) Al_2O_3.

adjusting 50 mM phosphoric acid to pH 2.24 with 4 M sodium hydroxide. The water was purified by a Millipore Simplicity™ water system (Millipore, Milford, MA, USA). All buffers and sample solutions were filtered through 0.45 μm syringe filters.

2.2. Nanodispersion preparation

As a result of van der Waals attractions, nanoparticles aggregate easily and therefore they were insoluble in common solvents [23,24]. Thus, we used long chain surfactants to dissolve the nanoparticles so as to avoid their aggregation [25–29]. Nanoparticles and β-CD were mixed in an agate mortar and homogenized for 40 min, followed by ultrasonication in the run buffer for about 1 h in an ultrasonic bath (KQ-50DE, Kunshan ultrasonic apparatus Ltd, PR China).

2.3. CE and the initial capillary treatment

Analyses were performed on a 1229 capillary electrophoresis system (Beijing Institute of New Technology Application, PR China). Detection was carried out by on-column measurement of UV absorption at 254 nm. Data were collected and processed with a 9423 chromatography integration instrument (Beijing Institute of New Technology Application, PR China). A new 50 cm long, 50 μm i.d., 375 μm o.d. polyimide-coated fused-silica capillary (Hebei Yongnian Optical Fiber Factory, Hebei, PR China) with an effective length of 35 cm was mounted into the CE system. It was flushed with 1.0 M sodium hydroxide for silanol activation (30 min), water (5 min), 0.1 M NaOH (5 min) followed by water (5 min). Finally, the run buffer solution was pumped through the capillary and the high voltage (l0 kV) turned on for about one h so as to equilibrate before use.

The sample was pressure-loaded at 100 mbar for 5 s before applying the separation voltages of +10 kV. The column temperature was fixed at 25 °C. Between the analyses, the capillary was washed sequentially with sodium hydroxide, water and run buffer, each for 3 min.

2.4. FTIR spectroscopic measurements

All infrared spectra were recorded at room temperature with a Nicolet Nexus 670 FTIR spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and a KBr beam splitter. For each spectrum, a 32-scan interferogram was collected at a resolution of 4 cm^{-1}.

2.5. Equipment for XRD

X-ray diffraction analyses were performed by a PANalytical X'pert Pro MPD diffractometer (PANalytical, Holland), using Cu Kα radiation (40 kV, 40 mA), a flat sample holder and an X'celerator detector. Measurements were carried out in the range $5 < 2\theta < 80^\circ$ with a step of 0.033°. The scan step time was 15 s. The JCPDS data bank of standard X-ray powder spectra was used for phase identification [JCPDS (2002)].

3. Results and discussion

3.1. Characterization of nanoparticles

The pristine nanoparticles used in this study are MWNTs, PS, TiO_2 and Al_2O_3 nanoparticles. The surfaces of these nanoparticles were modified by β-CD. The nature of the surface groups attached to nanoparticles was investigated using FTIR and XRD spectroscopies.

Fig. 2 shows the FTIR spectra of MWNTs sample (Fig. 2A), β-CD-modified MWNTs nanoparticles (Fig. 2B), β-CD sample (Fig. 2C). A strong band at 2923.13 cm^{-1} in the spectrum of β-CD (Fig. 2C) is due to the stretching vibration of CH_2, and that at 1654.43 cm^{-1} is due to HOH bending of physically absorbed water. Bands at 1158.04 and 1028.54 cm^{-1} are assigned to the absorption of C–O, C–O–C of glucose units. The relative intensity of the transmittance band at 947.89 cm^{-1} (C–O–C symmetrical stretching bands of five-membered ring) and 757.19 cm^{-1} (pyranose ring vibration) are the characteristic peaks of the rings of β-CD [30–32]. Comparing the spectrum of MWNTs (Fig. 2A), the corresponding bands of MWNTs can be found in the FTIR spectrum of β-CD-modified MWNTs nanoparticles (Fig. 2B). The corresponding bands in Fig. 2B are 1653.19, 1408.00, 1160, 1081.08 cm^{-1}. It can be seen that the characteristic MWNTs nanoparticles peaks were slightly shifted to short wavelengths when modified with β-CD. For example, the peaks at 1652.37 cm^{-1} were shifted to 1653.19, 1404.97–1408.00, 1155.72–1160 and 1079.45–1081.08 cm^{-1}. This discrepancy could be attributed to the interaction by β-CD on the surface of MWNTs nanoparticles. From Fig. 2B, the presence of β-CD can be judged by the characteristic bands of 2921.51, 1408.00, 1296.00, 1249.55, 1104.70, 1081.08, 1029.62, 947.15, 757.19, 704.65, 608.86, 576.51 and 530.16 cm^{-1}. Hence the modification of MWNTs with β-CD may be confirmed. A similar spectral analysis was applied to the PS nanoparticles and β-CD-modified PS nanoparticles. The characteristic absorption bands of PS nanoparticles are as follows: the aromatic C–H stretching bands at 2921.47 cm^{-1}; the skeletal vibration bands of the benzene ring at 1601.20 and 1452.39 cm^{-1}; the out-of-plane bending band of C–H in the benzene ring at 757.06 and 697.83 cm^{-1}. For comparison, the characteristic peaks of PS nanoparticles can be confirmed by the bands of 2922.62, 1607.28, 1455.12, 757.19 and 702.70 cm^{-1}; the peaks at 2922.62, 1298.98, 1250.16, 1105.20, 1081.08, 946.99, 702.70, 611.89 and 578.59 cm^{-1} are due to the presence of β-CD. Similarly, in the spectrum of β-CD-modified PS nanoparticles, the shifts to the short wavelengths were also shown as following when modified with β-CD: 2921.47–2922.20, 1601.20–1607.78, 757.06–757.19, 697.83–702.70 cm^{-1}, which were attributed to the presence of the interaction of β-CD and PS nanoparticles. Hence the modification of PS nanoparticles with β-CD can be confirmed.

XRD studies were carried out on Al_2O_3 nanoparticles (Fig. 3A) and β-CD-modified Al_2O_3 nanoparticles (Fig. 3B) compared to β-CD (Fig. 3C). From the similar peaks from $2\theta = 5^\circ$ to 40° in Fig. 3B and C, one can conclude on the

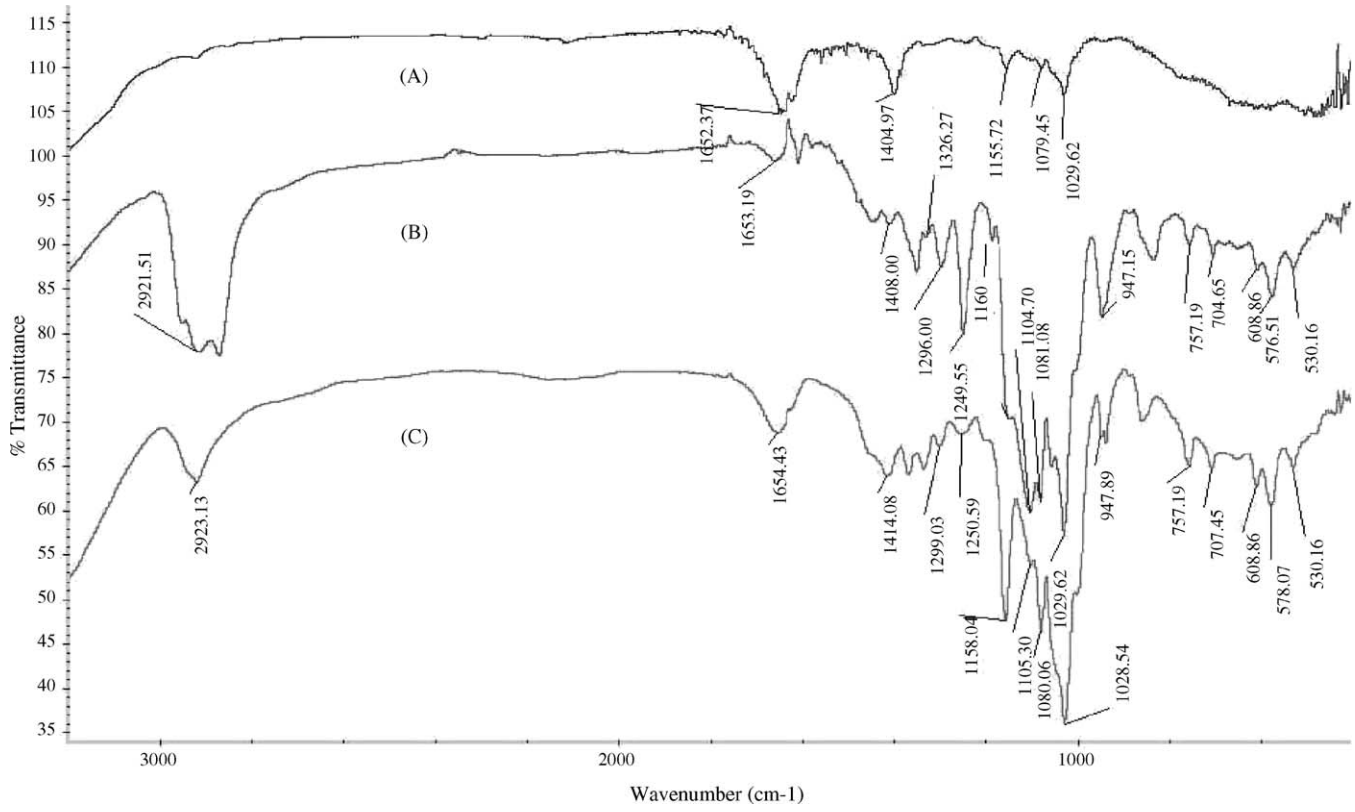

Fig. 2. FTIR spectra for the characterization of modified-MWNTs nanoparticles: (A) MWNTs; (B) β-CD-modified MWNTs nanoparticles; (C) β-CD.

interaction of β-CD and Al_2O_3 nanoparticles. Comparing the XRD spectrum of Al_2O_3 nanoparticles (Fig. 3A), we can also find the corresponding peaks of Al_2O_3 in Fig. 3B, which are marked with arrows. Similarly, through comparing the XRD spectra of TiO_2 nanoparticles, β-CD-modified TiO_2 nanoparticles and β-CD, it can be concluded that β-CD has likewise been modified on the surface of TiO_2 nanoparticles.

From the measurements of FTIR and XRD, the attachment of β-CD upon the surface of nanoparticles can be confirmed, supporting the successful modification of nanoparticles by the β-CD molecules.

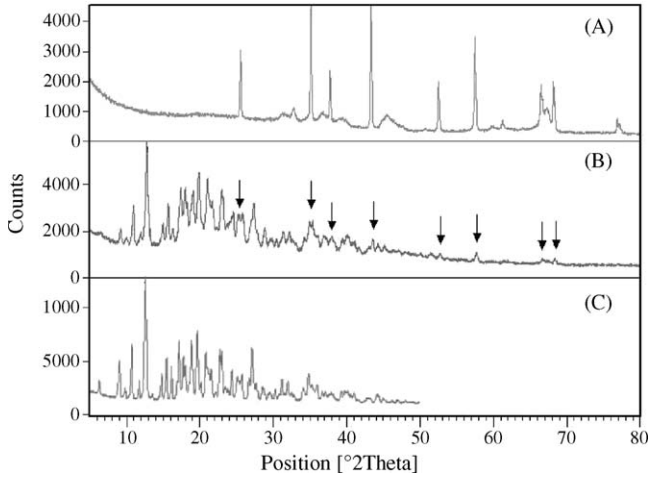

Fig. 3. XRD spectra for the characterization of modified-Al_2O_3 nanoparticles: (A) Al_2O_3 nanoparticles; (B) β-CD-modified Al_2O_3 nanoparticles; (C) β-CD.

3.2. Enantioseparation with β-CD-modified nanoparticles as chiral selector

Fig. 4A shows the effect of modified-nanoparticles in the enantiomeric separation. We compared the electropherograms of the enantiomeric separation of clenbuterol by using CE with four kinds of β-CD-modified nanoparticles (Fig. 4A, b–e) and with the comparable amount of β-CD as chiral selector (Fig. 4A, a). It is obvious that introducing β-CD-modified nanoparticles can substantially enhance the enantioseparation of clenbuterol. The reason that we obtained poor enantiosepartion when using β-CD alone is that the concentration of β-CD in the run buffer is 5 mM, which is much lower than the optimum β-CD concentration of 18 mM [33]. The role of modified-nanoparticles in the enantioseparation mechanism may be based on the fact that β-CD-modified nanoparticles present a large surface area platform for organized media, allowing a better contact and interaction with the analytes [34], which can be concluded from the obvious improvement of chiral separation.

Four kinds of β-CD-modified nanoparticles, β-CD-MWNTs, β-CD-PS, β-CD-TiO_2 and β-CD-Al_2O_3 were studied. As shown in Fig. 4A (b–e), the enantioseparation enhancement of modified-MWNTs is most prominent compared to the other nanoparticles, which can be explained by the stereoporous interfacial layer and the largest surface area of MWNTs.

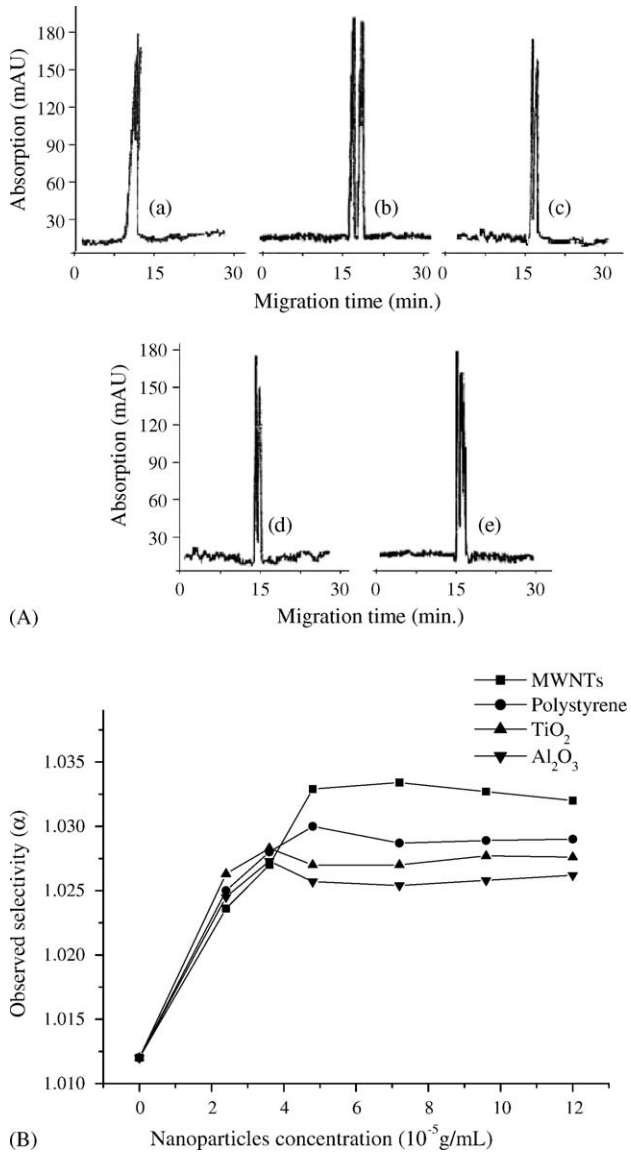

Fig. 4. Enantioseparation with β-CD-modified nanoparticles as chiral selector. (A) Electropherograms illustrating the influence of β-CD-modified nanoparticles upon the enantioseparation of clenbuterol enantiomers: (a) comparable amount of β-CD as chiral selector adding TX100; (b) 4.8×10^{-5} g mL^{-1} β-CD-modified MWNTs as chiral selector stabilized by TX100; (c) 4.8×10^{-5} g mL^{-1} modified-PS nanoparticles as chiral selector stabilized by TX100; (d) 3.6×10^{-5} g mL^{-1} modified-TiO_2 nanoparticles as chiral selector stabilized by TX100; (e) 3.6×10^{-5} g mL^{-1} modified-Al_2O_3 nanoparticles as chiral selector stabilized by TX100. Buffer composition: 50 mM phosphoric acid buffer (pH 2.24). The detector was on the cathodic side of the capillary and the detection wavelength was 254 nm. (B) Variation in enantioseparation as a function of modified-nanoparticle concentration. (■) Modified-MWNTs as selectors; (●) modified-PS nanoparticles as chiral selector; (▲) modified-TiO_2 nanoparticles as chiral selector; (▼) modified-Al_2O_3 nanoparticles as chiral selector. Replicate measurements were determined no less than three times at each concentration point. R.S.D.s (relative standard deviations) are less than 4%. Run buffer: 50 mM phosphoric acid buffer (pH 2.24).

The MWNTs consist of concentric cylinders with an interlayer spacing of 3.4 Å and a diameter typically in the order of 10–20 nm, exhibiting unique electronic properties, which are expected to disperse better in the presence of surfactant. Thus, a larger platform like a network can be made after modification with β-CD to enhance enantioseparation [8,12,35].

In addition, the variation in enantioseparation as a function of modified-nanoparticle concentration is shown in Fig. 4B. The increased effect would vanish with increasing modified-nanoparticles concentration above a certain value. The reason for these observations could be explained in the terms of the available localization sites for the enantiomers. When the localization sites are saturated for enantiomers, any further increase of the modified-nanoparticles concentration would not result in increased enantioseparation.

3.3. The suspension of β-CD-modified nanoparticles stabilized by different kinds of surfactants

The presence of surfactants is intended to promote the dispersion of modified-nanoparticles in the run buffer [28]. In this study, three kinds of surfactants were examined in dispersing modified-MWNTs nanoparticles. As shown in Fig. 5A, with modified-MWNTs nanoparticles, the enhancement of clenbuterol enantioseparations are more distinctly stabilized by TX100 than by NaDDBS and SDS. Fig. 5B visualizes the TEM observations of modified-MWNTs under the stabilization of three surfactants. The different dispersing capabilities of three kinds of surfactants would be explained in terms of graphite–surfactant interactions, alkyl chain length and headgroup size [26,36]. It is shown in Fig. 5B that TX100 has superior dispersing capabilities, thus a larger platform can be made by β-CD-modified nanoparticles under the stabilizing effect of TX100, which may lead to the best enantioseparation.

In addition, we also demonstrated that the best enantioseparation of clenbuterol was solely dependent on the β-CD-modified nanoparticles. TX100 plays only the role of disperser of the modified-nanoparticles into the run buffer. We did not observe the obvious enantioseparation effect when TX100 was added to the run buffer and the β-CD run buffer, which implies that the role of TX100 surfactant cannot be assigned an enantioseparational function.

3.4. Effect of run buffer concentration upon enantioseparation

The addition of salt to nanoparticle solutions can induce aggregation to some extent, which might affect the improvement of enantioseparation [28]. Experiments with varying run buffer concentrations from 25 to 100 mM were performed to investigate this concentrational effect upon enantioseparation with the modified-nanoparticles. As shown in Fig. 6, for MWNTs and PS nanoparticles, when increasing the buffer concentration above 50 mM, the observed decreased enantioseparation is most likely due to the conglomeration of modified-nanoparticles in the run buffer of high concentration, apart from the Joule heating effect. As to the modified-TiO_2 and Al_2O_3 nanoparticles, the phenomenon is less notable, which is most likely due to their smaller extent length.

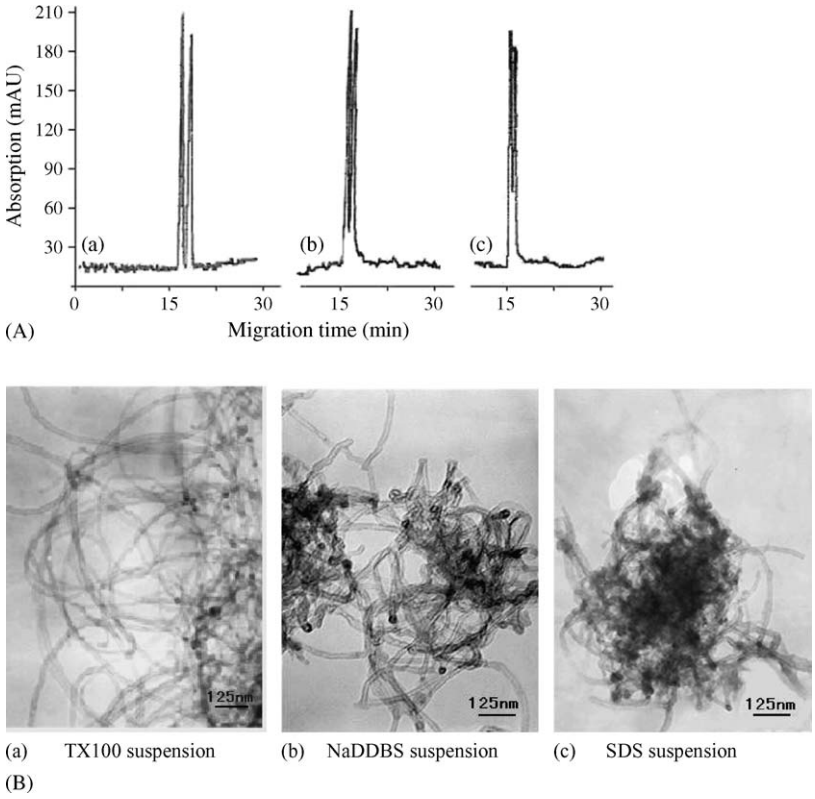

Fig. 5. Dispersing abilities of different kinds of surfactants. (A) Electropherograms of enantioseparation of clenbuterol with three surfactants stabilizing the β-CD-modified-nanoparticles: (a) stabilized by TX100; (b) stabilized by NaDDBS; (c) stabilized by SDS. Run buffer composition: 50 mM phosphate (pH 2.24) with 4.8×10^{-5} g mL^{-1} modified MWNTs. The detector was on the cathodic side of the capillary and the detection wavelength was 254 nm. (B) TEM images of β-CD-modified MWNTs stabilized by three kinds of surfactants.

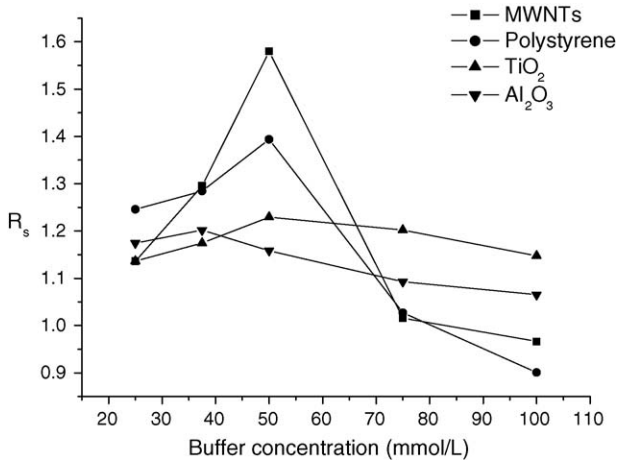

Fig. 6. Effects of run buffer concentration on enantioseparation: (■) 4.8×10^{-5} g mL^{-1} modified-MWNTs as selectors; (●) 4.8×10^{-5} g mL^{-1} modified PS nanoparticles as chiral selector; (▲) 3.6×10^{-5} g mL^{-1} modified TiO_2 nanoparticles as chiral selector; (▼) 3.6×10^{-5} g mL^{-1} modified Al_2O_3 nanoparticles as chiral selector.

4. Conclusions

A new class of modified nanoparticles as chiral selectors is being introduced for the enantioseparation of chiral compounds. Comparing to the results obtained with a comparable low amount of β-CD as chiral selector alone, we got the enhancement of clenbuterol enantioseparation by β-CD modified nanoparticles. And we obtained successful enantioseparation by β-CD-modified MWNTs nanoparticles stabilized by TX100 in the run buffer. This may be due to the fact that single layer β-CD modified on the surface of MWNTs nanoparticles forms a large surface area platform with the β-CD organofunctional groups, which can serve as a novel pseudostationary chiral-phase. The best enantioseparation of clenbuterol with modified-MWNTs nanoparticles stabilized by TX100 is assigned to their better tubular structure with larger surface area so as to attach a single layer β-CD. It was concluded that TX100 has the best dispersing ability in promoting the dispersion of modified-nanoparticles, which is due to its benzene ring and alkyl chain length. In addition, when increasing the modified nanoparticles concentration above a certain value, the increased effect will vanish because of the saturation of the available localization sites for the enantiomers. Above a certain concentration, any further increase of the nanoparticles concentration does not lead to further enhancement of the separation because of the conglomeration of the cited particles. It can be stated that nanoparticle-modified electrophoresis avoids the need to pack the capillary with a chiral stationary phase for specific applications; hence the involvement of other retaining mechanisms can be eliminated.

The successful applications of nanoparticles in the separation of the clenbuterol enantiomers as reported in this paper is most

likely to be readily extended to other classes of analytes and not in the least to nanoparticles applications in CE and other areas in the physicochemical and life sciences.

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