

# Particles Size Estimation of Polydopamine Based Polymeric Nanoparticles Using Near-Infrared Spectroscopy Combined with Linear Regression Method

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## Abstract

The particle size is considered as a fundamental property of nanoparticles used for cargo delivery (CDS) purpose. The objective of this study was the particles size quantification of polydopamine nanoparticles (PDANS) via the near infrared spectroscopy (NIRS) combined with chemometrics tools. The successful synthesis of PDANS was proved using several characterization methods. Compared with the model extracted using raw spectral data, the accuracy and stability of the new model extracted from pre-processed data were significantly improved. The PDANS particle size samples have been predicted with acceptable accuracy. The correlation ( $R^2$ ) between NIRS and the TEM granulometric data was 99.81%, while the root mean square error of calibration *RMSEC* was 0.196 nm. This research shows that NIRS combined with a regression method is a viable tool for the quality determination of CD system.

## Keywords

Near Infrared Spectroscopy, Particle Size Effect, Nanoparticles, Linear Regression

## 1. Introduction

IR spectroscopy plays an important role for evaluation of drug quality in industrial and research process especially for organic ingredient with abundant CH, OH, SH, or NH groups. Near-Infrared Spectroscopy (NIRS) (780 - 2595 nm), is a noninvasive and eco-friendly analytical technique that presents a promising alternative for cargoes delivery system (DDS) qualitative and quantitative analysis [1] [2]. NIRS is known as a rapid and nondestructive analytical method with

no sample preparation [2]. The sensitivity of NIRS spectral signals to any physical factors including particle size, the crystallinity ratio, solid surface roughness, coating thickness, temperature [1] [3] [4] [5] [6] [7] and chemical parameters such as analytes ratio, moisture ratio [8], concentrations and chemical composition; the ingredient distribution [9] could be of great interest in order to understand and evaluate new designed DDS.

For any drug delivery system, the determination of drug and the container physiochemical properties is vital for estimation of *in vivo* delivery and the study of the kinetics and release behaviour [10]. A good characterization of the designed system could lead to a good understanding to the designed system, by the way an accurate estimation of the therapeutic effect [11]. Importantly, the drug substrate design and a precise investigation of the physiochemical properties including particle size are primordial for understanding of the possibility of DDS leakage by enhanced Plasmon Resonance effect (EPR) [12] [13], besides its capacity of drug loading in case of chemotherapy or photothermal or photodynamic effect in case of other physical therapeutic modalities [10].

The determination of particle characteristics using conventional electronic microscope or laser diffractometer with high accuracy and reproducibility was always a challenging inversion problem [14], besides the nonavailability of such apparatus in every lab. NIRS instead is largely available apparatus and noninvasive quantitative and qualitative analysis method. This reliable and precise estimation of the DDS physiochemical properties could be achieved by NIRS as a non-destructive method and a precise quantitative tool when chemometrics is used.

The paper is structured around two main points presented in two parts. One part is the characterization results of the designed PDA based nanoparticles (PDANS), prepared for further drug delivery purposes. The accuracy of the nanostructures size and morphology is primordial for biomedical application [12], thus a set of prepared PDANS of multiple particle sizes was prepared and analysed for computational modelling using near infrared spectroscopy. The NIRS spectra of polymeric nanoparticles is considered as a response of the inherent absorption properties caused by its chemical component such as chemical structure or analyte ratio and scattering phenomena related to its physical characteristics such as particles' size and morphology [1] [2]. The NIRS spectral data are complex and need further chemometrics methods for extraction and interpretation of the desired information [3] [9].

In the present study, in order to prove the importance of NIRS for various DDS properties estimation, partial least square method (PLS) were used to evaluate the NIR spectra acquired for PDANS particle size and correlate it to transmission electron microscope primary analysis method. The accuracy of modelling process was by several correlation indexes.

## 2. Materials and Methods

### 2.1. Reactants

Dopamine hydrochloride DA-HCl (~35% - 37%) was purchased from Aladdin.

Sodium hydroxide (NaOH) ( $\geq 96\%$ ) were obtained from Sinopharm Chemical Reagent. The ultrapure water used for solution preparation was prepared using Millipak filter of 0.22  $\mu\text{m}$  pore size Millipore in Milli-Q system. Ethanol absolute was purchased from Tianjin Hengxing Chemical preparation. All chemical reagents were used as received without any purification.

## 2.2. Methods

### 2.2.1. Preparation of Polydopamine Nanoparticles

The PDA nanoparticles (PDANS) with different particles size were prepared by the oxidation and self-polymerization of dopamine hydrochloride [15]. Briefly, different amount (mg) of dopamine hydrochloride was dissolved in specific volume "VdiH<sub>2</sub>O" (mL) of deionized water, at various temperatures and under vigorous stirring, a volume VNaOH of 1N NaOH solution was added. After 5 h, the obtained dark black solution was centrifuged (13,000 rpm) and then washed several times with deionized water. All large-size materials were removed by 4000 rpm centrifugation. The obtained samples were washed several time with deionized water and ethanol, and then freeze-dried to form black powder. The optimized experimental conditions can be scaled up to obtain different size of PDANS particles as summarized in **Table 1**.

### 2.2.2. General Characterization Method

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet FT-IR 5700 spectrometer the samples were prepared using potassium bromide (KBr) pastille. Few milligrams of PDANS powder were mixed with 100 mg of KBr. The

**Table 1.** Experimental condition for synthesis polydopamine nanoparticles.

Experimental Conditions					
Sample N	DA-HCl mass (mg)	VdiH <sub>2</sub> O (mL)	VNaOH /n:n( $\mu\text{l}$ )	Rtemp ( $^{\circ}\text{C}$ )	dTEM (nm)
1	180.00	90.00	760/1:0.65	40	~135
2	360.00	90.00	760/1: 0.32	50	~950
3	180.00	90.00	760/1:0.65	20	~170
4	153.18	79.59	400/1:0.40	40	~285
5	360.00	90.00	760/1:0.32	70	~1350
6	153.18	79.59	400/1:0.40	25	~180
7	119.70	90.00	312/1:0.40	30	~290
8	153.18	79.59	600/1:0.60	30	~275
9	180.00	90.00	094/1:0.80	50	~221
10	270.00	90.00	880/1:0.50	30	~650
11	360.00	90.00	1880/1:0.80	50	~520
12	180.00	90.00	760/1:0.65	30	~250

V: Volume; Rtemp: Room temperature; DA-HCl: Dopamine hydrochloride; dTEM: TEM particles diameter.

FTIR were recorded for 2  $\text{cm}^{-1}$  resolution over the range of 600 - 4000  $\text{cm}^{-1}$  through diffuse reflection contact angle after 64 scans. UV-Vis full range absorption spectra were collected on a (Lambda 750S) spectrophotometer at 480 nm excitation wavelength.

### 2.2.3. Modelling Reference Method

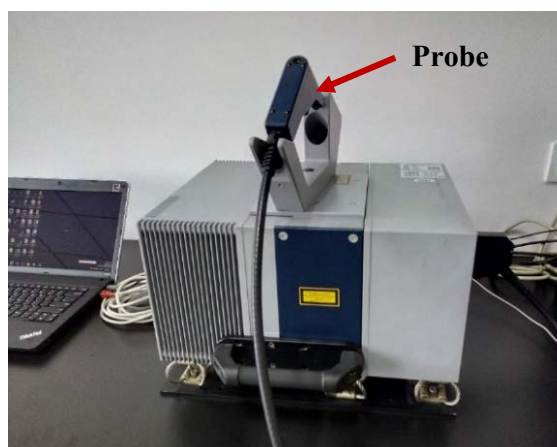
Transmission electron microscope (TEM) images were performed on Hitachi H-7650 microscope operating at an accelerating voltage of 100 kV. The samples were prepared by adding one drop of nanoparticles solution (0.1 mg/mL) onto a 300 mesh carbon film coated copper grid. The specimens were then air dried for 15 minutes. TEM have been used as reference method for multivariate analysis.

### 2.2.4. Modelling Secondary Method

A set of 12 samples of different particles size PDNS (As illustrate in **Table 1**). Every sample was ultrasonically dispersed in high purity water at the same concentration (2 mg/mL) and then its spectral data was collected on MATRIX-F BRUKER NIRS apparatus equipped with solid probe (as illustrated in photographs of **Figure 1**) with an integrating sphere. The samples were positioned in glass tubes and the probe was positioned perpendicularly on the bottom of the sample holder. The spectra of each sample were collected in the reflectance mode. Each spectrum was an average of 32 scans in the range of 4000 - 11,000  $\text{cm}^{-1}$ . The data treatment was proceeded on OPUS 5.0 software. Furthermore, all the experiment was conducted at a temperature of 25°C and at humidity of 60%. The mean of the three spectra collected from one sample was used for subsequent analysis. The NIRS data was used as secondary method.

## 3. Results and Discussion

Before you begin to format your paper, first write and save the content as a 12 samples of the PDA based polymeric nanoparticles were synthesized by neutralization of dopamine hydrochloride with NaOH and spontaneous autoxidation in air, which leads to a gradual formation of dark brown solution.



**Figure 1.** Photograph of NIRS equipment (with optic fibre probe).

The prepared nanoparticles have been characterized and evaluated through various analysis method. The **Figure 2** illustrates the experimental processed discussed in our manuscript.

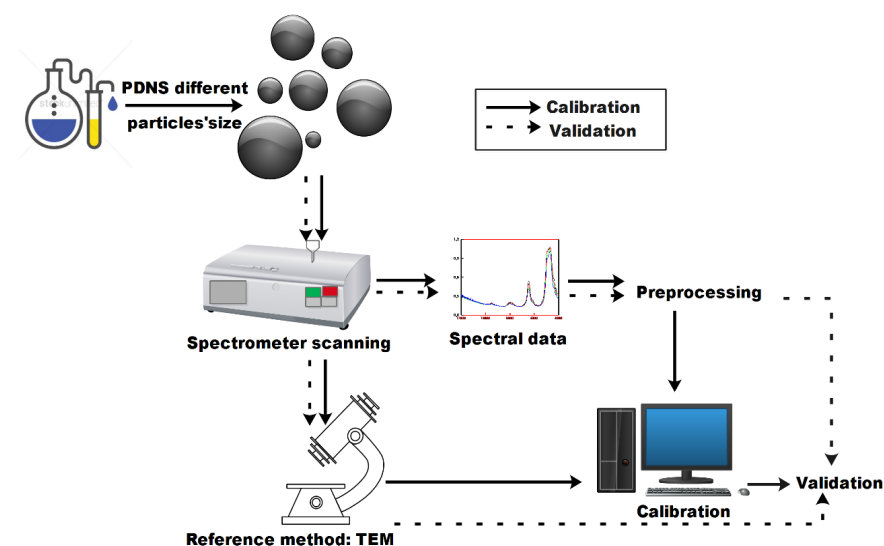
### 3.1. Structural Analysis of PDANS

The PDANS FTIR spectra illustrated in **Figure 3(a)** reveals the presence of two peaks at  $1621\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$  attributed to the characteristics absorption of the phenyl groups. The peaks at  $1288\text{ cm}^{-1}$  and  $1382\text{ cm}^{-1}$  are assigned to the scissoring of  $\text{CH}_2$  and OH of the PDA catechol groups, respectively [16] [17]. The wavelength band ranges from  $2800$  to  $3700\text{ cm}^{-1}$  are assigned to the hydroxyl and amine group stretching of the dehydroxyindole units of PDA [2] [3]. The PDANS UV-visible spectrum shows a broad characteristic absorption peak at  $208\text{ nm}$  as illustrated in **Figure 3(b)** [17].

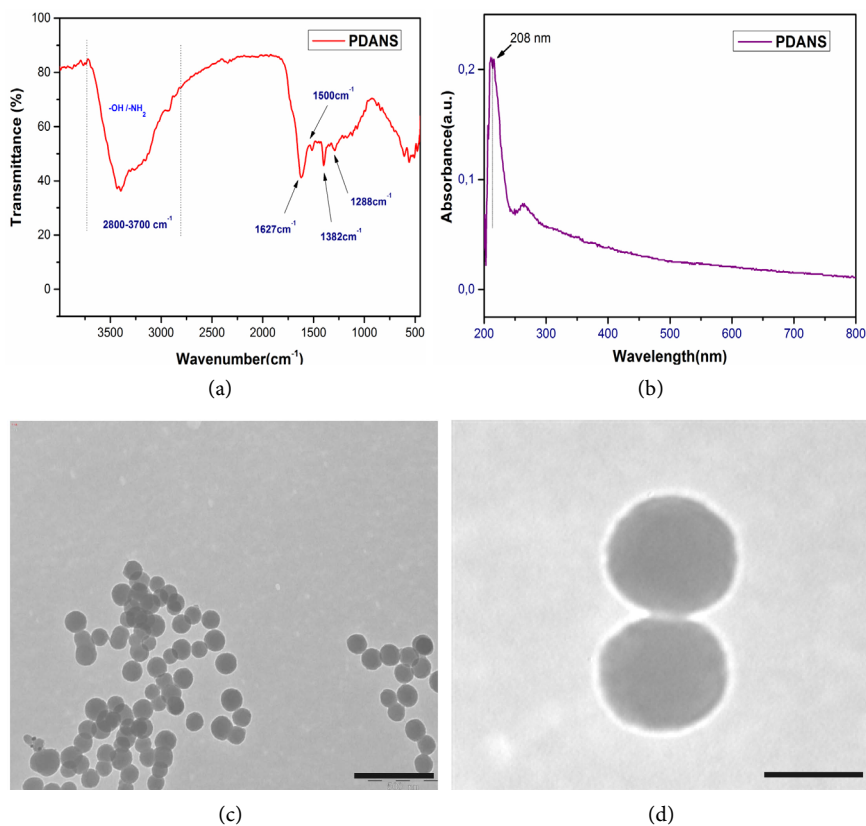
### 3.2. Morphological Analysis of Synthesised PDANS (Reference Method)

Transmission electron microscope images of synthesised PDANSs as shown in **Figure 3(c)** and **Figure 3(d)** indicates well spherical and uniform shaped nanoparticles. The  $135\text{ nm}$  sized particles presented in **Figure 3(c)** and **Figure 3(d)** have been used for FTIR and UV-Vis analysis. The average particle size of the all synthesised samples was organized in **Table 1**. The results reveal that the particle diameter was highly affected by the concentration of dopamine hydrochloride (DA-HCl). The TEM particle size is directly proportional to the DA-HCl amount and inversely proportional to the reaction temperature and NaOH volume.

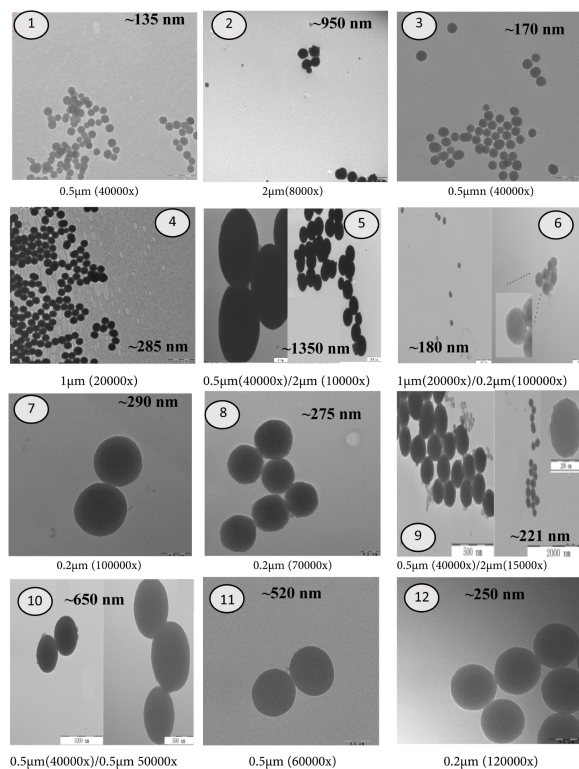
If the NaOH to DA-HCl ratio is more than 1:1 the reaction product is just amorphous polydopamine and not nanoparticles. The TEM images for the all 12 samples are presented in **Figure 4**.



**Figure 2.** Schematic illustration of the experimental procedure.



**Figure 3.** PDANS (~135nm): (a) FTIR spectrum; (b) UV-Vis spectrum; (c) TEM micrograph, scale bare is 500 nm; (d) TEM micrograph, scale bare is 100 nm.



**Figure 4.** TEM images of synthesized PDANS at different particles size.

## 3.2. Computational Modelling of PDANS Particles' Size Using NIRS with Linear Regression Methods (Secondary Method)

### 3.2.1. Samples Preparation

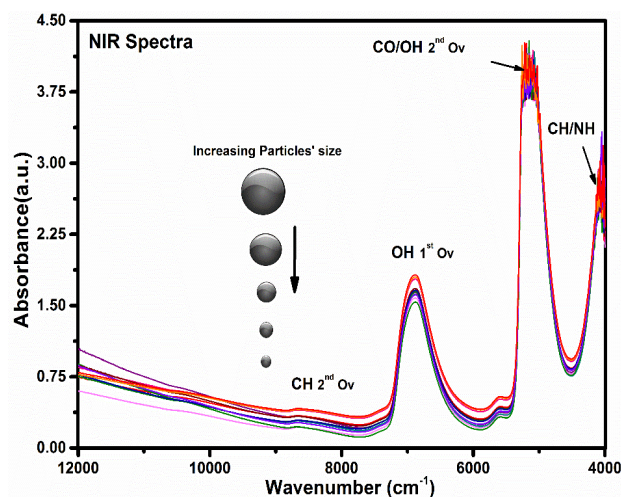
Previously synthesized samples as illustrated in **Table 1** were collected and ultrasonically dispersed in high purity water at similar concentration of 2.5 mg/mL. The prepared samples were left in dark just before analysis at room temperature.

### 3.2.2. Spectral Measurements

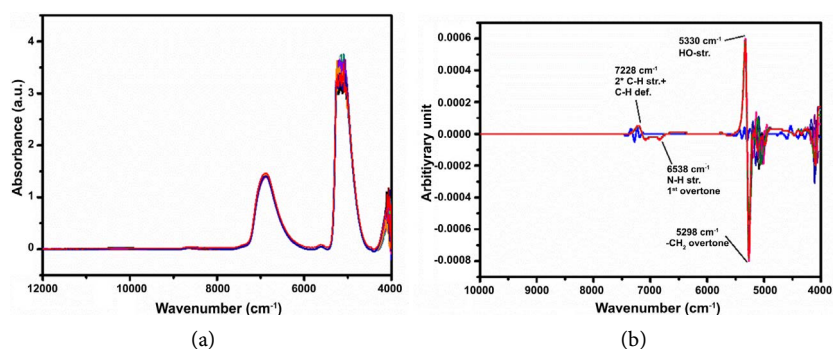
About one drop of freshly prepared samples were scanned with NIRS using the optic fibre probe and saved in absorbance mode. A reference scan was taken once in every three samples. The NIR spectra were collected and saved as illustrated in **Figure 5**. The main features of the spectra are the absorption bands at [8925 - 7802], [7312 - 5986], [5380 - 4500] and  $4029.7\text{cm}^{-1}$ , which are assigned to the second overtone of C-H stretching of PDA catechol groups; first overtones of O-H stretching of water and PDA phenyl groups and two combinations bands of C = O stretching /second overtone of O-H stretching and CH/NH of quinone groups, respectively [10] [18]. The spectra reveal high similarities due the presence of the same chemical properties for the prepared PDANS. The slight variation in spectral data is mainly caused by the differences in the particles size.

### 3.2.3. Spectra Preprocessing

Before the start in the systematic procedure of calibration development, the raw spectra was treated using various preprocessing method including the baseline correction as illustrated in **Figure 6(a)** and the second derivative in order to achieve a better model performance. The standard normal variance is strongly not advised to use because it can eliminate the effect of the particle size effect on NIRS spectra [2], which could mistake our NIRS quantification data. The second derivative highest variations shown in **Figure 6(b)** are similar with the highest peaks in the raw NIR spectra around  $5336, 5279, 5102, 4989$  and  $4095\text{cm}^{-1}$ .



**Figure 5.** Raw NIR spectra of PDANS dispersion in high purity water of 2.5 mg/mL.



**Figure 6.** (a) NIR spectra after baseline correction using Rubberband Corrections; (b) second derivative NIR spectra of PDANS samples.

### 3.2.4. The Selection of Calibration and Validation Set

For the extraction of calibration and validation model, some statistical parameters should be calculated as index of the model performance, which are the model correlation coefficients ( $R^2$ ) and the root mean square error ( $RMSE$ ). They were calculated using Equation (1), (2), (3) and (4) [19] [20]:

$$R^2 = \left\{ 1 - \frac{\sum_{i=0}^n (y_i - \hat{y}_i)^2}{\sum_{i=0}^n (y_i - \bar{y}_i)^2} \right\} \quad (1)$$

Calculated as the sum of squares about mean of Y over the sum of squares about regression line.

$$RMSEC = \sqrt{\frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{n-1}} \quad (2)$$

Calculated as the square root of the sum of squares between true value (lab values) and the predicted values in case of cross validation.

$$RMSEP = \sqrt{\frac{\sum_{i=1}^m (y_i - \hat{y}_i)^2}{m}} \quad (3)$$

Calculated as the square root of the sum of squares between true value (lab values) and the predicted values by prediction model.

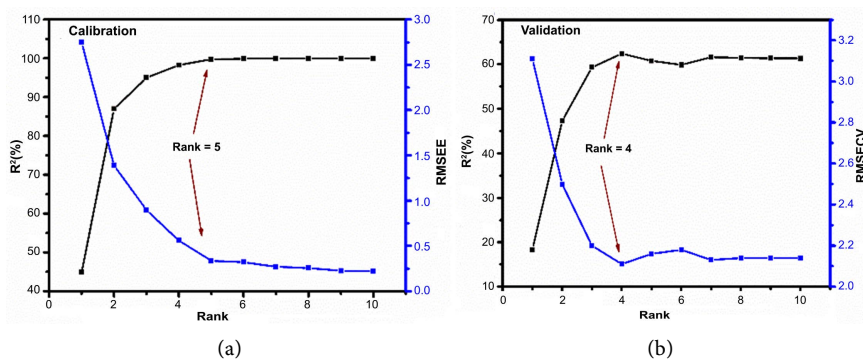
$$RMSEE = \sqrt{\frac{1}{R-N-1} \sum_{i=1}^n residues_i^2} \quad (4)$$

Calculated in case of test set validation determined from residues values.  $R$  is also known as the number of PLS factors.

The determination of the optimum rank is primordial step before the extraction of the calibration model, it can be determined by plotting the  $R^2$ ,  $RMSEE$  and  $RMSECV$  values versus the rank. The determination of optimal rank simplified the model development process and performs the model selection.

The determination of the optimized factor of the model variable matrix was analysed and presented in the **Figure 7(a)** and **Figure 7(b)** for the calibration and validation models, respectively. The results reveals an optimized factor





**Figure 7.** The correlation coefficient and root mean square of error versus PLS factors for (a) calibration set and (b) validation set.

number (Rank) of 5 and 4 for calibration and validation models, respectively. Obviously, both models are affected by the factors number, moreover, the models improved remarkably after changing the factors to number equal to or more than the optimized one. The differences between the calibration and validation models for default rank number of 1 and for an optimized rank number was illustrated in the **Figure 8(a)** and **Figure 8(b)** and a significant improvement in the models was noticed even by looking to the values of  $R^2$ ,  $RMSEE$  and  $RMSECV$  for calibration and validation set in **Table 2**.

### 3.2.5. The Influence of Spectral Pre-Processing

To determine the impact of spectral region selection on the calibration and validation model a comparison between the models parameters  $R^2$ ,  $RMSEC$ ,  $RMSEV$  was conducted at full and short range spectral region that contains more spectral data. According to the results presented in **Table 3**, the more appropriate spectral region for extraction of the best calibration and validation model ranging in  $9048.6 - 4026.7 \text{ cm}^{-1}$ .

### 3.2.6. The Calibration and Validation Results

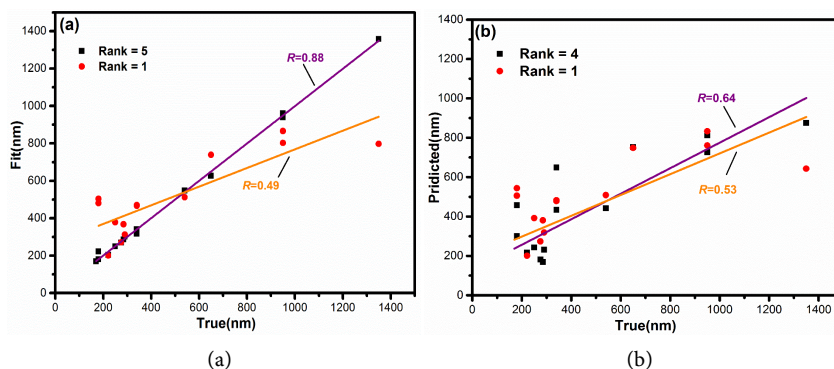
In order to set up a robust reliable and an optimized prediction capability, regression models should be determined through a set of preprocessing methods using optimized PLS factors number and well-established spectral regions. For our investigated PDANS system the best calibration and validation model is the one determined after using offset elimination method, baseline correction and second derivative spectral preprocessing. The optimized rank was 5, and 4 for calibration and validation model, respectively. The models demonstrate a high correlation between both the lab and predicted values. At  $9048.6 - 4026.7 \text{ cm}^{-1}$ , the model parameters  $R^2$ ,  $RMSEC$  for calibration model were 99.81% and 0.196 nm respectively, for validation model  $R^2$  and  $RMSECV$  were 70.67%, 1.87 nm respectively. The PLS models constructed for the quantitative evaluation of the particles size estimation were demonstrated to be predictive with high accuracy of our synthesised samples. The optimized models illustrated in **Figure 9** was used for estimation of the accurate particle size of known sample ( $d_{\text{TEM}} = 135$

**Table 2.** Difference between models parameters determined for default and optimized rank.

Model	Default Rank		Optimized Rank	
	$R^2$ (%)	RMSE (nm)	$R^2$ (%)	RMSE (nm)
Calibration	58.98	2.37	98.27	0.201
Validation	25.84	2.98	62.41	1.99

**Table 3.** Comparison between models parameters of full and short range spectral region for an optimized rank.

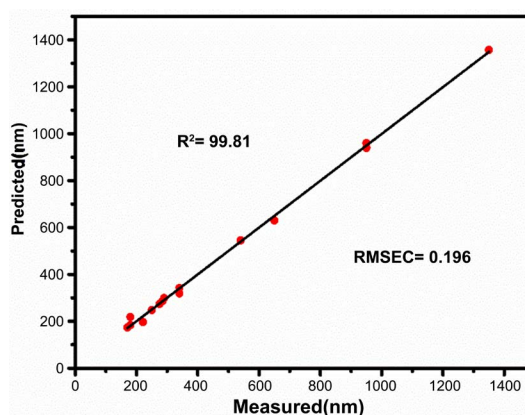
Spectral region	Calibration model		Validation model	
	$R^2$	RMSE	$R^2$	RMSE
Wavenumber ( $\text{cm}^{-1}$ )				
12000.0 - 4000.0	98.27	0.201	62.41	1.99
9048.6 - 4026.7	99.81	0.196	70.67	1.87
8000.0 - 4000.0	99.81	0.195	69.48	1.90
7997.5 - 5971.1/5519.4 - 4508.9	99.83	0.177	52.33	2.38
7997.5 - 5971.1/5626.4 - 3999.7	99.81	0.191	69.11	1.91

**Figure 8.** (a) The calibration and (b) the cross validation models for default and optimized Rank.

nm), while the accurate value was estimated to be 135.6 nm using NIRS model. The analysis of a real data set of PDANS granules size can be given using this robust calibration procedure (see **Figure 9**) and TEM as reference method.

#### 4. Conclusion

In conclusion, our paper introduces NIRS combined with chemometrics as tool for analysis of several physio-chemical properties of designed DDS based on polydopamine nanoparticles at different particles size. The elaborated PDANS as DDS have been monitored with NIRS. Predictive models have been extracted of the NIR versus the TEM granules with and without spectral pre-treatment. Applying robust preprocessing methods as well as model parameters seem to increase the quality of spectral data remarkably compared with non-pre-processed data. Correlation coefficient and root mean square of prediction have been used



**Figure 9.** The Correlation curve between NIR predicted and measured values for PDANS particles size.

to select the suitable preprocessing method for our designed system. Our findings allow the PDANS granules which is an illustration of drug nanocarrier to be in-line monitored with NIRS and controlled effectively. As a perspective, a considerable understanding of NIRS combined with chemometrics tool would contribute remarkably for development of high quality DDS. The collected results could be easily extended for analysis of further samples of released DOX from our designed DDS. A better understanding of the process by NIRS with chemometrics will contribute to developing high-quality therapeutic agent delivery systems.

### Acknowledgements

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