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ELECTROPHORESIS

RESEARCH ARTICLE

The interaction between silica flat substrate and functional group–modified nanoparticles

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Abstract

Inspired by nature, the research of functionalized nanoparticles and nanodevices has been in-depth developed in recent years. In this paper, we theoretically studied the interaction between functional polyelectrolyte brush layer–modified nanoparticles and a silica flat substrate. Based on the Poisson–Nernst–Planck equations, the mathematical model is established. The changes of the volume charge density and electric field energy density when the nanoparticle interacts with the silica flat substrate under multi-ions regulation were investigated. The results show that when there is a strong interaction between the silica flat substrate and nanoparticles, such as the distances between the nanoparticle and silica flat substrate, which are 2 or 5 nm, the isoelectric point shift under the influence of silica flat substrate and the total charge density in the brush layer is jointly controlled by the cations in the solution and the volume charge density of the brush layer. With the increase of the distances between the nanoparticle and silica flat substrate, the regulation of the volume charge density of the brush layer dominates. These results will provide guidance for the movement mechanism of functionalized nanoparticles in silica nanochannels.

KEYWORDS
charge density, electric field energy density, interaction, nanoparticles, silica flat substrate

1 | INTRODUCTION

With the development of the technology of combining the new theory and characterization tools to describe polymer brush layers, people have a further understanding of the uniqueness of the brush layer in recent years [1]. For example, the surface of nanoparticles or devices is modified by polyelectrolyte (PE) with a few nanometers to form a brush layer that can change the surface properties [1–3]. This surface modification technique is mainly used for ion current rectification [4–7], nanobiosensors [8, 9], DNA sequencing [10–13], biomedicine [14, 15], material transport [16, 17] and energy collection [16, 18, 19]. When the PE brush layer–modified nanoparticles or devices are put into the electrolyte solution, the charge properties of the PE brush layer will also change due to the change of ion concentration, and some interesting phenomena will happen. For example, it will change the velocity of nanoparticles passing through nanopores [12, 13, 17, 20, 21] and the ion selectivity in nanochannels [5, 22, 23].

Abbreviations: IEP, isoelectric point; PE, polyelectrolyte; PNP, Poisson–Nernst–Planck.

When the nanoparticles modified by the PE brush layer are in contact with electrolyte solution, the reactions of deprotonation and protonation will occur in the PE brush layer, and the positive or negative volume charges are generated in the brush layer [2, 3]. The volume charge is mainly related to the H^+ concentration such as changing the concentration of the solution and the pH value to change the surface charge density of particles or adjusting the thickness of the brush layer to change the charge density [3, 7, 24, 25]; the electric field energy density is also affected by the charge density [2]. We have come to know from the existing researches that the interaction occurs when two charged objects are close to each other, that is, the properties of the solution such as the local ion concentration between two objects will be different from the properties far away from the two objects [26–30]. Just as two negatively charged particles are close to each other, it will produce a nonuniform distribution of ions around the particles, which will affect the distribution of space charge density around them. At present, many researches are focused on the interaction of metal materials or silica. In fact, in the application of nanobiosensors, when the PE brush layer–modified nanoparticles are interacted with the wall of silica nanochannels, the ion concentration in the PE brush layer will be quite different from that in other positions.

A mathematical model of the interaction between nanoparticles modified by a PE brush layer and a silica flat substrate was established by Poisson–Nernst–Planck (PNP) equations in this paper. As the PE brush layer–modified nanoparticles are widely used in biomolecular transport, colloidal research and drug transport [25, 31–35], we used the PE brush layer to modify the surface of nanoparticles, investigated the interaction between the silica flat substrate and nanoparticles, studied the effects of pH value and the concentration of electrolyte solution on the volume charge density and the energy density of electric field at the bottom of particles.

2 | MATHEMATICAL MODEL

A silica flat substrate is placed in a KCl solution, a nanoparticle with a diameter of D_p is placed above it, as shown in Figure 1. The nanoparticles are modified by the functional groups P~NH_2 and P~COOH (such as lysine) [5], the thickness of the brush layer is d_m, and w is the distance between the silica flat substrate and nanoparticles. The pH of the electrolyte solution can be adjusted by KOH and KCl; thus, there are four ions in the solution (K^+, H^+, Cl^- and OH^-). In the nanoscale, the PE brush layer can be regarded as a single chain uniformly connected on the surface of nanoparticles, which is equivalent to completely wrapping the whole nanoparticle in the PE brush layer, so the influence of nanoparticle surface properties can be ignored. When the repeating units of functional groups are small enough ($N \leq 20$), the deformation of the PE brush layer can be ignored [5, 36].

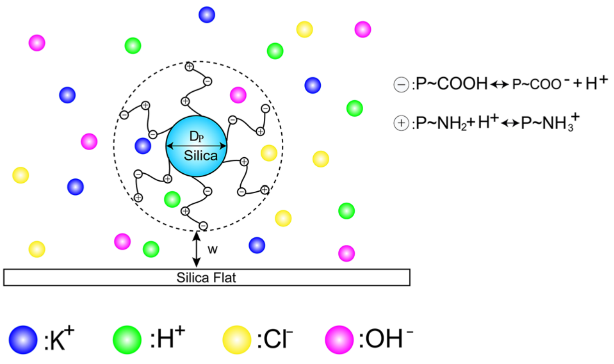

FIGURE 1 Schematic diagram of the interaction between functional group–modified nanoparticles and silica flat substrate

The PNP equations are used to describe the ion transport and electrostatic,

$$-\varepsilon_0\varepsilon_f\nabla^2\phi = F\sum_{i=1}^{4} z_i c_i = \rho_e \tag{1}$$

$$\nabla\cdot N_i = \nabla\cdot\left(-D_i\nabla c_i - z_i\frac{D_i}{RT}Fc_i\nabla\phi\right) = 0 \tag{2}$$

where ε_0 and ε_f represent the permittivity of the vacuum and the relative permittivity of the solution. c_i, D_i and z_i in the previous equations represent the molar concentration, diffusion coefficient and valence of the ith ionic species ($i = 1$ for H^+, $i = 2$ for K^+, $i = 3$ for Cl^- and $i = 4$ for OH^-), respectively. F is the Faraday constant. N_i is the ionic fluxes. The normal ionic flux on the surface of the nanoparticle is 0, that is, $n \cdot N_i = 0$. R is the universal gas constant, ϕ is the potential in the solution, and T is the temperature in the solution. The electric potential ϕ at infinity is set to 0.

Biological macromolecules generally have the characteristics of pH-regulating, so the reactions of protonation and deprotonation are occurred in the PE brush layer [3, 5], as shown in the following:

$$P \sim COOH \leftrightarrow P \sim COO^- + H^+ \tag{3}$$

$$P \sim NH_2 + H^+ \leftrightarrow P \sim {NH_3}^+ \tag{4}$$

The equilibrium constants of the previous reactions are set as K_a and K_b,

$$K_a = \frac{[P \sim COO^-][H^+]}{[P \sim COOH]} \text{ and } K_b = \frac{[P \sim {NH_3}^+]}{[P \sim NH_2][H^+]} \tag{5}$$

where $[H^+] = 10^{-pH}\exp(-\phi/\phi_0)$ represents the H$^+$ concentration in the PE brush layer, and the other brackets denote the volume site density in the PE brush layer of corresponding functional groups. Thus, the volume charge density of the PE brush layer can be obtained as follows:

$$\begin{aligned}\rho_m &= 1000F\left(\left[P \sim NH_3{}^+\right] - \left[P \sim COO^-\right]\right)\\ &= 1000F\left(-\frac{K_a\kappa_a}{K_a + [H^+]} + \frac{K_b\kappa_b\left[H^+\right]}{1+K_b\left[H^+\right]}\right)\end{aligned} \qquad (6)$$

where $\kappa_a = [P \sim COO^-] + [P \sim COOH] = N\sigma_m/1000d_m n_a$ and $\kappa_b = [P \sim NH_3{}^+] + [P \sim NH_2] = N\sigma_m/1000d_m n_a$ represent the net volume site density of the functional groups. σ_m is the grafting density (generally from 0.05 to 0.6 chains/nm^2) [5, 37]. N is the repeated unit of zwitterionic functional groups and n_a is the Avogadro constant.

It is assumed that the volume concentrations of the four ions remain unchanged, that is, $c_i = C_{i0}$. Due to the electroneutrality of the solution, the concentration of different ions in the solution can be obtained as follows [3, 5]:

$$C_{10} = 10^{-pH+3} \text{ and } C_{40} = 10^{pH-11} \qquad (7)$$

$$C_{20} = C_{KCl} - C_{10} + C_{40} \text{ and } C_{30} = C_{KCl} \text{ (pH > 7)} \qquad (8)$$

$$C_{20} = C_{KCl} \text{ and } C_{30} = C_{KCl} + C_{10} - C_{40} \text{ (pH} \leq 7) \qquad (9)$$

The concentration of H$^+$ can effectively affect the volume charge density, the average volume charge density of the PE brush layer ρ is defined as follows:

$$\rho = \frac{1}{d_m}\int_{R_P}^{R_P+d_m} \rho_m dy \qquad (10)$$

Thus, the total charge density of the PE brush layer ρ_t can be obtained:

$$\rho_t = \rho + \rho_e \qquad (11)$$

There are SiOH groups on the surface of silica flat substrate, and the deprotonation and protonation reactions are as follows:

$$SiOH \leftrightarrow SiO^- + H^+ \qquad (12)$$

$$SiOH + H^+ \leftrightarrow SiOH^+ \qquad (13)$$

In the following, K_C and K_D are set as the equilibrium constants of the previous reactions,

$$K_C = \frac{N_{SiO^-}\left[H^+\right]_S}{N_{SiOH}};\ K_D = \frac{N_{SiOH_2{}^+}}{N_{SiOH}[H^+]_S} \qquad (14)$$

where N_{SiOH}, $N_{SiOH_2{}^+}$ and N_{SiO^-} are the site density of SiOH, $SiOH_2^+$ and SiO^- on the surface of silica substrate, respectively. $[H^+]_S$ represent the H$^+$ concentration at the interface of liquid and solid.

The total number of groups on the silica surface is expressed as follows:

$$N_{total} = N_{SiO^-} + N_{SiOH} + N_{SiOH_2{}^+} \qquad (15)$$

From Equations (14) and (15), the surface charge density of silica flat substrate is obtained,

$$\sigma = -FN_{total}\frac{K_C - K_D\left[H^+\right]_S{}^2}{K_C + [H^+]_S + K_D[H^+]_S} \qquad (16)$$

The electric field energy density of the PE brush layer is expressed as follows [2]:

$$\omega = \frac{1}{2}\varepsilon_0 E^2 \qquad (17)$$

The electric field strength of the PE brush layer E can be obtained by the following equations:

$$\nabla \cdot E = \frac{\rho_t}{\varepsilon_0} \qquad (18)$$

$$\oint_S \vec{E}\, dS = \frac{1}{\varepsilon_0}\int_V \rho_t dV \qquad (19)$$

Through the calculation of electric field energy density, we have come to know the electric field intensity and charge or discharge effect in the PE brush layer. The radius of the solution domain is d, the outer boundary is regarded as the far-field boundary. The far-field boundary radius of the solution is set to be much larger than the nanoparticle diameter D_p, so the influence of the solution boundary on the results can be ignored [26], as shown in Figure S1.

3 | RESULTS AND DISCUSSION

The COMSOL Multiphysics (version 5.0) is used to establish and solve the mathematical model, the mesh is drawn by free triangular, and the total number of triangles is about 74 810. Based on the model, the interaction between the PE brush layer–modified nanoparticles and silica flat substrate was studied under different pH values and electrolyte solution concentrations. The changes of electric field energy density and volume charge density in the PE brush layer were discussed. The other parameters are as follows: $\varepsilon_f = 80$, $F = 96490$ C/mol, $D_p = 20$ nm, $d_m = 6$ nm, $d = 600$ nm, $\sigma_m = 0.15$ chains/nm^2, $pK_a = -logK_a = 2.2(\alpha - carboxyl)$, $pK_b = -logK_b = -8.8(\alpha - amino)$

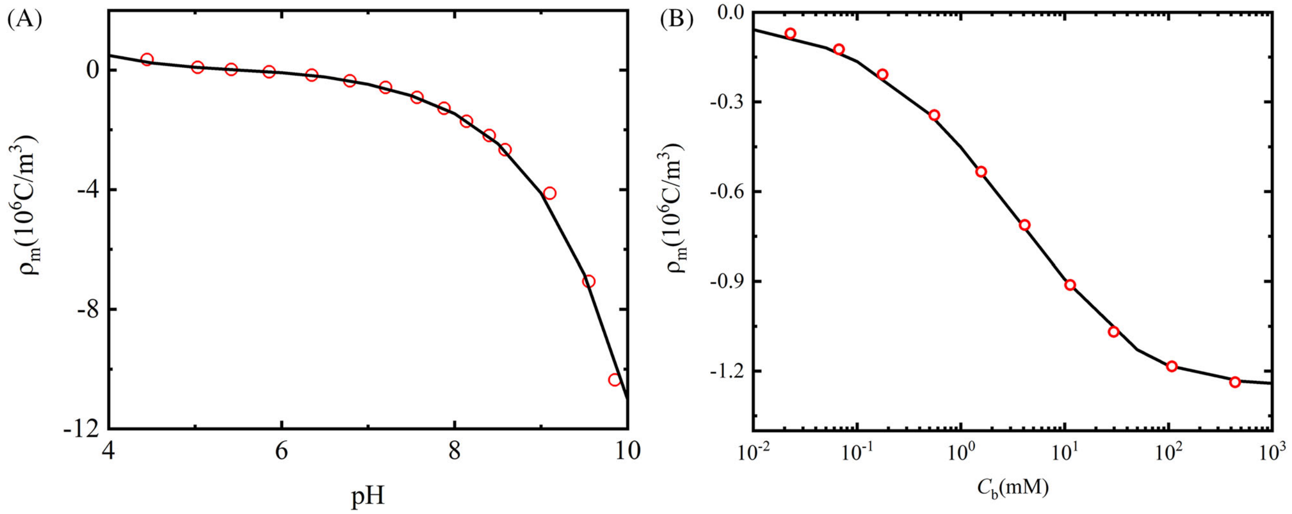

FIGURE 2 The relationship between the volume averaged charge density of a PE brush layer and pH (A). The relationship between the volume-averaged charge density of the PE brush layer and concentration (B). The black line represents our comparison results, and the red hollow circle represents the result of Zhou et al. [5]. PE, polyelectrolyte

[5], $N = 20$, $pK_C = -logK_C = 7.6$, $pK_D = -logK_D = 1.9$, $N_{total} = 8\ \text{sites/nm}^2$ [25], $D_i\ (i = 1, 2, 3, 4) = 9.31 \times 10^{-9}$, 1.96×10^{-9}, 5.30×10^{-9}, $2.03 \times 10^{-9}\ \text{m}^2/\text{s}$, $R = 8.31\text{J}/(\text{mol} \cdot \text{K})$, $T = 298\ \text{K}$, $\varepsilon_0 = 8.854 \times 10^{-12}\text{C/Vm}$, respectively. It should be noted that unless otherwise stated, the following research contents include volume charge density, total charge density, electric field energy density and ion concentration, which are all in the PE brush layer at the bottom of nanoparticles.

In order to verify the mathematical model, a PE brush layer–modified plate was put into the electrolyte solution and the concentration is 1 mol/m^3 (when the nanoparticle radius is large enough, it could be regarded as a plate), and other parameters were consistent. It can be seen in Figure 2, the numerical results of our model (black line) and Ref. [5] (red circle) are in good agreement. Obviously, the mathematical model is reliable.

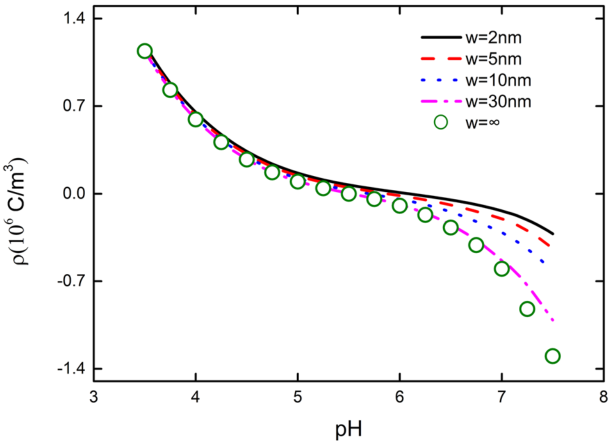

FIGURE 3 The relationship between the pH values and the volume charge densities under different distances between the nanoparticle and silica flat substrate, the concentration of KCl solution is fixed at 1 mol/m^3

3.1 | The effect of pH value on the volume charge density

When the PE brush layer interacts with the silica flat substrate, the solution charge density and H$^+$ concentration inside and outside the PE brush layer will be different, as shown in Figures S2 and S3. It means that the properties of the brush layer will change. By solving the mathematical model, the change law of the volume charge density was obtained when the interaction between the PE brush layer–modified nanoparticles and the silica flat substrate occurred.

Figure 3 shows that the volume charge density first decreases with the increase of pH value. The charge reversal occurs at a specific isoelectric point (IEP) and continues to increase the pH value, and the volume charge density will also increase. The phenomenon is consistent with the previous research [3]. By further observation of Figure 3, a special phenomenon occurs that the IEP shifts under the interaction between the silica flat substrate and nanoparticles. When the distance $w = 2$ nm, the volume charge density decreases to 0 at pH = 6.3, which is the IEP of the black curve. With the increase of the distance between the nanoparticles and the silica flat substrate, the IEP at the bottom of the nanoparticles shifts to the left. When $w = 5$, 10 and 30 nm, the curves reached the IEP at pH = 6.0, 5.8 and 5.55, respectively. In addition, the IEP of the PE brush layer without interaction is pH = 5.5 [2], which is the green

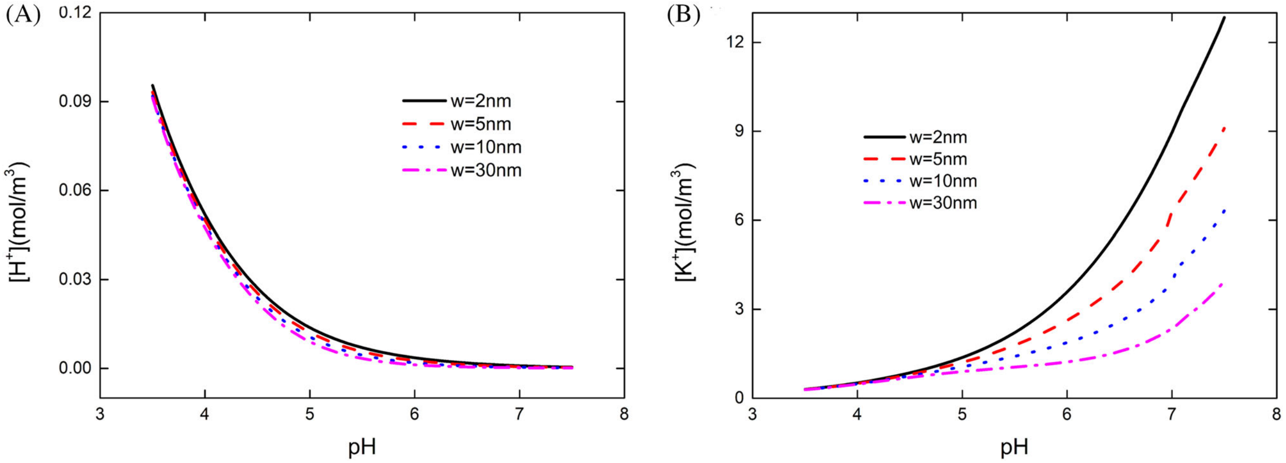

FIGURE 4 The relationship between the pH values and the ion-cation concentrations under different distances between the silica flat substrate and nanoparticles. (A) for H^+ and (B) for K^+

dot line in Figure 3. At the same time, due to the shift of IEP, with the decrease of the distance between the silica flat substrate and nanoparticle, the volume charge density will decrease. These phenomena can provide guidance for the movement of biomacromolecules in silica channels.

As the concentration of H^+ in the PE brush layer can affect the volume charge density, the size of H^+ concentration directly affects the reactions of protonation and deprotonation. The cation concentration diagram is drawn under different distances between the silica flat substrate and nanoparticles, as shown in Figure 4. As shown in Figure 4A, the H^+ concentration will decrease with the increase of the distance between the silica flat and nanoparticle under the same pH value, which means when the distance is small, the IEP of the PE brush layer corresponds to a larger pH value. Figure 4B describes the changes of K^+ concentration. It can be seen that with the decrease of the distance, K^+ is enriched in the PE brush layer at the bottom of the particles. It can even reach 12 times the K^+ concentration in the solution domain when the distance w is 2 nm. When pH > 3, the charge generated by the electric double layer of the silica flat substrate is negative, and with the increase of pH value, the charge will also increase [24, 25]. It is for the reason that when the nanoparticles interact with the silica flat substrate, a large number of cations at the bottom of the particles near the silica substrate are enriched. When the brush layer of the particles is positively charged, this enrichment phenomenon will be slightly weakened. Therefore, the volume charge density, H^+ concentration and K^+ concentration change little with the distances. When the PE brush layer of particles is negative, the enrichment degree of cations will be greatly improved, making the volume charge density, H^+ concentration and K^+ concentration change greatly with the change of distances. H^+ will be repelled by enrichment of K^+ [3], but when the nanoparticles interact with the silica flat substrate, this kind of repulsion almost has no effect so that it can be ignored. This also explains why the smaller the distance, the higher the H^+ concentration in the PE brush layer.

3.2 | The effect of electrolyte solution concentration on the volume charge density

When the interaction between nanoparticles and silica flat substrate occurs, ion enrichment occurs in the gap between nanoparticles and silica flat substrate. The pH value of the solution was fixed at 6.5, and the volume charge density was investigated by changing the concentration of the KCl solution. Figure 5 shows that the concentration of electrolyte solution C_{KCl} is set in the range of 1–100 mol/m^3. When the distance between the particles and silica flat substrate is 2 nm, with the increase of electrolyte solution concentration, the volume charge density increases and finally almost remains stable. When the distances are 5, 10 and 30 nm, with the increase of the electrolyte solution concentration, the volume charge density increases and then decreases, the concentrations at the turning points are 35, 21 and 18 mol/m^3, respectively. The main reason for the previous phenomenon is that the changes in electrolyte solution concentration will affect the H^+ concentration, resulting in the changes in volume charge density in the PE brush layer.

It can be seen from Figure 6 that when w = 5, 10 and 30 nm, corresponding to C_{KCl} = 35, 21 and 18 mol/m^3, the inflection points of H^+ concentration occurs. When pH = 6.5, the silica flat substrate is negatively charged and increases with the increase of electrolyte solution

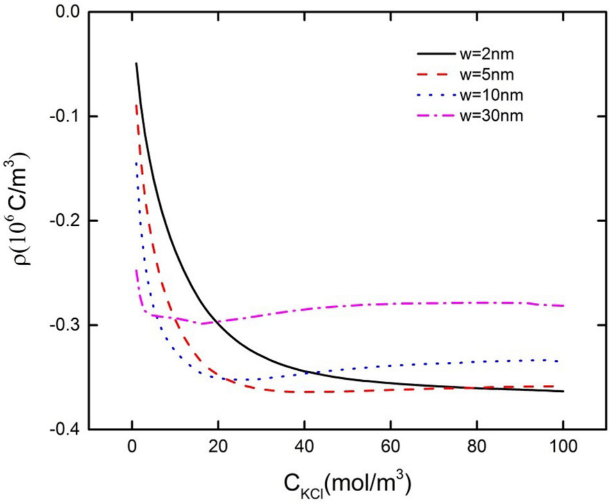

FIGURE 5 The relationship between the concentration of the electrolyte solution and the volume charge densities under different distances between the silica flat substrate and nanoparticles

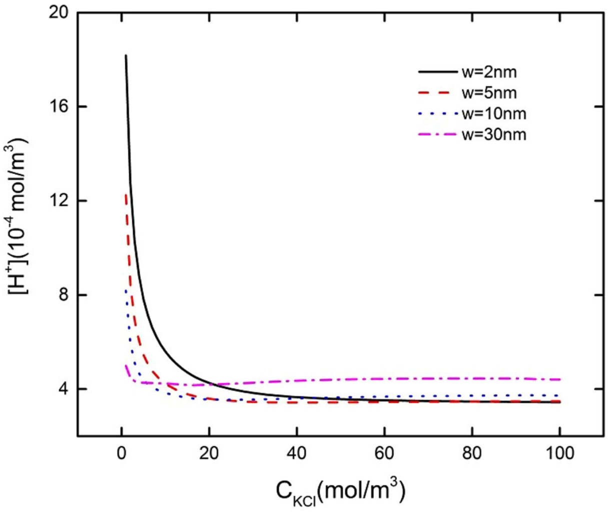

FIGURE 6 The relationship between the KCl solution concentration and H^+ concentration under different distances between the silica flat substrate and nanoparticles

concentration [26]. When $w = 2$, the H+ concentration in the PE brush layer decreases with the increase of the solution concentration due to the attraction of cations by the negatively charged silica flat substrate. When the solution concentration is large enough, the H+ concentration in the PE brush layer remains stable. When $w = 5$, 10 and 30 nm, the interaction between the silica flat substrate and nanoparticles is weakened. With the increase of the solution concentration, the silica flat substrate can attract more cations. But with the increase of K^+ in the solution, the attraction of the silica flat substrate to H^+ decreases. Thus, the PE brush layer can attract more H^+, which means the increase of H^+ concentration in the PE brush layer. The changes in H^+ concentration further explain the changes in the volume charge density in the PE brush layer.

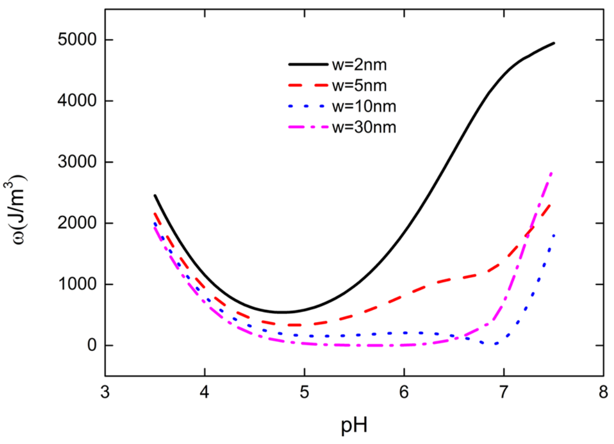

FIGURE 7 The relationship between the pH values and the electric field energy densities under different distances between the silica flat substrate and nanoparticles, and the concentration of KCl solution is fixed at 1 mol/m^3

3.3 | The effect of pH value on the electric field energy density

In order to further understand the interaction between the silica flat substrate and the nanoparticles, the relationship between the electric field energy density and pH value under different distances was studied. Figure 7 shows that under any distance, with the increase of pH value, the electric field energy density first decreases and then increases. The concentration of KCl solution is fixed at 1 mol/m^3. When pH < 6.55, the electric field energy density decreases with the increase of the distance between the silica flat substrate and particles. When pH = 6.55, the curves of $w = 10$ and 30 nm intersect, and the value at the intersection is about 148 J/m^3. When pH = 7.1, the curves of $w = 5$ and 30 nm intersect, and the corresponding electric field energy density is about 1863 J/m^3. By observing Figure 7, it is found that when $w = 10$ and 30 nm, the electric field energy density decreases to 0 at pH = 5.55 and 6.95, indicating that the electric field energy density decreases to 0 at these two points. It can be understood from Equations (17) and (19), the total charge density can affect the electric field energy density efficiently. Therefore, it is also necessary to study the relationship between the total charge density and the pH value under different distances.

It can be seen from Figure 8 that when $w = 2$ or 5 nm, the total charge density is always positive, and it first decreases and then increases with pH value. When $w = 10$ or 30 nm, the total charge density is initially positive, the charge reversal occurs at pH = 5.55 or 6.95, becomes negative,

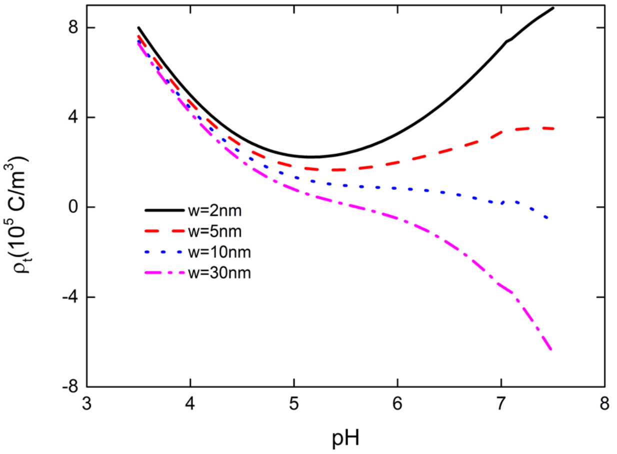

FIGURE 8 The relationship between the pH values and the total charge densities under different distances between the silica flat substrate and nanoparticles

decreases first and then increases with the increase of pH value. At the same time, when pH = 6.55, the number of total charge density of w = 10 nm is equal to that of w = 30 nm, but the polarity is the opposite. When pH = 7.1, the number of total charge density of w = 5 nm is equal to that of w = 30 nm, but the polarity is also the opposite. Because the silica flat substrate is always negative, when the particle is close to the silica flat substrate (such as w = 2 or 5 nm), a large number of cations are enriched in the PE brush layer, resulting in the volume charge density of the brush layer cannot be dominant, so that the total charge density is always positive. When the distance between the particles and the silica substrate is long (such as w = 10 or 30 nm), the interaction between the silica flat substrate and nanoparticle is weakened, the cations in the brush layer are no longer significantly enriched. Consequently, the polarity of the total charge density in the PE brush layer is dominated by the volume charge density. These results explain why the surface cations of biomacromolecules are enriched in silica nanopores.

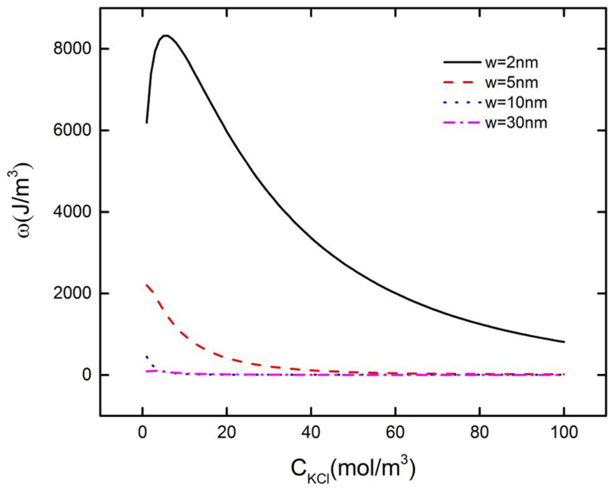

FIGURE 9 The relationship between the concentration of the electrolyte solution and the electric field energy densities under different distances between the silica flat substrate and nanoparticles

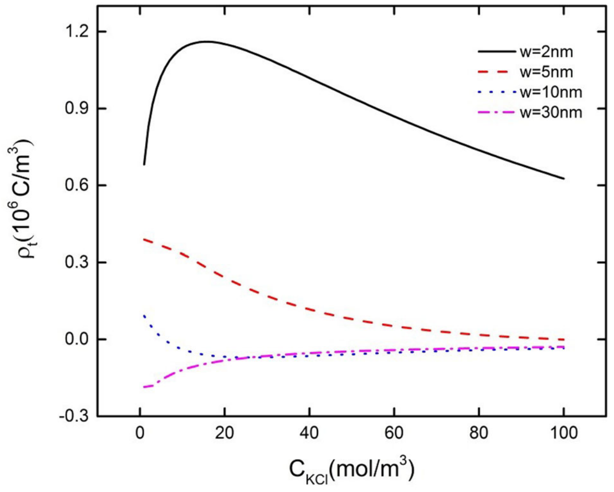

FIGURE 10 The relationship between the KCl solution concentration and the total charge density under different distances between the silica flat substrate and nanoparticles

3.4 | The effect of electrolyte solution concentration on the electric field energy density

Furthermore, the relationship between the electric field energy density and the concentration of the electrolyte solution was investigated when the pH value was fixed at 6.5, and the distance between the silica flat substrate and particles was different. Figure 9 shows that when w = 2 nm, with the increase of electrolyte solution, the electric field energy density first increases and then decreases, reaches the maximum at $C_{KCl} = 6\ mol/m^3$. When w = 5 and 10 nm, with the increase of the concentration of KCl solution, the electric field energy density will decrease and finally reaches a stable value. When w = 30 nm, the electric field energy density is almost unchanged due to the weak interaction between the silica flat substrate and nanoparticle. The relationship between the total charge density and the electrolyte solution concentration was studied to explain the previous phenomenon.

Figure 10 shows that when w = 2 nm, with the increase of the KCl solution concentration, the total charge density first increases and then decreases, reaches its maximum at $C_{KCl} = 6\ mol/m^3$. When w = 5 and 10 nm, with the increase of the KCl solution concentration, the total charge density decreases and finally remains stable. When w = 30 nm, the total charge density increases with the increase of the KCl solution concentration and finally remains stable. The main causes of the previous phenomena are analyzed by combining the Equation (17). When the interaction between the silica flat substrate and particles is strong at low electrolyte solution concentration, the cations in the gap between the nanoparticles and the silica flat substrate are enriched. The volume charge density is small, which leads to the increase of the total charge density with the increase of electrolyte solution concentration. With the increase of the electrolyte solution concentration, the volume charge density increases, which weakens the influence of the cations in the PE brush layer on the total charge density, and finally leads to the decrease of the total charge density with the increase of the electrolyte solution concentration. With the increase of the distance between the particles and the silica flat substrate, the cation enrichment in the gap between the particles and the silica flat substrate decreases. The total charge density is mainly affected by the volume charge density. For example, when w = 30 nm, the total charge will be negative at a low concentration of electrolyte solution.

4 | CONCLUDING REMARKS

When functional group–modified nanoparticles interact with silica flat substrate, the density of volume charge and electric field energy in the PE brush layer will change. The interaction between particles and silica flat substrate at different distances was investigated by controlling the pH value and the concentration of electrolyte solution. It can be seen from the results of this paper : (1) when the interaction between the silica flat substrate and nanoparticle is strong (such as w = 2 or 5 nm), the IEP in the PE brush layers are shifted under the influence of the silica flat substrate, which leads to the shift of IEP when there is no interaction or the interaction is small (such as w = 10 or 30 nm), under the strong interaction, the volume charge density of the PE brush layer can reach the zero point only at a higher pH value. At the same time, under the strong interaction, there will be cation enrichment between the silica flat substrate and nanoparticles, which leads to the decrease of the volume charge density with the increase of the electrolyte solution concentration. (2) When w = 2 or 5 nm, the total charge density is always greater than 0. When w = 10 or 30 nm, the total charge density changes to 0 at pH = 5.55 or 6.95, and charge reversal occurs, which leads to the equal electric field energy density at multiple pH values under different interactions. At the same time, under any intensity of the interaction, with the increase of the pH value, the electric field energy density first decreases and then increases. Under the strong interaction, the total charge density is controlled by the cation in the solution and the volume charge density. With the increase of the distance between the silica flat substrate and nanoparticles, the volume charge density gradually dominates. The previous results can provide guidance for the different motions of particles near the wall and away from the wall in the nanochannel of silica materials and provide ideas for the design of a new nanochannel.

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CONFLICT OF INTEREST

The authors have declared no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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