Gas adsorption behavior of silica photonic crystals with different size of initial particles

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The shift of photonic bandgap could be used to study the adsorption behavior of concentration. However, there are so many issues need to explore in this field, such as adsorption models and influence factors. In this paper, it is found that the size of initial particles has a great impact on the size of silica colloidal spheres and the volume fraction of pore, resulting in the different adsorption behavior on the surface of silica photonic crystals. The effect of initial particle size on colloidal spheres and volume fraction of pore are investigated. Furthermore, the effect of initial particle size on gas adsorption behavior has been discussed by using the volume fraction of adsorption vapor (Vvap). It can be seen that the trends of isopropanol adsorption differ from methanol and ethanol.

Key-words : Photonic crystal, Initial particle, Volume fraction of pore, Volume fraction of adsorption vapor, Photonic bandgap

1. Introduction

Photonic crystals (PCs) are highly ordered dielectric structures with a photonic bandgap (PBG) for electromagnetic waves, a band of frequencies in which light propagation is forbidden.¹ At the past decade, PBG has been reported to respond to external stimuli including temperature,²⁻⁴ humidity,⁵⁻⁹ pH value,¹⁰ mechanical force,¹¹ electrical fields,¹ chemicals¹²⁻²¹ and so on. Thus, PCs are expected to be applied to biological detection, temperature sensor, chemical sensor, and pH meter.²²,²³ The detection mechanism is based on the shift of PBG when PCs are exposed to different surrounding conditions.

So far, there are an increasing number of researchers to carry out the researches about the detection volatile organic compounds (VOCs) and small-molecular gases with low gas concentration by using PBG shifts.²⁴,²⁵ The influence factors, including the types of target gases, the concentration of gas, the chemical composition and morphologies of PCs, have been reported in the recent researches. We found the silica colloidal spheres are composed of initial particles by aggregation to decrease the surface free energy. The silica PCs with different initial particle size would exhibit different gas adsorption behavior, which has not been reported.

In this work, the silica PCs with different size of initial particles were obtained. The effect of initial particle size (Si) on the size of colloidal spheres (D) and the volume fraction of pore (Vpore) is discussed. The volume fraction of adsorption vapor (Vvap) is deduced from PBG shift. According to Replacing model proposed by our former publication,²⁶ capillary condensation and surface adsorption on colloidal spheres are employed to explain the effect of Si on the adsorption behavior of three alcohol vapor (methanol, ethanol, and isopropanol).

2. Experimental

2.1 Synthesis of silica particles with different sizes

In a typical synthesis, absolute ethanol (25 mL) dissolved in 20 mL of deionized (DI) water was added to varying concentration (1.73, 2.02, 2.31, 2.60, 2.88 mol/L) of ammonia with stirring for 10 min in the water bath at 40°C. The resulting transparent mixture was labelled as solution A. 12 mL tetraethoxysilane dissolved in 8 mL of absolute ethanol was dripped into solution A with fiercely stirring for 12 h in water bath at 40°C. The resulting solution of products was left undisturbed at room temperature (25°C) for 5 h in order to volatilize the residual ammonia. The resulting silica particles were washed three times with absolute ethanol upon centrifugation at 4,000 r.p.m. Then the white powder of silica particles was dried in an oven at 40°C.

2.2 Self-assembly of silica PCs

0.2 g silica powder was dispersed in 25 mL of absolute ethanol with ultrasound for 2 h to form silica suspension.
Two close clean substrates were vertically placed in the suspension, leading to the suspension sucked in between the two substrates. The silica PCs were obtained on the substrates when the dispersed ethanol was completely evaporated at 40°C. The double-substrate method combines capillarity and vertical deposition between two parallel substrates. These kinds of silica PCs were applied to characterize the scanning electron microscopy (SEM) images and X-ray diffraction (XRD) spectra.

2.3 Measurement of gas sensing performance
The custom vapor chamber based on cuvette was designed and assembled, which was comprised of a glass cuvette [used for ultraviolet–visual (UV–Vis) spectroscopy] stuck to substrate growth of silica PCs on the inner wall, a rubber sealing, a gas inlet and a gas outlet. As reference gas, nitrogen was injected through inlet before measuring gas sensing performance. After the transmittance spectrum of PCs kept constant, the target gas (methanol, ethanol, and isopropanol) with the concentration range from 1 ppb to 100 ppm was injected into the chamber. After reaching the adsorption equilibrium state, the reference gas was injected into the chamber again. During the adsorption–desorption process, the transmittance spectra were recorded at intervals.

3. Results and discussion
3.1 Different morphologies of silica PCs
Silica spherical particles were synthesized by Stöber method.27,28 A series of different particle size of silica spheres were obtained by controlling the concentration of ammonia during the synthesis process. The silica particles with sizes ranging from 235 ± 3 to 285 ± 5 nm were synthesized (shown as Fig. S1) by controlling the concentration of ammonia from 1.73 to 2.88 mol/L. The high-resolution SEM investigation shows that as-prepared silica spheres are composed of so many tiny-size initial particles [shown as Fig. 1(a)]. Certainly, the same phenomenon can be observed in other silica spheres with different particle size (Fig. S1). The XRD patterns with different silica samples were shown in Fig. 1(b) and Fig. S1. From the XRD patterns, it can be seen that the sole diffraction peak coincided with the JCPDS card (No. 29-0085) of amorphous silica. According to Scherrer equation, the sizes of initial particles with different silica samples were calculated. The results are listed in Table 1. It is indicated that the particle size of silica colloidal spheres will change with the size of initial particle size.

In order to explore the relationship between sphere size and initial particle size, the nitrogen physical sorption of different silica samples was measured (as shown in Fig. S2). The measured Brunauer–Emmett–Teller (BET) surface area and pore volume of silica with different particle size were used to calculate the volume fraction of pore ($V_{\text{pore}}$). According to the introduction of calculation method in Supporting Information, $V_{\text{pore}}$ of silica with different sphere size were obtained (shown in Table 1). From the results in Table 1, the size of initial particle ($S_{\text{in}}$) seems to have effect on the size of silica spheres ($D$) and volume fraction of pore ($V_{\text{pore}}$). The plots based on the relationship among $D$, $V_{\text{pore}}$ and $S_{\text{in}}$ are exhibited in Fig. 2. With the increasing of the size of initial particles, the trends of $D$ and $V_{\text{pore}}$ are almost opposite. Due to the high surface free energy, the initial particles are likely to aggregate to form the second particle (namely silica colloidal spheres) to decrease the surface free energy. Furthermore, with decreasing the size of initial particles, the agglomeration phenomena are obvious. From Fig. 2, when the size of initial particles smaller than 1.327 nm, the aggregation of initial particles resulted in the increase of size of colloidal

| Initial particle size, $S_{\text{in}}$ (nm)* | Silica sphere size, $D$ (nm)* | $V_{\text{pore}}$ (%)* |
|-----------------------------------------|-------------------------------|---------------------|
| 1.317                                   | 265                           | 6.05                |
| 1.327                                   | 275                           | 6.61                |
| 1.339                                   | 245                           | 8.29                |
| 1.410                                   | 235                           | 8.00                |
| 1.572                                   | 285                           | 5.27                |

*Measured from XRD. *Measured from SEM images. *Calculated from BET.
When the size of initial particles increases in range from 1.327 to 1.410 nm, the size of colloidal spheres decreases. The possible reason is that the surface free energy of initial particles decreases with increasing of initial particle size. It could decrease the free energy of system by aggregation of initial particles to a certain extent. Therefore, the number of initial particles involved in agglomeration is less than the smaller size of initial particles so that the size of colloidal spheres tends to reduce. When the size of initial particles increases in range from 1.410 to 1.572 nm, by reason of the great increasing of initial particle size, the colloidal particles grow larger due to agglomeration of initial particles. Thus, it can be seen that the size of initial particles has a great impact on the colloidal spheres size. However, the size of silica colloidal spheres seems to have greatly influenced the volume fraction of pore. According to Fig. 2, it can be observed that the $V_{\text{pore}}$ increases with the decreasing of silica spheres size, while it decreases with the increasing of colloidal spheres size. The $V_{\text{pore}}$ mainly depends on the specific surface area of colloidal spheres. The colloidal spheres with small particle size have high specific surface area, resulting in large volume fraction of pore.

3.2 Gas adsorption performance of silica PCs

From the SEM images (Fig. 1 and Fig. S1), the silica spheres are ordered along the three directions of space. It indicates that the silica spheres are arranged in a close-packed face-centered-cubic (fcc) structure. The structure of hexagonal alignment has been formed which corresponds to (111) plane of fcc.29,30

Figure S3 presents transmittance spectra of PCs recorded from silica spheres with the range of size from 235 to 285 nm. These spectra were measured using UV–Vis spectrophotometry at normal incidence ($\theta = 0^\circ$). A clear band in the optical transmittance spectrum is observed, which is attributed to the PBG in the (111) plane of fcc. The transmittance spectra also show the Bragg reflection spectral position scales with particle size; the Bragg reflection shifts linearly towards shorter wavelengths at smaller particle sizes (shown inset of Fig. S3). It is the major characteristics of PCs. According to the Bragg-Snell law, due to fcc (111) planes of silica PCs paralleling to substrate, central wavelength of PBG ($\lambda_c$) shifts linearly along silica particle size ($D$) as Eq. (1):

$$\lambda_c = 2\sqrt{\frac{2}{3}}n_{\text{eff}}D$$  

(1)

where $n_{\text{eff}}$ is the effective refractive index of silica PCs, $D$ is the diameter of silica colloidal spheres. The experimental results agree with the Bragg-Snell law. It indicates that the central wavelength of PBG can be controlled by the size of colloidal spheres. PBG is expected to respond differently to the environment due to the different size of initial particles.

In order to investigate the behavior of gas adsorption on the surface of silica PCs with different initial particle size, three kinds of alcohol vapor (methanol, ethanol, and isopropanol) with concentration from 1 ppb to 100 ppm were used as target gases. The transmittance spectra were applied to explore the sensing behavior of silica PCs in different target gases. Therefore, the relationship between central wavelength of PBG and adsorption–desorption time was obtained (shown as Figs. S4–S6). No matter what kind of target gases were altered, the PBG of silica PCs with different initial particle size had a redshift when the silica PCs were exposed to target gas with different concentration. When the reference gas was injected into the vapor chamber, the PBG had a blueshift. According to the reports13),29), the replacement of reference gas with target gas molecules in the pores changes the refractive index of PCs, causing redshift of the PBG. Thus, the difference of PBG at the initial state (when reference gas reached the equilibrium adsorption state on the surface of silica PCs) and at saturated adsorption state (when sensing gas reached the saturated adsorption state on the surface of silica PCs) would provide some information about adsorption behavior of target gas on the surface of silica PCs.

Strictly speaking, the amount of redshift of PBG ($\Delta \lambda$) is the qualitative explanation of effect of gas adsorption on light transmission in silica PCs. It could not quantitatively explain the gas adsorption on the surface of silica PCs. $\Delta \lambda$ only exhibits the value of difference between PBG at initial state and final state, which cannot offer enough information about the effect of types of target gases on adsorption behavior on the surface of PCs. Therefore, in this work, the redshift of PBG was transformed into volume fraction of adsorbed gas ($V_{\text{vap}}$), which represents the amount of gas adsorption in silica PCs.

3.3 The effect of initial particle size on gas adsorption performance of silica PCs

According to our earlier results,26) the adsorption behavior of VOCs vapor on silica PCs follows the Replacing model. In Replacing model, VOCs vapors are more likely to condensate in the interstitials between silica spheres to exhibit liquid–vapor menisci, not only simple adsorption on the surface of silica.
When the silica PCs exposure to reference gas, the effective refractive index at the initial state can be calculated using the Eq. (2) as following:

$$n_{\text{eff,0}} = \sqrt{n_{\text{SiO}_2}^2 V_{\text{SiO}_2} + n_{\text{ref}}^2 V_{\text{pore}}}$$  \hspace{1cm} (2)$$

where $V_{\text{SiO}_2}$ is the volume fraction of silica, $V_{\text{pore}}$ is the volume fraction of pore, $n_{\text{SiO}_2}$ and $n_{\text{ref}}$ are the refractive index of the silica and reference gas, respectively.

When the silica PCs are exposed to target gas, the effective refractive index at some point can be calculated using the Eq. (3):

$$n_{\text{eff}} = \sqrt{n_{\text{SiO}_2}^2 V_{\text{SiO}_2} + (V_{\text{pore}} - V_{\text{vap}}) n_{\text{ref}}^2 + V_{\text{vap}} n_{\text{vap}}^2}$$  \hspace{1cm} (3)$$

where $V_{\text{vap}}$ is the volume fraction of adsorption target vapor at some point, $n_{\text{vap}}$ is the refractive index of target vapor.

According to the Eqs. (1)-(3), the volume fraction of adsorption target vapor ($V_{\text{vap}}$) can be calculated by Eq. (4):

$$V_{\text{vap}} = \frac{n_{\text{eff}}^2 - n_{\text{eff,0}}^2}{n_{\text{vap}}^2 - n_{\text{ref}}^2} = \frac{(\lambda^1_{\text{c}})^2 - (\lambda^0_{\text{c}})^2}{8 D^2(n_{\text{vap}}^2 - n_{\text{ref}}^2)}$$  \hspace{1cm} (4)$$

where $\lambda^0_{\text{c}}$ and $\lambda^1_{\text{c}}$ are the central wavelength of PBG at the initial state and at some point, respectively.

As shown in Eq. (4), the amount of gas adsorption can be calculated by using the central wavelength of PBG at the initial and final state. Moreover, the volume fraction of adsorption vapor ($V_{\text{vap}}$) is taken into account the differences of refractive index of target gas and reference gas in

Eq. (4). Therefore, it can quantitatively describe the differences of gas adsorption on the surface of silica PCs.

The effect of initial particle size ($S_{\text{in}}$) on adsorption behavior of target gas has been investigated (shown in Fig. 3). Methanol and ethanol vapors have the similar adsorption rules [Figs. 3(a) and 3(b)]. When $S_{\text{in}}$ increases from 1.317 to 1.327 nm, the size of colloidal spheres ($D$) increases due to aggregate of initial particles; while the volume fraction of pore ($V_{\text{pore}}$) increases from 6.05 to 6.61%, resulting in weak capillary condensation because of the increase of the space among silica spheres at this stage. The gas adsorption on the surface of colloidal spheres increases with the increasing of colloidal sphere size. Since the decrement of capillary condensation is small, the $V_{\text{vap}}$ tends to increase at this stage. When $S_{\text{in}}$ increases from 1.327 to 1.339 nm, $D$ decreases due to decreasing of degree of aggregation; while $V_{\text{pore}}$ increases from 6.61 to 8.29%, leading to greatly decrease of capillary condensation. Thus, the $V_{\text{vap}}$ decreases at this stage. When $S_{\text{in}}$ increases from 1.339 to 1.410 nm, both $D$ and $V_{\text{pore}}$ decrease. The increasing of exposure effective surface area of colloidal spheres contributes to enhance the gas adsorption. Furthermore, the decrease of $V_{\text{pore}}$ is of great benefit to capillary condensation in the space among colloidal spheres. Therefore, the $V_{\text{vap}}$ increases remarkably at this stage. When $S_{\text{in}}$ increases from 1.410 to 1.527 nm, $D$ increases and $V_{\text{pore}}$ decreases, resulting in closely arrangement and decreasing of exposure effective surface area of colloidal spheres. However, the capillary condensation is obvious because of the decreasing of $V_{\text{pore}}$. Thus,
the $V_{\text{vap}}$ tends to slightly decrease. The summary of the results for adsorption of methanol and ethanol is listed in Table S1.

From Fig. 3(c), the behavior of isopropanol adsorption volume ($V_{\text{vap}}$) is very different from methanol or ethanol vapor. When $S_{\text{in}}$ increases from 1.327 to 1.339 nm, the $V_{\text{vap}}$ increases instead of decrease. The possible reason is that at the room temperature, the saturated vapor pressure of methanol, ethanol and isopropanol are 13.33, 8.00, and 5.87 kPa, respectively. Thus, isopropanol is more likely to happen capillary condensation compared to other two target gases. At this stage, the decrement of capillary condensation of isopropanol is smaller than methanol and ethanol. Therefore, the $V_{\text{vap}}$ trends to increase at this stage. When $S_{\text{in}}$ increases from 1.410 to 1.527 nm, the $V_{\text{vap}}$ decreases greatly, which is very different from methanol or ethanol. At this stage, the adsorption on the surface of colloidal spheres decreases and capillary condensation increases. But the increment of capillary condensation of isopropanol is smaller than methanol and ethanol. Thus, the $V_{\text{vap}}$ exhibits the significant reductions at this stage. The summary of the results for adsorption of isopropanol is listed in Table S2.

4. Conclusions

Silica colloidal spheres with different initial particle size have been obtained by controlling the concentration of ammonia. It is found that the size of initial particles has a significant impact on the size of colloidal spheres and volume fraction of pore. The volume fraction of adsorbed vapor ($V_{\text{vap}}$) is applied to quantitatively describe the adsorption behavior of target gases. The $V_{\text{vap}}$ for different VOCs vapors changes with size of initial particles. The change trends of $V_{\text{vap}}$ for methanol and ethanol are exactly similar. The change tendency of $V_{\text{vap}}$ for isopropanol is very different from the other vapors due to their different saturated vapor pressure, resulting in different capillary condensation in the space among silica colloidal spheres. The results demonstrate that the size of initial particles can produce great impact on the adsorption behavior on the surface of colloidal spheres by influencing the size of colloidal spheres and volume fraction of pore.

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