Vibrational features of confined water in nanoporous TiO_2 by Raman spectra*

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Raman spectra of confined water adsorbed in nanoporous TiO_2 are obtained in experiment. TiO_2 samples with different pore diameters under different humidity conditions are investigated. The results indicate that the symmetric vibrational mode of water molecule is destroyed when relative humidity decreases. This indicates that the interaction between water molecules and surface of TiO_2 becomes stronger when the distance between water molecules and surface turns smaller, and the interaction plays a major role in depressing the symmetric vibrational peak. The spectra of confined water in TiO_2 and Vycor are compared. When filling fractions are the same, their spectra show distinctions no matter whether they are in partial filling condition or in full filling condition. The spectra of HDO confined in TiO_2 with different filling fractions are compared with each other. There is no clear distinction among their vibrational peaks, and the peaks mainly relate to asymmetric vibration. Therefore, the interaction between water molecules and the wall of pore decouples the symmetric vibrational mode only, and the influences on asymmetric vibrational mode show little differences among different filling fractions.

Keywords: porous titanium dioxide, confined water, Raman spectrum, asymmetric vibration

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1. Introduction

Water is the most abundant and common fluid in nature, and it is closely related to most natural phenomena and our life. Confined water has attracted considerable attention due to its significance in many fields of science, including biology,[1–3] nanofluidic devices,[4–9] geology,[10] etc. There are so much work on confined water in porous materials such as zeolite,[11–13] Vycor,[14,15] carbon nanotube,[16–26] etc. Physical characteristics of nanoconfined water is related to material, pore size, shape of wall, and chemical properties of surface, so the structure and dynamics differ from those of the bulk water.[27–33]

Titanium dioxide is a kind of functional material which is used in many areas, such as heterogeneous catalysis,[34,35] solar cell,[36] gas sensor,[37–39] white pigment, and it is also used as bone implants[40] because of its great biocompatibility. Almost all applications are based on the surface properties of titanium dioxide so that the surface science of titanium dioxide has become a hot spot in surface science researches in the last decades.[41] Especially, the water interacting with surface of titanium dioxide has been studied widely because many applications are related to this interaction.[42] Though a great deal of work has been done on the interaction between water molecules and surface of titanium dioxide, most of which are studied in vacuum condition, there are few reports on confined water in porous titanium dioxide. In many cases such as catalysis, porous titanium dioxide has been used to enlarge the interface between water and titanium dioxide.[43–45] Besides surface properties of substrate, it is essential to study the structure and dynamics of water molecules in porous titanium dioxide with considering other factors such as pore size or filling fraction of water as well.

The vibrational dynamics of water molecules can be measured by Raman spectroscopy,[46,47] and this method has been used widely to study the confined water in porous materials as well.[15,48–50] The relative intensities of Raman shift from different modes of vibration will change when water molecule adsorption happens in different environment. Most of these relevant researches focus on the substrate of silica. However, there is little work on studying the substrate of titanium dioxide. It is hard to realize appreciable signal-noise ratio of Raman spectrum, because the fluorescence background is so intensive that the background almost shields the Raman signal of water. Researchers choose deuteroxide D_2O to decouple the mode of symmetric vibration so that different modes of vibration can be analyzed separately.[47,51–54] In order to reveal the influences caused by filling fraction and pore size, D_2O is used to decouple symmetric vibration in this work.

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2. Experiment

In this work, three samples of porous titanium dioxide with different diameters(Sachtopore®-NP, ZirChrom Separations, Inc.) are used as porous absorbents. These porous materials are produced as chromatographic packing material, and they each have a great chemical stability and adsorption selectivity. The chemical purity of each of all the samples is 99.99%. The average diameters for three samples are 60 Å, 100 Å, and 300 Å separately, and they are denoted as S1, S2, and S3. The physical parameters of all samples are shown in Table 1. The samples are composed of 100% crystalline structure, and small angle x ray diffractions of these samples of porous titanium dioxide are shown in Fig. 1. From Fig. 1, it can be found that they are almost of anatase structure, and only a small quantity of rutile structure exists in S3.

Table 1. Physical parameters of the samples.

Sample	S1	S2	S3	S4
Substrate	TiO_2	TiO_2	TiO_2	Vycor glass
Pore diameter/Å	60	100	300	69
Specific surface area/(m^2/g)	100	55	15	130
Specific pore volume/(ml/g)	0.2	0.21	0.12	0.28

The Raman spectrum of water confined in Vycor porous glass (Corning Vycor®, code 7930) is used to compare with spectra of water in titanium dioxide samples. The average diameter of this Vycor glass is 69 Å, and specific surface area is 130 m^2/g. Vycor glass is comprised of SiO_2, B_2O_3, and Na_2O, and is produced by quenching and subsequent acid leaching. Unlike the sample of titanium dioxide, Vycor glass has an amorphous structure, and the concentrations of these three components are about 96%, 3%, and 0.4% respectively. Therefore, Vycor glass can be considered as a silica-based porous material which is denoted as S4 in our experiment.

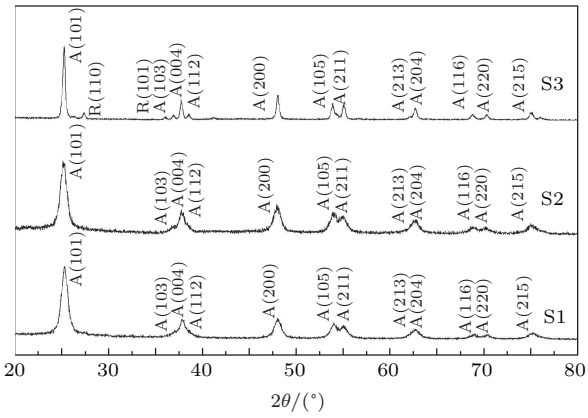


Fig. 1. XRD spectra of S1, S2, and S3, where A and R represent anatase and rutile respectively.

A method of using saturated salt solution to control relative humidity is adopted. The saturated vapor of each kind of saturated salt solution has special relative humidity at a certain temperature. The typical salts used in this work are bought from Jinke institute of fine chemical industry and the corresponding humidity values of saturated solutions are shown in Table 2.

The weight m_1 values of dry samples are measured by an analytical balance of Mettler AE240 with a sensitivity of 0.01 mg, then the dry samples are placed in adsorption box where the humidity is adjusted to some fixed value by corresponding saturated salt solution. This should be kept for 2 days to ensure that the adsorption reaches equilibrium. After the adsorption reaches equilibrium, the weight m_2 values of the samples are measured. When the weight m_3 values of the samples filled fully with water are measured finally, the corresponding filling fraction of water at each relative humidity can be written as

$$\phi = \frac{m_2 - m_1}{m_3 - m_1}. \tag{1}$$

It should be noticed that the fully filled case is not obtained in the 100% relative humidity, because there is free water on the outer surfaces of sample particles in this case. Furthermore, the surface water and water bridge between sample particles in the condition of 100% relative humidity can be observed even by naked eyes. Therefore, the filling fraction will be larger than 100% when the relative humidity reaches 100%. In this work, we think that the fully filled case is realized by absorbing in the saturated vapor humidity of saturated K_2SO_4 solution. This humidity is 97.6% at 20 °C which is very close to 100%, while there is observed no obvious free water existing even by DSC measurement. The samples reaching adsorption equilibrium are sealed into a specially designed sample cell which is made of stainless steel and can be sealed by a packing washer to prevent the confined water from evaporating. There is a slice of fused quartz glass with a thickness of 0.3 mm as optical window in the cell in order that the laser can penetrate in and scattering light can radiate out through the quartz glass window.

A Jobin Yvon T64000 Raman system is used to measure Raman scattering spectra of samples in the experiment, and wavelength of the laser is 532 nm. The laser with a power of 1 mW is focused on sample surface through the fused quartz window with a ×50 long focus objective. The integration time is set to be 140 ms per point with a spectral resolution of 1.4 cm^{-1}. All samples are prepared and measured at about 20 °C.

Table 2. Relative humidity values of different saturated salt solutions at 20 °C.

Salts	CsF	LiBr	LiCl	CH_3COOK	$MgCl_2$	K_2CO_3	NaBr	KI	NaCl	KCl	K_2SO_4
Relative humidity/%	3.8±1.1	6.6±0.6	12	23.1±0.3	33.1±0.2	43.2±0.4	59.1±0.5	69.9±0.3	75.5±0.2	85.1±0.3	97.6±0.6

3. Results and discussion

Figure 2 shows the dependences of filling fraction of samples S1, S2, and S3 on relative humidity. The 100% filling fraction means that the pores are filled completely. As mentioned in Section 2, the fully filled case is defined as absorbing in the saturated vapor humidity of saturated K_2SO_4 solution in which case the humidity is 97.6% at 20 °C. It can be found that the changes of Raman intensity for three samples are not identical, but different especially in the cases with relative humidity values ranging from 40% to 100%. The relative humidity rapidly increasing up to a value larger than 70% may be caused by the capillary condensation.

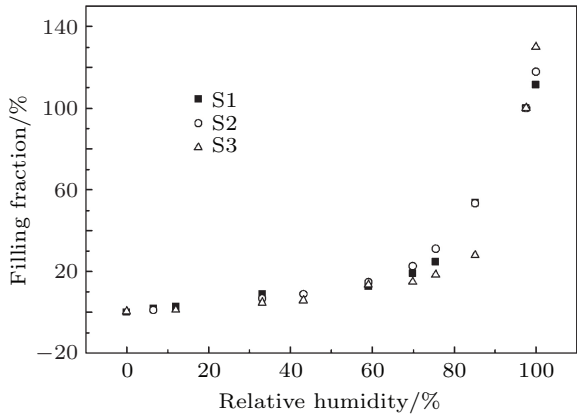


Fig. 2. Plots of filling fraction versus relative humidity for samples S1, S2, and S3.

The Raman spectra of samples S1, S2, and S3 normalized by peak intensity are shown in Fig. 3. As mentioned above, the filling fraction larger than 100% corresponds to the case of absorbing in saturated vapor of pure water because of the assumption of fully filled case. The weak peaks near 2900 cm^{-1} correspond to the character peak of C–H bond which comes from the organic residuals in samples.[55] Larger the filling fraction, the weaker the Raman peak at 2900 cm^{-1} is. For all these three samples as shown in Fig. 3, the obvious trend can be found that the mode of symmetric vibration peaks near 3200 cm^{-1} or less when the filling fraction decreases. For S3, there are no data for the case with filling fraction ranging from 30% to 100% because the filling fraction falls down so rapidly in this humidity range that no salt solution can be used in this experiment to obtain corresponding humidity, which can be found from Fig. 2 as well.

For the cases with lower filling fractions, the Raman spectra mainly indicate the vibrational information of water molecules near the interface of the substrate where the titanium dioxide substrate affects features of water molecule strongly. This indicates that the main action of the substrate is to weaken the symmetric vibration of H–O–H, so the asymmetric vibration dominates for the cases with lower filling fractions. For S3, when filling fraction is lower than 30%, the symmetric vibrational peak nearly vanishes, and there are little differences among the cases with filling fractions lower than 30%. However, there are still apparent peaks existing for S2 until its filling fraction is lower than 20%. For S1, even the filling fraction is lowered to 20%, the component of symmetric vibration in Raman peak still exists, and it vanishes mostly only when the filling fraction reaches 10%.

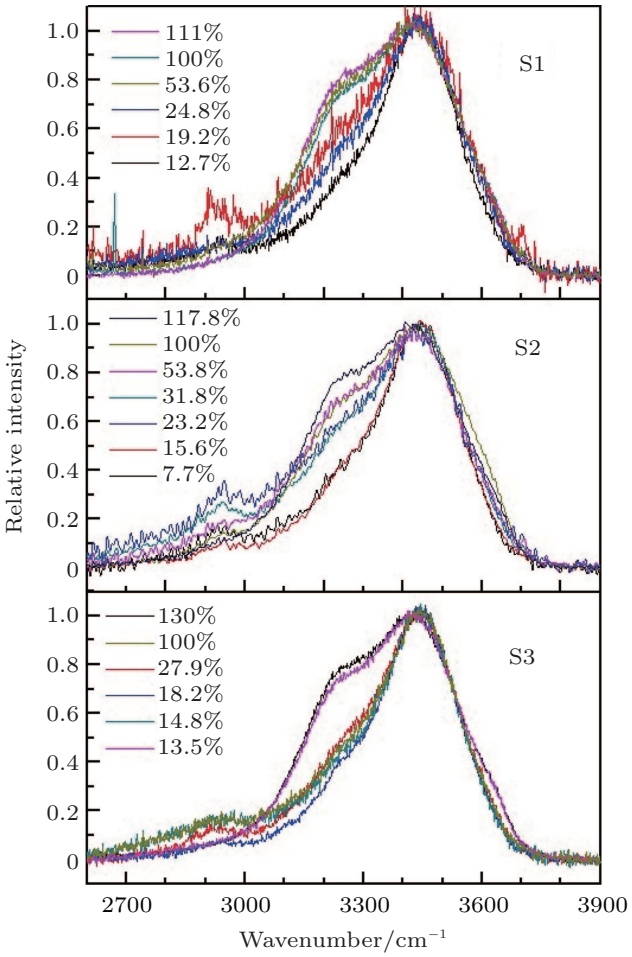


Fig. 3. (color online) Comparisons of stretching band of water adsorbed in S1, S2, and S3 among different filling fractions.

In order to ascertain the influence caused by interface of the substrate materials, the Raman peaks of water in both porous titanium dioxide and silicon dioxide are compared in Fig. 4. Here we choose S2 which has a similar pore size to S4 to compare its Raman spectrum with that of S4 of silicon dioxide.

In Figs. 4(a)–4(c), the filling fractions of water are nearly equal. It can be seen that the Raman peaks from water in S2 and S4 are distinct especially when the lower filling fraction occurs. Though the distinction turns smaller and smaller with filling fractionincreasing, it still exists even though the filling fraction reaches 100%. The Raman peaks are also different from that obtained from bulk water in the case with 100% filling fraction. This indicates that the vibrational features of water confined in nanoporous material depend on not only pore

size, but also elements of material. The lower symmetric vibrational peak of water in TiO_2 also shows that the stronger interaction occurs at the interface of TiO_2, which may be caused by dissociative adsorption of water molecule on the surface of TiO_2.[42,56–59]

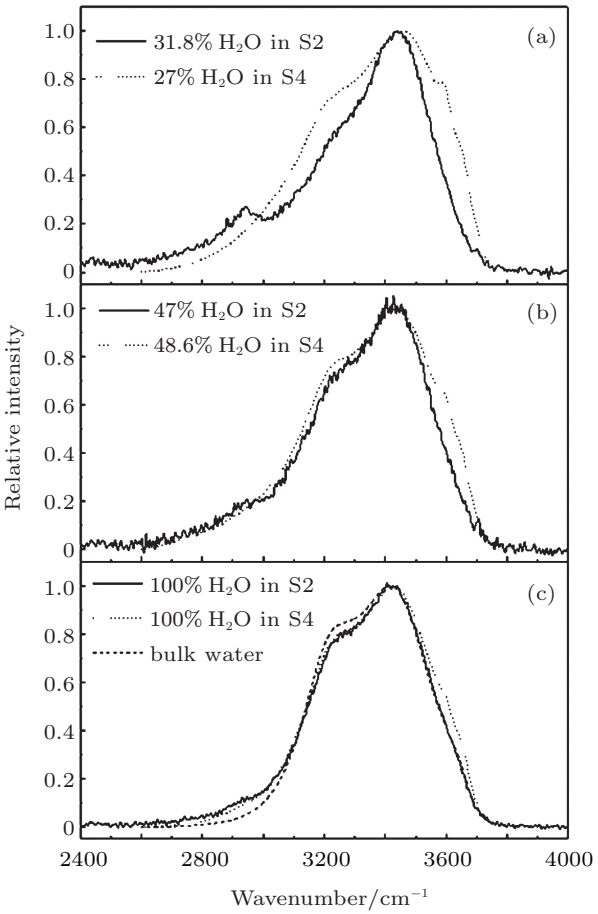


Fig. 4. Comparisons among the stretching bands of H_2O adsorbed in S2 and S4 with similar filling fractions.

To further study the influence caused by TiO_2, D_2O is used to decouple the bond of H–O–H,[47,51–54] so that we can confirm whether the TiO_2 has an influence on the asymmetric vibration of water molecule. When D_2O and H_2O are mixed together, a dynamic equilibrium can be realized according to the following chemical equation:

$$H_2O + D_2O \rightleftharpoons 2HDO. \tag{2}$$

Based on the following equation:

$$K = \frac{[HDO]^2}{[D_2O]\,[H_2O]}, \tag{3}$$

the equilibrium constant equals 4 approximately.[60] The latest result shows the equilibrium constant is 3.86.[61] The mixture with a volume fraction ratio of 9:1 between D_2O and H_2O is used. When equilibrium is reached, the mixture composed of only D_2O and HDO is taken, and the fraction of H_2O is taken to be nearly zero. The vibrational peaks of D–O and D–O–D correspond to Raman shift at about 2600 cm^{-1}, therefore there is no influence on detecting the peak of H–O at about 3450 cm^{-1}. Subsequently the S1 samples with different filling fractions are prepared by this mixture, and the Raman spectra are shown in Fig. 5.

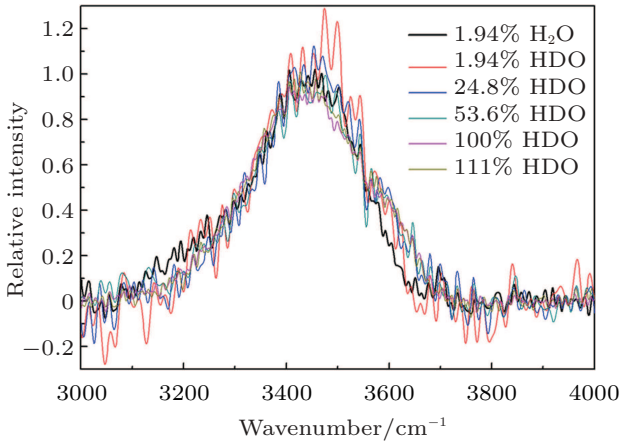


Fig. 5. (color online) Raman spectra of HDO with different filling fractions in S1.

Because there exists only a small fraction of HDO in the mixture we prepared, single-noise ratio of Raman peak of H–O is poor, but we can still compare the results well as shown in Fig. 5. It can be found that there is almost no difference among the cases with different filling fractions. The result of the case with very low filling fraction of H_2O is also shown in Fig. 5, and it accords very well with the results of the cases absorbing H–D–O. This indicates further that the interface destroys the symmetric vibration of H–O–H, and has little influence on the asymmetric vibration of H–O.

4. Conclusions

Confined water absorbed in nanoporous materials such as TiO_2 and SiO_2 is realized by the method of saturated vapor of saturated salt solution in this work. Based on Raman measurements, the vibrations of water molecule confined in nanoporous materials are studied in detail, and the results show that the features of confined water are very different from those of bulk water. The main conclusions can be obtained as follow.

(i) Absorbing isotherms of water in porous TiO_2 materials with different pore sizes are not the same, especially when the relative humidity is larger than 40%.

(ii) The vibrational peaks of water molecule in TiO_2 samples with different pore sizes have the same changing trend with filling fraction of water. When the filling fraction lowers, the symmetric vibrational peak of water at about 3200 cm^{-1} turns weaker. For the case with the same low filling fraction in porous TiO_2 with different pore sizes, the symmetric vibrational peaks have different intensities. Thereof, it can be concluded that both pore size and filling fraction of water can exert an influence on the symmetric vibration of water.

(iii) There is a distinct difference between confined water in porous TiO_2 and that in porous SiO_2, which indicates that the vibrational features of confined water depend strongly on the substrate material. TiO_2 surface can destroy the symmetric vibrational mode of water more strongly, which may correspond to dissociative absorption of water molecules on the interface of TiO_2.

(iv) The asymmetric vibrational peaks of H–O, which are measured by adsorbing HDO to decouple the H–O–H symmetric vibration, show no difference, so the substrate of TiO_2 affects only the symmetric vibration of water, rather than asymmetric vibration.

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