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Effect of hydrogenation on the microwave absorption properties of BaTiO₃ nanoparticles[†]

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Microwave absorbing materials (MAMs) have numerous important applications in electronic communications, signal protection, radar dodging, *etc.* Although it has been proposed as a promising MAM, $BaTiO_3$ has a high reflection coefficient at the interface with air, causing a large reflection. Thus, its efficiency of microwave absorption is not satisfactory. Here, we report that hydrogenation has largely improved the microwave absorption of $BaTiO_3$ nanoparticles. Hydrogenation is performed on $BaTiO_3$ nanoparticles by treating pristine $BaTiO_3$ nanoparticles at 700 °C for 4 hours in a pure H₂ environment. The enhanced microwave absorption efficiency with a reflection loss value (-36.9 dB) is attributed to the increased resonance of polar rotations with the incident electromagnetic field which is amplified by the increased interfacial polarization caused by the built-in electrical field along the boundaries between different grains created within these nanoparticles.

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Introduction

Microwave absorbing materials (MAMs) play important roles in electronic communications, signal protection, radar dodging, etc.1-4 Traditional mechanisms for microwave absorption include dipole rotation and ferromagnetic resonance due to the alignment of the polar groups or the strongly interacting electron spins to the electromagnetic field in the microwave field.1-4 The main-stream MAMs investigated so far are carboneous materials⁵⁻⁹ and ceramic ferroelectrics such as barium titanate,^{4,10-13} lead zirconate titanate,⁴ ferrites and ferromagnetic materials.^{4,10,14} For example, with carbon nanotubes, a permittivity value of 10-16 can be obtained in the microwave range of 2-18 GHz,8 and it can be tuned with the chirality, diameter, length, and doping of carbon nanotubes.9 The permeability of ferromagnetic fillers such as ferrites and carbonyl iron decreases dramatically in the GHz range.⁴ However, for ceramic ferroelectrics such as BaTiO₃, a large microwave reflection and low microwave absorption are observed, i.e. in the high frequency range, due to their large reflection coefficients at the

interface with air,⁴ although they have been considered as promising MAMs.¹⁵

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The interactions between matter and electromagnetic irradiation depend not only on the frequency of the alternating electromagnetic field, but also on the structure, phase, surface and composition of the materials. In order to be a strong absorber, the material has to be able to allow the electromagnetic wave to enter (impedance matching characteristic) and get entirely absorbed (attenuation characteristic) in the microwave region. Recently, we have demonstrated that by altering the lattice structures of TiO₂ nanoparticles using hydrogenation processes, the interactions of TiO₂ nanoparticles with electromagnetic irradiation changed dramatically not only in the high frequency (visible-light & infrared) region,^{16,17} but also in the low frequency (microwave) region.^{18,19} The hydrogenated TiO₂ nanoparticles featured with a layer of an amorphous lattice on the outside of the crystalline core.16,20 The electronic structures of the crystalline core and the amorphous shell were different,16,21 which was suggested to cause a built-in electric field and to facilitate the charge transfer processes.²² The hydrogenated TiO₂ nanoparticles also displayed dramatic changes in their dielectric constants and showed excellent absorption in the microwave regions when compared to normal TiO₂ nanoparticles, which traditionally were not a good MAM.18,19 A collective-movement-ofinterfacial-dipole (CMID) mechanism was proposed to explain the enhanced microwave absorption with a collective interfacial polarization amplified microwave absorption (CIPAMA).18,19 The CMID was based on the increased interfacial polarization and charge accumulations caused by the built-in electrical field along the boundaries between different grains within these nanoparticles from the hydrogenation process.18,19

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Here, we report that hydrogenation brings in a large microwave absorption for BaTiO₃ nanoparticles, although pristine BaTiO₃ nanoparticles do not show much absorption. Hydrogenation changes the color of BaTiO₃ nanoparticles from white to gray and their optical absorption from the UV region to the visible-light region. A large reflection loss value (-36.9 dB) has been obtained with hydrogenated BaTiO₃ nanoparticles in the microwave region, which corresponds to an absorption efficiency larger than 99.9997%. This enhancement is ascribed to the increased efficiency of the resonance of charge rotations with the incident microwave electromagnetic field due to the increased interfacial polarization caused by the built-in electrical field along the boundaries between different grains created within these nanoparticles created by the hightemperature hydrogenation process. Thus, this study shows that hydrogenation plays an important role in the interactions of BaTiO₃ nanoparticles with the electromagnetic irradiation and may revive their opportunities as promising MAMs.

Results and discussion

Hydrogenated BaTiO₃ nanoparticles were obtained by heating pristine BaTiO₃ nanoparticles at 700 °C for 4 hours in a pure hydrogen environment. Pristine BaTiO₃ nanoparticles were obtained by reacting barium hydroxide and tetrabutyl titanate in a water/ethanol solution within a sealed glass bottle at 70 °C for 1 h. No organic or polymeric surfactant was used in the synthesis. Fig. 1 shows the transmission electron microscopy (TEM) images of pristine and hydrogenated BaTiO₃ nanoparticles. As seen from Fig. 1A, the size of the primary particles of pristine BaTiO₃ nanoparticles was around 20–30 nm in diameter, secondary particle size around 100 nm and larger aggregates around 200 nm. The high-resolution TEM (HRTEM) image in Fig. 1B shows clear lattice fringes of one BaTiO₃



Fig. 1 TEM images of pristine (A and B) and hydrogenated (C and D) $BaTiO_3$ nanoparticles.

nanoparticle. This indicated that the pristine $BaTiO_3$ nanoparticles were highly crystallized.

Fig. 1C shows the TEM image of hydrogenated BaTiO₃ nanoparticles. The particles aggregated with each other. The particle size was around 100 and 200 nm for smaller and bigger particles. The average size of the BaTiO₃ nanoparticles after hydrogenation was bigger than that of the pristine BaTiO₃ nanoparticles. Meanwhile, the surface of the particles became much smoother than that of pristine BaTiO₃ nanoparticles. This was likely attributed to the particle fusion and growth during the high-temperature hydrogenation process, similar to that in hydrogenated TiO2 nanoparticles.18,19 The HRTEM image in Fig. 1D shows that the clear lattice fringes throughout the entire particle in the pristine BaTiO₃ nanoparticles were lost for the hydrogenated BaTiO₃ nanoparticles, instead only some weak and local lattice fringes were observed here and there with amorphous structures lacking clear lattice fringes (also see Fig. S1[†]). Fig. S1[†] further shows a HRTEM image of hydrogenated BaTiO₃ nanoparticles. As marked by the red dotted lines, an amorphous phase was found not only within one nanoparticle but also at the interface between two nanoparticles. This hinted that hydrogenated BaTiO₃ nanoparticles had mixed crystalline and amorphous phases. Overall, the pristine BaTiO₃ nanoparticles were highly crystalline, while the hydrogenated BaTiO₃ nanoparticles were mixed with crystalline and amorphous phases, consistent with the XRD and Raman results shown below. Based on our previous studies on hydrogenated TiO₂ nanoparticles,^{18,19} it was likely that hydrogen induced the reorganization of the atoms in primary BaTiO₃ nanoparticles and stabilized the amorphous phase between different primary BaTiO₃ nanoparticles during the fusion of these nanoparticles in the hydrogenation process, which led to the smoother surface of the fused nanoparticle surface and unchanged crystalline grain size as observed from the TEM and XRD results, respectively.

Fig. 2A shows the X-ray diffraction (XRD) patterns of the pristine and hydrogenated BaTiO₃ nanoparticles. Both pristine and hydrogenated BaTiO₃ nanoparticles had strong diffraction peaks, suggesting that highly crystalline phases existed in both nanoparticles. Their diffraction patterns matched well with the standard BaTiO₃ structure (PDF #00-031-0174). The crystalline grain size was calculated using the Scherrer equation: $\tau = (K\lambda)/(K\lambda)$ $(\beta \cos \theta)$, where τ is the mean size of the ordered (crystalline) domains, which may be smaller than or equal to the grain size, *K* is the shape factor with a typical value of 0.9, λ is the X-ray wavelength, β is the line broadening full width at half maximum (FWHM) peak height in radians, and θ is the Bragg angle.^{16,18} The crystalline grain size of both the pristine and hydrogenated BaTiO₃ nanoparticles was around 24.0 nm in diameter based on the (110) diffraction peak near $2\theta = 31.3^{\circ}$ and the (200) peak near 44.9°. Apparently, the hydrogenation process did not change the crystalline grain size of BaTiO₃ nanoparticles, even though the particle size was increased after hydrogenation from the TEM measurements. For pristine BaTiO₃ nanoparticles, the size of the primary particles was around 20-30 nm in diameter from the TEM measurement and the crystal grain size was around 24.0 nm based on the XRD diffraction pattern, so the



Fig. 2 (A) XRD patterns, (B) Raman, (C) UV-visible reflection, and (D) FTIR absorption spectra of (a) pristine and (b) hydrogenated $BaTiO_3$ nanoparticles.

primary particle was most likely single crystalline, and the larger particles agglomerated from the primary particles. On the other hand, the hydrogenated BaTiO₃ nanoparticles seemed to be mostly aggregated with many different crystalline grains as their particle sizes were around 100 and 200 nm.

Raman scattering measurements were taken to further investigate the structural properties of these BaTiO₃ nanoparticles. The peaks near 200 and 541 cm⁻¹ were assigned to the E(TO) modes²³ and the F_{1u} cubic phase modes. The peak near 317 cm^{-1} came from the splitting of the cubic silent F_{2u} mode. The peaks around 124, 317 and 734 cm⁻¹ were attributed to the E(LO) modes. The peaks around 837 and 1096 cm⁻¹ were not attributed to the intrinsic vibrational mode of the BaTiO₃ nanoparticles in a previous study,24 but were more likely due to the presence of lattice hydroxyl groups residing on the defect sites within the BaTiO₃ nanoparticles.^{25,26} These characteristic vibrational peaks of BaTiO₃ were not observed for the hydrogenated BaTiO₃ nanoparticles, instead only a broad and featureless fluorescence background was seen. This meant that an amorphous phase existed in the hydrogenated BaTiO₃ nanoparticles and their vibrational fingerprints were lost. However, the XRD pattern of hydrogenated BaTiO₃ nanoparticles showed strong diffraction peaks and a highly crystalline nature. Therefore, it seemed that hydrogenated BaTiO₃ nanoparticles had a crystalline/amorphous mixed nature, and the featureless fluorescence background of the amorphous phase shadowed the vibrational features of the crystalline phase. This conclusion was consistent with the TEM measurements.

The UV-visible reflection spectra of pristine and hydrogenated $BaTiO_3$ nanoparticles are shown in Fig. 2C. Pristine $BaTiO_3$ nanoparticles only absorbed light from 395 nm to the UV region and reflected almost all the light from 400 nm to the near-infrared region. In contrast, hydrogenated $BaTiO_3$ nanoparticles absorbed more than 50% of light from 400 nm wavelength to the near-infrared region, and absorbed almost all the light in the UV region. Compared to the white colour of the pristine BaTiO₃ nanoparticles, the colour of the BaTiO₃ nanoparticles changed to gray. If a material absorbs 100% light across the entire visible-light, it shows a completely black color. If only a certain percentage across the entire visible-light region is equally absorbed, it is partially black or gray. So, gray is similar to black, although black materials absorb more. Thus, it is reasonable to believe that they may share some similar behaviours. The increased light absorption in the visible and near-infrared regions of the hydrogenated BaTiO₃ nanoparticles seemed to be caused by the amorphous phase formed by the hydrogenation process. This assignment was based on the similar findings in black TiO2 and ZnO nanoparticles with the amorphous phase either formed by hydrogenation or other processes,16,27-29 where the black color was due to the disturbance of the crystalline lattice by hydrogenation or other processes, and the corresponding electronic structures were changed.16,27-29 These optical property changes caused by the structural alterations were summarized in a recent review article on TiO₂ nanoparticles, where the changes of the bulk or surface lattice structures could bring in electronic and optical property changes.30 Thereby, the dramatic optical property change of BaTiO₃ nanoparticles was attributed to the amorphous phases in the nanoparticles as revealed from the TEM and Raman results. The colour of the hydrogenated BaTiO₃ was only grey and not black like that in hydrogenated black TiO_2 , which was possibly related to the extent of the effect of hydrogenation on the electronic structure and optical property changes were not as much as that in TiO₂, as their crystal structures, chemical bonding and electronic structures were apparently different, leading to different perturbations from the hydrogenation process.

Fig. 2D shows the Fourier transform infrared (FTIR) absorption spectra of pristine and hydrogenated BaTiO₃ nanoparticles. Both had similar FTIR features with several absorption bands around 3514, 1463, 1360 and below 1000 cm⁻¹. The first three bands were attributed to the vibrational modes (stretching and bending) from the surface hydroxyl groups and molecularly chemisorbed or physisorbed water.16 The large absorption band below 1000 cm⁻¹ was attributed to the lattice vibrational modes of the BaTiO₃ nanoparticle lattice. Compared to the pristine BaTiO₃ nanoparticles, the hydrogenated BaTiO₃ nanoparticles had much weaker IR absorption peaks from the OH groups. In other words, the hydrogenated BaTiO₃ nanoparticles had fewer hydroxyl groups than the pristine BaTiO₃ nanoparticles. This was likely due to the loss of the hydroxyl groups during the heating process, which was consistent with the results from the Raman measurements where the peaks around 837 and 1096 cm⁻¹ from hydroxyl groups were not observed for the hydrogenated BaTiO₃ nanoparticles. Meanwhile, the hydrogenated BaTiO₃ nanoparticles had much weaker absorption below 1000 cm^{-1} from the lattice vibrational modes than the pristine BaTiO₃ nanoparticles, suggesting possible existence of the amorphous phase. This was consistent with the findings from Raman and HRTEM results.

The microwave absorption properties were evaluated with the complex permittivity and permeability values of the materials. The real parts ε' and μ' of the complex permittivity and permeability are related to the stored electrical and magnetic energy within the medium, respectively. The imaginary parts ε'' and μ'' are related to the dissipation (or loss) of electrical and magnetic energy. The dielectric and magnetic dissipation factors tg $\delta_{\varepsilon} = \varepsilon''/\varepsilon'$ and tg $\delta_{\mu} = \mu''/\mu'$ provide a measure of how much power is lost in a material *versus* how much is stored.^{18,19}

The complex permittivity and permeability values were measured for BaTiO₃ nanoparticles/epoxy composites, where the BaTiO₃ nanoparticles were dispersed in the paraffin wax matrix. Fig. 3A shows the ε' values of pristine and hydrogenated BaTiO₃ nanoparticles/epoxy composites. Pristine BaTiO₃ nanoparticles/epoxy composites displayed a slow increase in the ε' value from 8.2 to 10.1 in the frequency range of 1.0–18.0 GHz; while the hydrogenated BaTiO₃ nanoparticles/epoxy composites displayed a slow increased gradually from 17.6 at 1.0 GHz to 19.3 at 7.7 GHz, decreased to 16.6 at 8.6 GHz, increased to 20.1 at 12.2 GHz and decreased to 6.0 at 18.0 GHz.

The ε'' values of pristine and hydrogenated BaTiO₃ nanoparticles/epoxy composites are shown in Fig. 3B. Pristine and hydrogenated BaTiO₃ nanoparticles/epoxy composites showed relatively constant ε'' values around in the frequency range of 1.0–8.0 GHz. In the frequency range of 8.0–18.0 GHz, the ε'' value of pristine BaTiO₃ nanoparticles/epoxy composites increased from 0.2 to 1.5 with a small bump of 0.5 around 9.4 GHz, while the ε'' value of hydrogenated BaTiO₃ nanoparticles/ epoxy composites increased to 0.43 around 3.6 GHz, then decreased to 0.2 at 5.3 GHz, increased to 2.9 around 8.1 GHz, decreased to 0.9 at 10.0 GHz, increased to 8.9 at 15.1 GHz, and finally decreased to 8.0 at 18.0 GHz. One small peak at 5.3 GHz, a medium peak at 8.1 GHz, and a large and broad peak around 15.1 GHz were observed. Overall, hydrogenated BaTiO₃



Fig. 3 Frequency dependence of (A) the real part (ε'), (B) the imaginary part (ε'') of the complex permittivity, and (C) the real part (μ') and (D) the imaginary part (μ'') of the complex permeability of pristine and hydrogenated BaTiO₃ nanoparticles in the microwave region.

nanoparticles showed much higher ε'' values than pristine BaTiO₃ nanoparticles.

Fig. 3C shows the μ' values of pristine and hydrogenated BaTiO₃ nanoparticles/epoxy composites. The μ' of pristine BaTiO₃ nanoparticles increased slowly from 1.07 at 1.0 GHz to 1.14 at 5.0 GHz, then decreased to 0.94 at 18.0 GHz. The μ' of hydrogenated BaTiO₃ nanoparticles was lower than that of pristine BaTiO₃ nanoparticles in the region of 1.0-15.7 GHz and higher in the region of 15.7–18.0 GHz. The μ' of hydrogenated BaTiO₃ nanoparticles increased slowly from 0.96 at 1.0 GHz to 1.07 at 4.3 GHz, then decreased to 0.90 at 12.5 GHz, increased to 1.3 at 17.1 GHz and decreased to 1.2 at 18.0 GHz. Fig. 3D shows the μ'' values of complex permeability for pristine and hydrogenated BaTiO₃ nanoparticles/epoxy composites. The μ'' value for pristine BaTiO₃ nanoparticles decreased from about 0.16 at 1.0 GHz to 0.03 at 12.0 GHz and then slowly increased to 0.09 at 18.0 GHz. The μ'' value of hydrogenated BaTiO₃ nanoparticles decreased from about 0.43 at 1.0 GHz to 0.05 at 11.2 GHz, increased to 1.0 at 17.0 GHz and decreased to 0.82 at 18.0 GHz. The μ'' of hydrogenated BaTiO₃ nanoparticles was higher than that of pristine BaTiO₃ nanoparticles. The changes of the μ' and μ'' values of hydrogenated BaTiO₃ nanoparticles were likely from the changes of the crystal field and the magnetic properties due to the change of the crystal symmetry after hydrogenation as seen from the Raman spectrum that hydrogenated BaTiO₃ nanoparticles had lower tetragonality than pristine BaTiO₃ nanoparticles, and the possible contribution from the possible oxygen vacancies created in the hydrogenated BaTiO₃ nanoparticles. Oxygen vacancies can possess unpaired electrons and introduce magnetic resonance.

The tg δ_{ϵ} values of pristine and hydrogenated BaTiO₃ nanoparticles are shown in Fig. 4A. The tg δ_{ϵ} value of pristine BaTiO₃ nanoparticles was around 0.02 from 1.0 GHz to 8.0 GHz, and increased to 0.15 at 18.0 GHz with a small peak around 11.0 GHz. For hydrogenated BaTiO₃ nanoparticles, it was around 0.02 from 1.0 GHz to 7.0 GHz, then increased to 0.17 at 8.0 GHz, decreased to 0.05 at 10.0 GHz, and finally increased to 1.4 at 18.0 GHz. Fig. 4B shows the frequency dependent magnetic dissipation factor, tg δ_{μ} for pristine and hydrogenated BaTiO₃ nanoparticles. The tg δ_{μ} values of pristine BaTiO₃ nanoparticles decreased from 0.15 at 1.0 GHz to 0.03 at 12.0 GHz and then increased to 0.09 at 18.0 GHz. The tg δ_{μ} value of hydrogenated BaTiO₃ nanoparticles decreased slowly from 0.45 at 1.0 GHz to



Fig. 4 Frequency dependence of (A) electrical (tg δ_{ϵ}) and (B) magnetic (tg δ_{μ}) dissipation factors of pristine and hydrogenated BaTiO₃ nanoparticles in the microwave region.

0.04 at 10.8 GHz, increased to 0.80 at 16.6 GHz and finally decreased to 0.70 at 18.0 GHz. Both the tg δ_{ϵ} and tg δ_{μ} values of hydrogenated BaTiO₃ nanoparticles were larger than pristine BaTiO₃ nanoparticles. This testified that hydrogenated BaTiO₃ nanoparticles had higher efficiency in dissipating the electrical and magnetic energies of the microwave electromagnetic irradiation.

The microwave reflection loss (RL) curve can be calculated according to the following equations:

$$Z_{\rm in} = Z_0(\mu_{\rm r}\varepsilon_{\rm r})^{1/2} \tanh[j(2\pi f d/c)(\mu_{\rm r}\varepsilon_{\rm r})^{1/2}] \tag{1}$$

 $RL(dB) = 20 \log|(Z_{in} - Z_0)/(Z_{in} + Z_0)|$ (2)

$$RL(dB) = 10 \log_{10}(P_i/P_r)$$
 (3)

where *f* is the frequency of the electromagnetic wave, *d* the thickness of the absorber, *c* the velocity of light, Z_0 the impedance of free space, Z_{in} the input impedance of the absorber, RL (dB) the reflection loss in dB, P_i is the incident power, and P_r the reflected power.³¹

According to eqn (1) and (2), the simulations of the RL of the pristine and hydrogenated BaTiO₃ nanoparticles with a thickness of 3.0 mm are shown in Fig. 5A. The RL (dB) value of pristine BaTiO₃ nanoparticles decreased from -0.1 at 1.0 GHz to -21.1 at 18.0 GHz with a small dip of -5.1 at 11.3 GHz. The hydrogenated BaTiO₃ nanoparticles showed two sharp dips of the RL with values of -16.4 and -36.9 dB around 8.1 and 11.9 GHz, respectively. A material with a RL value less than -30 is regarded as an excellent absorber, as from eqn (3), this corresponds to 99.999% reflection loss or absorption. This indicated that hydrogenated BaTiO₃ nanoparticles had excellent reflection loss of microwave irradiation at these frequencies. The power reflection loss is shown in Fig. 5B. Hydrogenated BaTiO₃ nanoparticles showed power losses larger than 99.999% around 8.1 and 11.9 GHz, while pristine BaTiO₃ nanoparticles had a 99.99% power loss near 18 GHz. So, hydrogenation improved the reflection loss or absorption of the microwave irradiation and shifted its peak position to lower frequencies. Meanwhile, it was noticed that the reflection loss was smaller than that of the pristine BaTiO₃ nanoparticles when the frequency was above 15 GHz even though the permittivity and permeability values were higher. This could be understood as follows. As seen from eqn (1)-(3), the reflection loss was determined by the co-play of



Fig. 5 Frequency dependence of (A) reflection loss and (B) the power reflection ratio of pristine and hydrogenated BaTiO₃ nanoparticles in the microwave region.

complex permittivity and permeability values. A large reflection loss was observed only with matched permittivity and permeability values.^{31,32}

The hydrogenated BaTiO₃ nanoparticles had a better microwave absorbing performance (-36.9 dB) than the BaTiO₃ nanostructures reported from other groups.^{11,32-35} For example, composites of BaTiO₃ nanotubes (~10 nm in diameter) and polyaniline only displayed the largest microwave absorption of -3.7 dB at 8.84 GHz,¹¹ and composites of BaTiO₃ nanotubes (~10 nm in diameter) and paraffin wax had a maximal reflection loss of -21.8 dB.32 The good microwave absorption performance of BaTiO₃ nanotubes in the paraffin wax was attributed to the nanotubes' high interface areas and hollow structures which led to a complicated interface polarization and intensive dielectric relaxation.³² This explanation was, however, not persuasive for their study of BaTiO₃ nanotubes and polyaniline composites.¹¹ In other studies, BaTiO₃ and BaTiO₃/polyaniline composites showed a microwave absorption of -9.5 and -13.8 dB at 6.8 and 11.6 GHz, respectively,³³ BaTiO₃/polypyrrole composites had a maximum reflection loss value up to -28 dBaround 5.5 GHz.34 BaTiO3 flakes with an average size of 500 nm after annealing at 1250 °C reached a maximal reflection loss of -27 dB at 12 GHz with 80 wt% mass loading in a polyurethane matrix,35 and composites of BaTiO3 nano-torus and epoxy resin displayed a maximum reflection loss of -28.38 dB at 11.36 GHz.36 Their excellent absorption performance was attributed to the increased interface area and the more complicated interface polarization of the BaTiO₃ nano-torus structures,³⁶ due to longer trapping time of microwave within the matrix by much reflection or scattering in the concaves or pores of the nano-torus.36 Obviously, the hydrogenated BaTiO₃ nanoparticles showed superior microwave absorbing performance (-36.9 dB).

However, the explanations for the enhanced microwave absorption of the various nanostructured BaTiO3/epoxy composites have not been convincing so far. For example, in the study of the nano-torus structures, the wavelength of the 11.36 GHz microwave was 26.4 mm, the size of these BaTiO₃ nanotorus was around 40-100 nm in diameter, and the thickness of the sample made of the nano-torus/epoxy resin composites was 2.8 mm.²⁷ Because of this, the multiple reflection or scattering mechanism seemed difficult to understand, as the size of these nanostructures or the entire composite was much smaller than the wavelength of the microwave irradiation. On the other hand, traditional mechanisms for microwave absorption include dipole rotations,37 and ferromagnetic resonances.38,39 The traditional dipole rotation mechanism did not work well here, as the hydrogenated BaTiO3 nanoparticles had fewer polar groups than the pristine BaTiO₃ nanoparticles as seen from the Raman and FTIR results. However, the contribution of the magnetic resonance mechanism could not be excluded as both the real part (μ') and the imaginary part (μ'') of the complex permeability changed after hydrogenation. Meanwhile, based on our previous studies on the enhanced microwave absorption of hydrogenated TiO2 nanoparticles,18,19 we pondered this enhancement could be more likely due to the contribution of the increased interfacial polarization and charge accumulations caused by the built-in electrical field along the boundaries

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between different grains within these nanoparticles from the hydrogenation process.^{18,19} Both hydrogenated BaTiO₃ and TiO₂ nanoparticles shared similar structural and optical characteristics when compared to pristine BaTiO₃ and TiO₂ nanoparticles, respectively, that is, both had long-wavelength absorption in the visible-light region, fewer hydroxyl groups, amorphous lattices in addition to the crystalline phases and many disorder/crystalline interfaces. The crystal planes along the interface are normally different even if the crystalline phases are the same, and different crystalline planes have different lattice structures. Hence, defects and dangling bonds are commonly seen along the interfaces for charge accumulation.40,41 Moreover, different planes will have different electronic structures, e.g. different conduction and valence band positions. As a result, there is a mismatch between the electronic structures of the crystalline planes along the interfaces. This causes charge imbalance and redistribution along the interface to introduce a polarization effect, and the built-in internal electrical field along the interfaces.18,19,22,42 The higher the interfacial area, the stronger the polarization. The polarization is more obvious near the interface or surface, *i.e.* a few atomic layers. As seen from the TEM images, in the pristine BaTiO₃ nanoparticles, the primary nanoparticles were only loosely aggregated together to form large particles and the interfaces between these primary nanoparticles might only cause a small or moderate interfacial polarization effect. In the hydrogenated BaTiO₃ nanoparticles, intimate contact between primary nanoparticles was expected during the heating process in forming large aggregated particles, thus leading to a large interfacial polarization effect. Moreover, the hydrogenated BaTiO₃ nanoparticles had additional interfaces between the amorphous and crystalline phases. These interfaces benefited the microwave absorption due to a built-in electric field.^{18,19,42} So, overall, the interfacial polarization effect was largely enhanced for the hydrogenated BaTiO₃ nanoparticles, which increased the microwave absorption. This explanation echoed the CMID in the hydrogenated TiO₂ nanoparticles and the recent findings of partially oxidized titania nanotubes which displayed large microwave absorption due to the interfacial electrical field formed at the boundaries of crystalline and amorphous phases inside the nanotubes.42 Meanwhile, it was possible that some oxygen vacancies were created in the hydrogenated BaTiO₃ nanoparticles since the oxygen vacancy was the primary factor in determining the disorder of BaTiO₃.^{43,44} The O vacancy from the BaO-terminated surface previously was found to induce magnetism from the unpaired electrons that were localized in the O vacancy basin and contributed to the magnetism on BaTiO₃(001) surfaces.⁴⁵ Thus, the microwave absorption of the hydrogenated BaTiO₃ nanoparticles might have magnetic resonance from oxygen vacancies.45

Conclusions

In summary, we have demonstrated here that hydrogenation can improve the microwave absorbing performance of the BaTiO₃ nanoparticles besides apparent UV-visible absorption and colour changes. The enhancement in the microwave absorption efficiency is suggested to be due to the increased interfacial polarization caused by the built-in electrical field along the intimate boundaries between different grains created within these nanoparticles during hydrogenation, along with possible contribution of the magnetic resonance based on the change of complex permeability. As a consequence, this study demonstrates that hydrogenation can change the interactions between matter and electromagnetic irradiation not only in the high frequency ranges (visible-light and near-infrared), but also in the low frequency ranges (microwave absorption).

Methods

Synthesis

BaTiO₃ nanoparticles were prepared from a precursor solution consisting of barium hydroxide, tetrabutyl titanate, ethanol, and deionized (D.I.) water. The solution was stirred at room temperature for 15 min and then maintained at 70 °C for 1 h. The white precipitates were filtered, washed with D.I. water, and dried at 80 °C to obtain pristine BaTiO₃ nanoparticles. These pristine BaTiO₃ nanoparticles were then hydrogenated at 700 °C for 4 hours to obtain hydrogenated BaTiO₃ nanoparticles.

Characterization

XRD was performed using a Rigaku Miniflex XRD instrument with Cu K α as the X-ray source (wavelength = 1.5418 Å). The Raman spectra were collected on an EZRaman-N benchtop Raman spectrometer. The excitation wavelength was 785 nm. The spectrum range was from 100 cm^{-1} to 3100 cm^{-1} . The spectrum collection time was 4 seconds. The spectrum was averaged three times to improve the signal-to-noise ratio. The TEM study was performed on a FEI Tecnai F200 TEM with an electron accelerating voltage of 200 kV. To prepare the TEM sample, a small amount of the nanoparticles was dispersed in water, dropped onto a thin holey carbon film, and dried overnight. The UV-visible absorption spectra were collected on an Agilent Cary 60 UV-Vis spectrometer equipped with a fiber optical reflectance unit. MgO powder was used as the reference material. The FTIR spectra were collected using a Thermo-Nicolet iS10 FT-IR spectrometer with an attenuated total reflectance (ATR) unit. BaTiO₃ nanoparticles were pressed onto the ZnSe crystal of the ATR unit, and the measurements were performed in air at room temperature.

Electromagnetic property measurement

The complex permittivity and permeability of pristine and hydrogenated $BaTiO_3$ nanoparticles were measured in the frequency range of 1–18 GHz using a HP8722ES network analyzer. The $BaTiO_3$ nanoparticles were dispersed in melting paraffin wax. The content of $BaTiO_3$ nanoparticles was 60 wt%. The mixture was cast into a ring mold with a thickness of 2.0 mm, an inner diameter of 3 mm, and an outer diameter of 7 mm. The measurements were performed at room temperature.

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