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The origin of the strong microwave absorption in black TiO₂

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In this study, the mechanism of the strong microwave absorption in black TiO_2 nanoparticles has been investigated both experimentally and theoretically. In experiment, the amorphous TiO_2 nanoparticles/paraffin wax composites show the reflection loss (RL) of -4.0 dB, which is much smaller compared with the RL of -49.0 dB in those core/shell structure ones. Theoretically, the calculation illustrates that the accumulated charge of 10^{13} cm^{-3} at the core/shell interface results in the plasmon resonance with the incident microwave frequency at 9.3 GHz and 27.0 GHz. The microwave absorption enhancement of the black TiO_2 nanoparticles is proposed to originate from the synergy mechanism between their crystalline-cores and amorphous-shells, rather than the defects and impurities in amorphous phase. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4948456]

Black TiO21 nanoparticles in the crystalline-core/ amorphous-shell structures synthesized through hydrogenation process had been exploited as highly efficient photocatalysts for harvesting solar energy in the visible region. Surprisingly, this nanomaterial also exhibits extraordinary capability in absorbing microwaves, with reflection loss (RL) values reaching -49.0 dB (99.99999%).² Such highly efficient microwave absorption is unusual, considering the facts that their sizes are much smaller than the microwave wavelengths and being a wide-band-gap semiconductor, pristine TiO₂ is normally inert to microwave. Generally, microwave absorbing materials (MAMs) are classified into three types, i.e., ferromagnetic,^{3–5} ferroelectric,^{6–8} or sort of conductive matter,^{9–11} where ferromagnetic resonances, dipole rotations, and electronic diffusive transport characterize, respectively, their microwave absorbing ways. Among them, ferromagnetic resonance certainly cannot account for the microwave absorbing of black TiO₂ since it is a nonmagnetic material. For the other two mechanisms, it depends on reasonably figuring out their dipoles or current sources.

In fact, black TiO₂ represents a type of semiconductor nanomaterials that are produced by the so called disorderengineering. Like black TiO₂, this technique, i.e., highpressure high-temperature treated surface hydrogenation, which makes other oxide semiconductor nanoparticles^{12,13} possess the similar crystalline-core/amorphous-shell structures and absorb microwaves well. That core-shell crystalline-amorphous feature has been known as playing the key roles^{1,14,15} in deciding the visible photocatalytic performance of black TiO₂. That is the shell-disorder(amorphous) lifts up the valence band maximum (VBM) which results in the visible solar absorption and the crystalline/amorphous interface prompt the charge separation which improves the energy conversion efficiency. However, for the microwave region of μeV s, how these nano-complexes contribute to their absorption needs to examine. One plausible explanation is to ascribe the enhanced absorption to the impurities or defects in the amorphous region, such as hydroxyl (OH) groups,¹⁶ which contribute the dipoles in response to microwaves. In this case, black TiO₂ is regarded as a traditional amorphous material, and the crystalline parts are not necessary for its microwave absorbing performance. But, other mechanisms can also be proposed if one considers the synergy effects between the cores and shells. Due to the band mismatch between their crystalline and amorphous phases, charges¹⁷ or dipoles^{13,18} will accumulate near the interface where they interact strongly with microwave in certain ways.² If the later understanding is correct, that actually means that "disorder-engineering" opens up a way of making highly efficient MAMs with oxide semiconductors. However, currently such a mechanism is still not confirmed unless the first possibility can be unequivocally ruled out with solid evidences.

In this study, with the aim of providing a clear understanding on the mechanism of black TiO_2 absorbing microwaves, we synthesized TiO_2 nanoparticles in totally amorphous structure and compared their microwave response with those in engineered core-shell ones. Moreover, based on the finite element method (FEM) simulations, we further proposed the synergy mechanism to explain the novel microwave behaviors in "disorder-engineering" semiconductor nanoparticles.

The amorphous TiO₂ nanoparticles were prepared by a facile pulse laser ablation (PLA) approach,¹⁹ where the Nd:YAG pulsed laser (Continuum PRII-8000, = 355 nm, pulse duration = 8 ns, frequency = 10 Hz, power = 1.0 W,

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instantaneous power = 12.5 MW) was used to irradiate the anatase TiO₂ powder suspended in deionized water. The nanosecond laser pulses render the nanoparticles melting and quenching alternatively in every 8 ns. After such high frequency melting-quenching process continuously repeated for 1 h, those anatase nanoparticles can be totally converted into amorphous structures.

Fig. 1 presents the field-emission scanning electron microscopy (SEM) images of these anatase TiO₂ nanoparticles before and after PLA, together with their X-ray diffraction (XRD) spectra. Obviously, the "potato" shapes of ablated TiO_2 particles, as shown in Fig. 1(b), verify that they had sustained the temperature high enough to liquidize and reshape them from those much smaller anatase nanoparticles (Fig. 1(a)). With XRD characterization, their crystal structures were analysed as shown in Fig. 1(c). Before PLA, the TiO₂ particles present the typical anatase XRD features, with those peaks identified as the (101), (103), (004), (112), (200), (105), (211), (213), (204), and (116) lattice planes of anatase. But after PLA, those diffraction peaks belonging to the (110), (101), and (111) planes of rutile appear at 27.4° , 36.1°, and 41.3°. Moreover, after laser irradiation, their XRD peaks become much broader and show much lower intensity, that indicates the amorphous nature of these PLA particles. By analysing the peak profiles of these particles, we can also estimate their percent crystallinity, from the intensity ratio of the crystalline component to the sum of both the crystalline and the amorphous.^{20,21} Accordingly, we found, after PLA, the percent crystallinity of TiO2 particles decreases dramatically from about 97.4% to 19.4%, i.e., being converted (mostly) into amorphous form.

The amorphization of these TiO_2 particles upon laser ablation is also confirmed with the transmission electron microscopy (TEM) and the selected area electron diffraction (SAED) analysis. The clear lattice fringes in those TEM images as shown in Figs. 2(a) and 2(b) reveal that the pristine anatase nanocrystals are highly crystallized. In comparison,



FIG. 1. SEM images of anatase TiO_2 nanocrystals before (a) and after (b) laser ablation, and their XRD spectra (c).



FIG. 2. TEM images and SAED patterns of anatase TiO_2 nanocrystals before (a)–(c) and after (d)–(f) laser ablation.

that the fringes blur almost everywhere in the TEM images as shown in Figs. 2(d) and 2(e) indicates the lattices of PLAprocessed particles are mostly disordered. Furthermore, the difference between these crystalline and amorphous particles is also manifested by their SAED patterns. In Fig. 2(c), the anatase particles show the crystalline feature with the SAED pattern with regular clear diffraction dots, whereas the ablated ones present their amorphous nature with those rings in a milky diffraction background (Fig. 2(f)).

To investigate the microwave absorption performance of TiO₂ upon amorphization, we measured the complex relative permittivity $\varepsilon_r (= \varepsilon' - j\varepsilon'')$ and permeability $\mu_r (= \mu' - j\mu'')$ of both nanoparticles.² With these frequency-dependent constants, we can calculate their reflection loss (RL) values according to the transmission line impedance equation as follows,²² in the case that a layer of nanoparticles with a given thickness is coated on a perfect conductor ground

$$RL(dB) = 20 \lg |(Z_{in} - Z_0)/(Z_{in} + Z_0)|, \qquad (1)$$

$$Z_{in} = Z_0 \sqrt{\mu_r / \varepsilon_r} \tanh[j(2\pi f d/c) \sqrt{\mu_r \varepsilon_r}], \qquad (2)$$

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

Following the same way as on black TiO_2 ,² the microwave-band dielectric ($\varepsilon', \varepsilon''$) and magnetic (μ', μ'') constants of the amorphous and crystalline TiO₂ nanoparticles were measured as dispersed in paraffin wax (in the

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measurement, the contents of TiO_2 were 60 wt. %, so the electromagnetic properties belong to the TiO₂ nanoparticles/ paraffin wax composites). Upon amorphization, the most notable change of these parameters comes from ε' , whose value increases by about 40% from \sim 5.7 to \sim 7.8 as plotted in Fig. 3(a). That indicates amorphization, or structural disorder, has indeed brought more electric dipoles or charges into these TiO₂ nanoparticles. Whereas both of their μ' values remain as low as about 1.0 as shown in Fig. 3(c). That evidences, as expected, that lattice disorder with hydrogenation will not bring more magnetic moments. As to imaginary parts ε'' and μ'' both get a little larger after structural amorphization, as shown in Figs. 3(b) and 3(d), respectively. While the imaginary parts of permittivity and permeability reflect directly the electrical and magnetic energy losses, respectively, that means the amorphization will not enhance microwave absorption as much as black TiO₂. From their calculated RL values as shown in Fig. 3(e), the amorphous TiO₂ can absorb microwaves more efficiently in the range of 1.0–16.0 GHz, whereas the crystalline TiO_2 performs better in the range of 16.0-18.0 GHz. In comparison with the RL value of $-49.0 \, \text{dB}$ of black TiO₂,² their extreme RL values can approximately reach only -4.0 dB. Therefore, the contribution solely from the amorphous part of black TiO₂ can be taken as trivial in its overall microwave absorption performance.

Now that neither crystalline cores nor amorphous shells can contribute independently to the microwave performance of black TiO₂, its greatly enhanced absorption must originate from their crystalline/amorphous interface and the synergy effects between these two phases. Our previous experimental¹



FIG. 3. Measured dielectric permittivity (a) and (b) and magnetic permeability (c) and (d) of the crystalline and amorphous TiO_2 particles/paraffin wax composites, and their calculated RL values (e) in the microwave region between 1.0 and 18.0 GHz.

and theoretical¹⁴ works had revealed that the hydrogenationengineered amorphization can lift up the VBM to as large as 2.18 eV and thus shrink effectively the band gap of black TiO₂ in its shell region. That means an indeed heterojunction, with band offset of at least 2 eV, forms at the crystalline-core/ amorphous-shell. As shown schematically in Fig. 4, to keep the Fermi level constant through the interface, the electronic bands have to bend near the interface, which induces the charge accumulation. Since confined in the thin layers around the interface, the accumulated charges may oscillate collectively, if with the proper density, in response with microwaves. Such collective interface charge oscillations resemble the plasmons in nanoshell structures.^{23,24} Like those surface ones, under resonance condition, such interface plasmons can interact strongly with electromagnetic waves, including microwave, and results in strong absorption as well. To examine the possibility of the plasmon-enhanced microwave absorption, we simulated the resonance behaviors of interface plasmons excited by microwaves, with the FEM calculations. To simulate the black TiO₂ nanoparticles, a spherical coreshell model was built with a crystalline core in radius of 100 nm, an amorphous shell in thickness of 10 nm, and the accumulated interface charges in density of 10^{13} cm⁻³. By the Drude model, the dielectric function of the shell layer can be evaluated as

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + j\omega\gamma},\tag{3}$$

where $\omega_p = (n_e e^2 / \epsilon_0 m^*)^{1/2}$ is the plasma frequency of the free electron gas, and γ is the collision rate of the electrons. n_e , e, and m^* are, respectively, density, charge, and effective mass of electrons. Here, we set $m^* = 0.8m_e$, $^{25}\gamma = 1 \times 10^{10}$ Hz, and ϵ_{∞} to 6.76. In this core/shell model system, the evoked plasmons can be taken as due to the hybridization between the fixed-frequency plasmon mode ω_{sp} of a nanosphere and that



FIG. 4. Schematic energy band diagram of the crystalline-core/amorphousshell interface in black TiO₂, and the electron accumulated. Grey, red, and black balls represent the titanium, oxygen, and hydrogen atoms, respectively.



FIG. 5. Simulated electric field distributions for the symmetric "bonding" (a) and the antisymmetric "antibonding" (b) plasmons at resonance, of a spherical core/shell model with a crystalline core in radius of 100 nm and an amorphous shell in thickness of 10 nm; and the electric field enhancement factor $|E|^2/|E_0|^2$ (black line) and absorption cross-section $\sigma(abs)$ (red line) of the modelled core/shell nanoparticle under the incident light from 1.4 GHz to 40.0 GHz (c).

 $\omega_c (= \sqrt{2}\omega_{sp})$ of a nanocavity.²³ Their "bonding" plasmon is symmetric with lower energy, whereas their "antibonding" is antisymmetric and with higher energy. The coupling strength between the sphere and cavity modes is dependent on the shell thickness, and the ratio between the inner and outer radii of the shell plays a decisive role in determining the frequencies of the hybrid plasmon modes.

Figs. 5(a) and 5(b) show the electric field distributions for the symmetric and the antisymmetric plasmons at the resonance frequencies of 9.3 GHz and 27.0 GHz, respectively. And in Fig. 5(c), their electric field enhancement factor²⁶ (defined as the ratio of the total electric field intensity $|E|^2$ to the incident light intensity $|E_0|^2$) and absorption spectra (by calculating the absorption cross-section $\sigma(abs) = W_{abs}/P_{in}$, where W_{abs} is the integrated resistive heating, and P_{in} is the incident energy flux) are presented with significant frequency-dependent enhancement in the range from 1.4 GHz to 40.0 GHz. That demonstrates clearly that, if with proper interface charge carriers, here 10^{13} cm⁻³ is reasonably rather small and convincingly possible, interface plasmons can be excited in the microwave ranges, and with much enhanced electric field these plasmons can be most responsible for microwave absorption of black TiO₂.

In summary, with a facile PLA technique, we synthesized the amorphous TiO_2 nanoparticles and compared their microwave response with the crystalline anatase ones and those core/shell structure black TiO_2 nanoparticles. Although also in black color, the amorphous TiO_2 nanoparticles have been found to perform behavior similar as the crystalline particles in absorbing microwaves in the range of 1.0–18.0 GHz. It elucidates that the contribution from the impurities or defects in amorphous region is indeed trivial in the overall microwaveabsorbing performance of black TiO₂. Moreover, with the help of FEM calculations, we demonstrated the collective oscillations of accumulated interface charges, i.e., plasmons, can be evoked in resonance with microwaves at a reasonably charge density, and their strong electric field enhancement can explain highly efficient microwave absorption of black TiO₂. Therefore, the strong microwave absorption in black TiO₂ indeed originates from the synergy effect between its crystalline-core and amorphous-shell. These results in fact indicate that "disorder-engineering" illuminates a way of making highly efficient MAMs with oxide semiconductors.

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