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Binder-free TiO\textsubscript{2} hydrophilic film covalently coated by microwave treatment

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HIGHLIGHTS

- Binder-free blue TiO\textsubscript{2} film was covalently coated on the substrate by microwave.
- Chemical bonds between hydroxyl groups of blue TiO\textsubscript{2} and substrate were formed.
- Chemical bonds of Ti–O–Si and Ti–O–Ti kept the film integrity and strength.
- High film thickness (above 38 \(\mu\text{m}\)) and strong adhesion force (15.2 N) were achieved.
- Efficient visible-light photocatalysis for VOCs degradation was realized.

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ABSTRACT

A binder-free attachment method for TiO\textsubscript{2} on a substrate has been sought to retain high active photocatalysis. Here, we report a binder-free covalent coating of phase-selectively disordered TiO\textsubscript{2} on a hydroxylated silicon oxide (SiO\textsubscript{2}) substrate through rapid microwave treatment. We found that Ti–O–Si and Ti–O–Ti bonds were formed through a condensation reaction between the hydroxyl groups of the disordered TiO\textsubscript{2} and Si substrate, and the disordered TiO\textsubscript{2} nanoparticles themselves, respectively. This covalent coating approach can steadily hold the active photocatalytic materials on the substrates and provide long-term stability. The binder-free disordered TiO\textsubscript{2} coating film can have a thickness (above 38 \(\mu\text{m}\)) with high surface integrity with a strong adhesion force (15.2 N) against the SiO\textsubscript{2} substrate, which leads to the production of a rigid and stable TiO\textsubscript{2} film. This microwave treated TiO\textsubscript{2} coating film showed significant volatile organic compounds degradation abilities under visible light irradiation. The microwave coated selectively reduced TiO\textsubscript{2} realized around 75% acetaldehyde degradation within 12 h and almost 90% toluene degradation after 9 h, also retains stable photodegradation performance during the cycling test. Thus, the microwave coating approach allowed the preparation of the binder-free TiO\textsubscript{2} film as a scalable and cost-effective method to manufacture the TiO\textsubscript{2} film that shows an excellent coating quality and strengthens the application as a photocatalyst under severe conditions.
1. Introduction

Currently, the energy crisis and environmental pollution are becoming serious global concerns. Due to the above worldwide issues, human civilization development has been relatively restricted, and public health faces severe detrimental impacts from various pollutants [1]. For tackling energy and pollution problems, titanium dioxide (TiO$_2$) has attracted great interest due to the excellent photocatalytic activity since the discovery of TiO$_2$ water splitting to hydrogen gas phenomena under near ultra-violet (UV) light by Fujishima and Honda at 1972 [2]. As one of the most promising photocatalysts, TiO$_2$ showed favorable heterogeneous photocatalytic properties and has been applied in various fields, such as environmental pollutants degradation [3,4], antibacterial materials for sterilization in the hospital system or food industry [5], self-cleaning coatings [6], light-driven water splitting, and CO$_2$ reduction [7], among others [8]. Moreover, the inert, non-toxic, and economic nature makes TiO$_2$ more favorable in the development and industrial process without the introduction of environmental issues [9]. During the ongoing COVID-19 coronavirus pandemic, TiO$_2$ as a potential, environment-friendly antivirus agent will gain more concerning in the practical applications [10-12].

Recently, researchers found that the disordered surface on TiO$_2$ can effectively reduce the bandgap and dramatically increases visible light absorption [8,13]. Our group has reported a visible-light-driven high photocatalytic performance of the phase-selectively disordered blue P25 TiO$_2$ nanomaterials, which are disordered rutile (R$_d$) phase and ordered anatase (A$_o$) crystalline phase Li-P (R$_d$/A$_o$) TiO$_2$, and ordered crystalline rutile (R$_o$) and disordered anatase (A$_d$) Na-P (R$_o$/A$_d$) TiO$_2$, respectively [8,14,15]. The selectively disordered phase that has many hydroxyl groups can enhance visible light absorption, and the unchanged crystalline phase can provide high charge separation [8].

Meanwhile, most current applications and research of the TiO$_2$ needs to be loaded or coated on the substrates as a loading medium (silicon dioxide, conductive glasses, activated carbon or polymer, etc.) [16-18]. Multiple events can easily cause a detachment problem of the loaded active catalysts such as 1) wind, rain, and other natural processes in ambient conditions; 2) shearing force in the agitated reaction chamber; 3) high-temperature annealing process and catalytic reaction conditions, and so on. For solving the detachment problems, several deposition methods have been developed, such as plasma or thermal spray [17], sol-gel process [19], and sinter coating [20]. However, the abovementioned approaches require high energy, high temperature, and complex processes [21]. The conventional TiO$_2$ deposition strategies lack the robust interfacial binding ability for fulfilling long-term or severe environmental applications, which will result in easy detachment from the substrate with a loss of activity.

Several types of the binder for TiO$_2$ coating have been tested, such as tetraethylorthosilicate (TEOS) and Poly(vinylidene fluoride) (PVDF) [22, 23]. Even though the binding ability with long-chain binders is enhanced between TiO$_2$ and substrates, the efficiency in the TiO$_2$ applications can decrease due to the large portion of the non-active binder composition. Therefore, the formation of a strong adhesive bond of TiO$_2$ to substrates without a binder has become a significant issue in practical applications.

To produce the binder-free TiO$_2$ film, several important questions must be addressed: 1) Is it possible to form covalent bonds between TiO$_2$ nanoparticles and any substrates, and also covalent bonds between TiO$_2$ nanoparticles by themselves? 2) What are the best functional groups to form the covalent bonds between TiO$_2$ and the substrate; and also, what is the best way to activate the functional groups? 3) If the functional groups are hydroxyl groups, what is the best way to form chemical bonds? 4) Finally, is it possible to form the chemical bonds through a condensation reaction between hydroxyl groups by microwave irradiation?

Herein, we report a binder-free adhesion method for hydrophilic TiO$_2$ film on substrates via a condensation reaction between hydroxyl groups of the phase-selectively reduced TiO$_2$ nanoparticles and the silicon oxide substrate by microwave treatment. It is expected that the phase-selectively reduced TiO$_2$ nanoparticles that have many hydroxyl (-OH) functional groups can be chemically attached to the hydrophilic SiO$_2$ substrate via covalent ether bonding (-O-) through a few minutes of microwave treatment due to the rapid and uniform oscillation among polar moieties (especially hydroxyl groups). In this approach, a strong binding force exists among reduced TiO$_2$ nanoparticles to maintain good film integrity. The covalent coating methods can hold the active photocatalyst material steady on the substrates and provide long-term stability, resulting in high photocatalytic performance.
5 min (output power: 700 W) for thin and thick film coating cases to ensure that the ethanol solvent was fully removed. At first, a glass container with 8 cm diameter was put at the center of the microwave oven, and its cap was punched and installed a soft tube which was connected to the outside of the chamber through the microwave oven top hole. Then, we put the 10 × 10 mm square hydroxylated SiO$_2$ substrate into the glass container followed by dropping the TiO$_2$ suspension (0.2 ml and 0.5 ml for thin and thick coating samples, respectively) on the substrate. The cap of the glass container is tightened to prevent the evaporated ethanol vapor release to the oven chamber. To create good microwave treatment uniformity during the coating process, a slow manual rotation from top of the oven through the connected soft tube was given to the reaction container during the treatment, which is like turntable function. For the thick film coating treatment, two cycles of treatments were conducted. At first, the 0.2 ml suspension was spread on the substrate and followed by 2 min microwave irradiation and then the additional 0.3 ml TiO$_2$ suspension was added followed by the further 3 min microwave irradiation. After microwave irradiation treatment, the TiO$_2$ nanoparticles were tightly coated on the SiO$_2$ substrates. The unbound TiO$_2$ powder was removed with a compressed air gun.

2.5. Material characterization

The SmartLab JD3643 N diffractometer performed the powder X-ray diffractometer (XRD) for crystal structure characterization. The water contact angle (WCA) of treated SiO$_2$ substrates was determined by using SEO PHX300. X-ray Photoelectron Spectrometer (XPS) spectra were obtained from Thermo ESCALAB250 with a twin-crystal, micro-focusing monochromator. And, before the XPS measurements, the samples are loaded in the chamber and initiated the vacuum. For the sake of XPS measurement accuracy, the top few layers of samples are sputtered away to avoid the typical surface carbon contamination. JEOL JSM7600F SEM was utilized to obtain the coated film surface and cross images. The microwave coated TiO$_2$ film binding force was analyzed by a Mecmesin MultiTest 2.5 Tester. The electron paramagnetic resonance (EPR) analysis was conducted by X-band CW-EPR, QM09 under room temperature with 2.97 mW, 100 KHz modulation frequency and 1G modulation amplitude conditions. FTIR spectra were measured with a Bruker Vertex 70/80 FTIR spectrometer.

2.6. Volatile organic compounds (VOCs) degradation

The photocatalytic activity was evaluated by degrading the common VOCs (acetaldehyde and toluene) under visible light in a transparent Tedlar gas bag. TiO$_2$ film samples (300 mg catalyst loading amount) were placed in the 3-L Tedlar bag. Acetaldehyde concentration was detected by a gas detector (Gastek, MODEL GV-100) and toluene gas concentration was determined through gas chromatograph-FID (Younglin Instrument, YL6500). A 100 W white LED lamp (Giolite) was used as a visible light source (wavelength: 420–680 nm). The average light intensity on the catalyst was 0.6 W cm$^{-2}$. After the absorption-desorption equilibrium was achieved, the light lamp was illuminated. The acetaldehyde and toluene gas were diluted to 100 ppm (initial concentration) with airflow. The VOCs removal ratio was calculated as

$$\eta(\%) = \frac{(A/A_0)}{100\%},$$

where $A$ and $A_0$ are acetaldehyde concentration (ppm) before and after the light irradiation, respectively.

3. Results and discussion

The reduced TiO$_2$ (R$_d$/A$_0$ and R$_d$/A$_3$) were selectively disordered rutile and anatase phase, respectively, while kept intact in another crystalline phase. Fig. 1 describes the phase structure of the three types of TiO$_2$. The reduced TiO$_2$ has a large amount of hydroxyl (-OH) groups, existing as Ti–OH in the disordered region of R$_d$/A$_0$ and R$_d$/A$_3$ TiO$_2$. Further, the SiO$_2$ substrates also keep a sufficient portion of Si–OH groups after the hydroxylation process. Herein, the reduced TiO$_2$ is phase-selectively covalently bonded on the hydroxylated SiO$_2$ substrates via microwave treatment for effective VOC degradation photocatalysis (Scheme 1). To clarify the covalent binding among the reduced TiO$_2$ and SiO$_2$ substrate, we conducted various characterizations and analyses.

3.1. The characterisation of selectively reduced TiO$_2$ (R$_d$/A$_0$ and R$_d$/A$_3$) and P25

The crystal structure of three TiO$_2$ (R$_d$/A$_0$ and R$_d$/A$_3$ TiO$_2$, and pristine P25) were first characterized by XRD, as shown in Fig. 2(a). The P25 TiO$_2$ is a commercial product consisting of a mixture of anatase and rutile crystalline phases. The mix of anatase and rutile crystalline phases was concluded after comparing the P25 TiO$_2$ with the standard card of anatase (JCPS 21–1272) and rutile (JCPS 21–1276). The red and blue triangles were used to index the anatase and rutile phase, respectively. To form the disordered phase that leads to producing the hydroxyl groups by breaking the Ti–O bond in the crystal lattice, the alkali metals (i.e., Li and Na) were used as reductants in EDA solution. For the R$_d$/A$_0$ TiO$_2$ case, the rutile phase XRD peaks disappeared with only anatase crystalline remaining. Inversely, the most dominant anatase phase in P25 becomes disordered, and the rutile crystalline remains intact in the R$_d$/A$_3$ TiO$_2$ product. The interface between the crystalline phase and reduced disordered region in R$_d$/A$_0$ and R$_d$/A$_3$ TiO$_2$ can efficiently separate the excitons and profoundly enhance photocatalytic performance [8].

The Ti–O–Ti bond can be broken down in the reduction process of raw P25 TiO$_2$, and the coordinated state of Ti$^{4+}$ decreases to Ti$^{3+}$. Fig. 2(b) shows EPR data among the two kinds of disordered TiO$_2$, exhibiting the unpaired electron in the compounds. This is indicative that the reduced TiO$_2$ samples produce Ti$^{3+}$ by catching the electron of the alkali metal. Moreover, the bonded O after forming Ti$^{3+}$ will capture the protons in the environment to neutralize the negative charge, producing Ti–OH. The Ti$^{3+}$ EPR peak is located around 350 and 361 mT, and shows the highest intensity in the R$_d$/A$_3$ TiO$_2$ sample (+19.8 & –13.8 a.u.) while the pristine P25 sample has no response. Compared with the XRD data, the Ti$^{3+}$ amount follows the order of R$_d$/A$_3$ > R$_d$/A$_0$ > P25, since the disordered phase proportion of anatase in R$_d$/A$_3$ TiO$_2$ is higher than the disordered rutile portion in the R$_d$/A$_0$. UV–VIS absorption spectroscopy was used to evaluate the light absorption ability for these materials. According to the UV–VIS results shown in Fig. 2(c), R$_d$/A$_0$ and R$_d$/A$_3$ TiO$_2$ retained broad and high-intensity visible absorption at wavelengths longer than 400 nm rather than poor visible absorption of traditional P25. Increasing the range and amount of photocatalyst light absorption is essential to the applications, which can give a robust photocatalytic performance in the environment.

To further characterize the TiO$_2$ chemical state, XPS analysis was
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Conducted, results are shown in Fig. 3. The two main peaks in Ti2p spectra were assigned to Ti2p$^{3/2}$ and Ti2p$^{1/2}$ by referring to the Zhao et. al (2014) report [26]. In terms of Ti2p, the peak position had been a lower shift to 457.95 eV in R$_o$/A$_d$ but did not change in R$_d$/A$_o$ TiO$_2$, when compared with pristine P25. The decrease of 0.26 eV binding energy in Ti2p of R$_o$/A$_d$, whose anatase portion is major, was due to the destruction Ti–O–Ti bond in the TiO$_2$ lattice. As shown in the Ti2p deconvolution spectra (Fig. 3a), the Ti$^{3+}$ reduced state in the R$_o$/A$_d$ and R$_d$/A$_o$ TiO$_2$ existed, also the Ti$^{3+}$ reduced state of R$_d$/A$_o$ TiO$_2$ sample was relatively more than that of R$_d$/A$_o$ TiO$_2$, which is match with the EPR spectra. Similarly, the Ti–O–H amount in the O1s spectra showed an obvious increment in R$_o$/A$_d$, confirmed with the deconvoluted peak at 531.4 eV of raw P25 O1s peak position. Based on the above XPS results, we concluded that both phase-selectively disordered reduced TiO$_2$ (R$_o$/A$_d$ and R$_d$/A$_o$) were successfully synthesized with OH groups. This approach is important for covalently microwave coating the TiO$_2$ films on the substrate and essential to give strong VOC photodegradation ability under visible light.

3.2. The hydroxylation of SiO$_2$ substrate

For most of the practical applications of the photocatalyst, proper loading can ensure the efficient function of the photocatalyst and retain long-term stability. The typical SiO$_2$ substrate was chosen as a loading medium due to its universal nature. To have hydroxyl groups on the substrate, surface modification is required to have a hydrophilic surface. The surface modification techniques of substrates have two general classes: plasma treatment (dry chemical method) and chemical etching (wet chemistry method). He et al. utilized an O$_2$ plasma for producing the hydrophilic property on their CNT (carbon nanotube) carpets.
However, even the amount of hydrophilic oxygen groups (C–O/OH) can be enriched by oxygen plasma processing, but it can be depleted through mild thermal treatment due to the relatively weak binding affinity between the attached functional group and their objects [27]. Further, the restoration phenomena of plasma-treated samples to the hydrophobic surface property with increasing time or temperature have been found frequently (Supplementary Fig. 7), so-called "aging" of the surface [28–30]. In the chemical etching approach, the surface defect can be produced by acid oxidation, thus converting to the hydroxyl group.

Moreover, the hydroxylation of the SiO2 substrate, a soak in the HNO3 solution can yield plenty of hydroxyl groups (Si–OH) by the etching of the substrate surface [32]. For covalent bonding TiO2 nanoparticles on the substrates, the SiO2 substrates need to be hydroxylated.

Fig. 3. The XPS spectra of the three kinds of TiO2 (a: Ti2p, and b: O1s). The Ti3+ chemical reduced state deconvoluted peaks were labelled in figure (a); besides, the O1s spectra are deconvoluted as green peaks. The corresponding XPS full spectra are provided in Supplementary Fig. 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 4. The hydroxylation process of SiO2 substrates. (a) WCA results of the initial SiO2 substrate, HNO3 etched SiO2 (E-Sub.), and HNO3 etched SiO2 followed by 30 s of O2 plasma treatment (Hydro. Sub.) from bottom to top; (b) and (c) shows the XPS spectra Si2p and O1s of the treated SiO2 substrate. The corresponding XPS full spectra are provided in Supplementary Fig. 2.
first, to conduct a condensation reaction among Si–OH and Ti–OH between the reduced TiO₂ and hydroxylated SiO₂ substrate. The hydroxylation process of the SiO₂ substrates was performed in two steps: 1) HNO₃ etching (E-Sub.), and 2) O₂ plasma treatment. The WCA and XPS analysis of the processed substrate in each step was performed as shown in Fig. 4. After nitric acid etching on the initial SiO₂ substrate surfaces, the WCA was decreased from 69.8° to 43.1° (Fig. 4a), and the binding energy of Si2p and O1s was shifted lower to 0.3 and 0.4 eV, respectively (Fig. 4b, c). The above changes in E-Sub indicated the Si–OH was produced through the breakage of the Si–O bonding of the SiO₂ substrate surface. To further convert the Si–O dangling bond into Si–OH and increase hydrophilicity, O₂ plasma was applied to E-Sub. As shown in Fig. 4a top image, the water drop was fully spread on the hydroxylated SiO₂ substrate, and no WCA can be measured. The XPS Si2p and O1s spectra of the hydroxylated SiO₂ substrate also were further shifted to lower binding energy due to the reduction by radicals in the O₂ plasma cloud.

The fully hydroxylated SiO₂ substrate maintained the superior hydrophilic surface and high percentage Si–OH on the substrate surface, which can uniformly distribute the TiO₂ suspension on the whole

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**Fig. 5.** The SEM images of P25 (a,d,g), R₆/A₆ (b,e,h), and R₆/A₀ (c,f,i) TiO₂ samples for describing the surface integrity. The raw powder state (a,b,c), covalent coated TiO₂ film top surface (d,e,f), and covalent coated TiO₂ film cross-section (g,h,i) images.

**Fig. 6.** The bonding state characterization of the TiO₂ powders and MW coated TiO₂ films. The Ti2p (a) and O1s (b) XPS spectra comparison of microwave coated TiO₂ film with initial powder state samples. The corresponding XPS full spectra are provided in Supplementary Fig. 4; (c) the ATR-FTIR spectra of R₆/A₀ MW TiO₂ films and initial powder. (“Microwave” is denoted as “MW” in the figure.)
substrate and produce plenty of condensation reaction sites. Finally, the combination of wet chemistry treatment and dry chemical processes gave a stable and permanent hydrophilic Si–OH enriched surface for covalently binding the disordered TiO$_2$ samples.

### 3.3. The covalent coating by rapid microwave treatment

The microwave oven has been applied in many organic synthesis reactions due to its effectiveness in inducing a condensation reaction between molecules which have permanent dipoles [33–35]. Polar molecules will be aligned in the electric field, and their alignment direction can be changed along with the electric field. The commercialized SIENO MAS-II microwave oven can generate 2.45 GHz microwaves, and it subsequently induces extreme agitation ($4.9 \times 10^9$ times) to the polar molecules. Therefore, the hydroxyl groups in the prepared R$_d$/A$_o$ and R$_o$/A$_d$ disordered and hydroxylated TiO$_2$ molecules can undoubtedly absorb the microwave irradiation and induce sufficient internal heat by agitation to initiate condensation reaction. The condensation reaction among the reduced TiO$_2$ and substrate was realized in a two-step. At the first, the SiO$_2$ substrate needs to exist sufficient permanent -OH groups which can be produced by an acid etching process. Then, the -OH groups on alkali metal reduced TiO$_2$ surface is supposed to form ether (-O-) bonding linkage through condensation reaction induced by microwave irradiation. Also, the -OH groups on reduced TiO$_2$ surface subsequently reacted, transfer to Ti–O–Ti for interconnections.

The TiO$_2$ samples were coated on the hydroxylated SiO$_2$ substrate after several minutes of microwave treatment. Comparisons among the SEM surface images show that microwave coated R$_d$/A$_o$ and R$_o$/A$_d$ TiO$_2$ had better surface integrity than P25 (Fig. 5 the second row, coated surface) under thinner coating conditions. However, it seems that the P25 layer contained most of the agglomerated particles and loose stacking. The raw powder TiO$_2$ materials (Fig. 5 the first row, powder) were fine particles, which were milled and treated by bath sonication to uniformly suspend TiO$_2$ in the solution. Additionally, the coating thickness is an essential parameter to evaluate the coating quality. Among the thin coating conditions, three types of TiO$_2$ candidates gave a 6.3–8.8 μm thickness, and the R$_d$/A$_o$ TiO$_2$ case retained a well-coating layer (Fig. 5 the third row, coated cross-section).

The intrinsic covalent binding can contribute to the good coating surface integrity among TiO$_2$ molecules and hydroxylated SiO$_2$ substrate. The XPS and Fourier-transform infrared spectroscopy (FTIR) analysis were performed to test the chemical binding state after rapid microwave coating treatment (Fig. 6). For characterizing the bonding information between the TiO$_2$ film and substrate, small amount TiO$_2$ suspension was dropped on the substrate and conducted microwave irradiation. The small loading amount of microwave treated TiO$_2$ is aimed to ensure the detection of film and hydroxylated substrate interface. Moreover, to determine whether the Ti–O–Si bonding and film-substrate interface information can be released during the spectroscopy survey, we collected the energy-dispersive X-ray spectroscopy (EDX) data.
Fig. 8. The SEM images of thick coated TiO2 films by rapid microwave treatment. The figures a), b), c), and d), e), f) represent film surface and cross-sectional images. Moreover, P25 (a, d), R6/A1 TiO2 (b, e), and R6/A1 TiO2 (c, f) are shown for comparison.

(EDS) data of MW R6/A6 TiO2 film samples through SEM analysis (Supplementary Fig. 3). Both Si, Ti, and O elements species uniformly distributed within the MW R6/A6 TiO2 film image. It indicated that the state information of Si and Ti elements at the interface between film and substrate could be detected under X-ray irradiation.

As shown in Fig. 6 a of XPS Ti2p spectra, the Ti–O–Si peak, which stays around deconvoluted 458.9 eV were indicated as a blue line peak with labels for the MW R6/A6 and R6/A6 TiO2 film sample [36]. Then, the Ti2pO2–2 of MW R6/A6 and R6/A6 TiO2 film showed 0.54, 0.90 eV binding energy shifting upward to 458.75 and 458.85 eV in comparison with the raw R6/A6 and R6/A6 TiO2 materials, respectively. However, no Ti–O–Si peak signal and Ti2p shift peak were observed in the MW P25 TiO2 film case. The above peak shifting phenomena can be assigned as the formation of Ti–O–Si and reconnection of Ti–O–Ti after the condensation reaction between OH groups. Due to the higher electronegativity of Si (1.90, Pauling scale) than Ti (1.54, Pauling scale), the hydroxyl groups on the surface can be covalently bonded to each other by the condensation reaction to form Ti–O–Ti among inter-particles. In this way, thick TiO2 loading can be realized rather than around the 1–10 µm thickness reported in most of the current literature. As shown in Scheme 2, the Ti–O–H groups of the disordered surface were connected through a condensation reaction of hydroxyl groups by forming ether O bonds.

To investigate whether the phase change happened in the reduced R6/A6, R6/A6, and P25 TiO2 films after microwave treatment, the thin and thick microwave coated TiO2 films were analyzed by XRD (Fig. 7). As shown in the XRD spectra Fig. 7b and c, the amorphous, disordered rutile in R6/A6 TiO2 and disordered anatase in R6/A6 TiO2 were not changed, maintaining the amorphous states. It was also observed that the TiO2 peak intensities were increased in the thicker coating than the thin coating cases. Besides, the SiO2 substrate peak intensity also follows the same trends, which decreased in the thick sample cases. Therefore, we provided the SiO2 substrate XRD pattern to track the substrate diffraction peaks. In Fig. 7 (d) SiO2 substrate XRD pattern, the main peak at 69.15° belongs to (100) planes of Si. And the other lower intensity peaks are associated with the silicon oxide species [38]. Besides, the reflection peak at 33° of pristine SiO2 substrate in Fig. 7 d is associated with the forbidden (002) reflection of Si surface through multiple diffractions and Renninger effect [39,40]. It can appear under XRD azimuth (α angle) rotation measurement after the substrate surface crystal was damaged during wet and dry chemical hydroxylation processes treatments. Subsequently, it disappears in the further TiO2 film microwave coating treatments process with the soft thermal heating. Also, the peaks near 62° and 67° in Fig. 7 a, b and d arose from the Cu and W in the X-ray sources. In Fig. 7 e, due to the utilization of Ni filter during XRD measurement, the Si (004) peak at around 69° became broader and the 62° and 67° peaks from X-ray sources were disappeared [41].

After obtaining the thick-coated samples, SEM images were collected again to characterize the surface state and thickness (Fig. 8). After the microwave treatment coating, the loosely attached or uncoated TiO2 particles were removed by an airflow gas gun. According to the top view images of the coated surface, the surface integrity of R6/A6 (Fig. 8b) and R6/A6 TiO2 (Fig. 8c) is retained better than P25 in the thick film (Fig. 8a). Besides, the R6/A6 TiO2 achieved 38.1 µm thickness with dense packing, and R6/A6 TiO2 realized 22.2 µm, as shown in (Fig. 8e and f). The P25 microwave coated film has a lower thickness value of about 9.6 µm (Fig. 8d), which is mainly due to weak interconnection bonds between particles to hold on the substrate surface. The phenomena further indicate that the phase selectively reduced TiO2 can give high-quality coating film by forming the covalent interconnection bonding.

3.4. The thick TiO2 loading through rapid microwave coating

To achieve a higher TiO2 loading amount while maintaining a good coating film, the connection between TiO2 particles is necessary. The phase-selectively disordered R6/A6 and R6/A6 TiO2 have disordered rutile and disordered anatase phases, respectively. In the region of the disordered phase, the hydroxyl groups on the surface can be covalently bonded to each other by the condensation reaction to form Ti–O–Ti among inter-particles. In this way, thick TiO2 loading can be realized rather than around the 1–10 µm thickness reported in most of the current literature. As shown in Scheme 2, the Ti–O–H groups of the disordered surface were connected through a condensation reaction of hydroxyl groups by forming ether O bonds.
Moreover, thick MW-coated R\textsubscript{d}/A\textsubscript{0} TiO\textsubscript{2} film in comparison with the R\textsubscript{d}/A\textsubscript{0} TiO\textsubscript{2} easily loosened the stacking according to the cross-sectional image texture. The loose stacking may be caused by orientation randomness of the large portion of the disordered anatase amorphous phase in the R\textsubscript{d}/A\textsubscript{0} TiO\textsubscript{2}. Fig. 9 shows the magnified images of thickly coated R\textsubscript{d}/A\textsubscript{0} TiO\textsubscript{2} cross-section. We can see that the R\textsubscript{d}/A\textsubscript{0} TiO\textsubscript{2} particles were tightly stacked on the substrate. These SEM images verified the good coating ability of R\textsubscript{d}/A\textsubscript{0} and R\textsubscript{o}/A\textsubscript{d} TiO\textsubscript{2} under rapid microwave irradiation treatment.

Further XPS analysis of the thick MW-coated TiO\textsubscript{2} films confirmed the description of Ti–O–Ti interconnection formation. As shown in Fig. 10a, a slight shift of the Ti\textsubscript{2p\textsubscript{3/2}} peak upward (~0.2 eV) is due to a Ti–O–Ti bond reformation produced from Ti–O–H state after condensation under microwave conditions. The reverse phenomena were observed in the R\textsubscript{o}/A\textsubscript{d} TiO\textsubscript{2} powder XPS when compared with pristine P25 due to the reduced state (Ti\textsuperscript{3+}) formation, shown in Fig. 3a. Furthermore, the O1s peak position among the thick MW-coated TiO\textsubscript{2} film samples was almost the same (Fig. 10b). These XPS results further proved the Ti–O–Ti forms an interconnection in the MW-coated R\textsubscript{d}/A\textsubscript{0} and R\textsubscript{o}/A\textsubscript{d} TiO\textsubscript{2} thick film samples.

3.5. Microwave-coated TiO\textsubscript{2} film adhesion force

To quantitatively characterize the coated film binding strength on the SiO\textsubscript{2} substrate, the Mecmesin MultiTest 2.5 Tester was used. The transparent adhesive tape (12-mm wide) was applied in the measurement. The force was conducted by pulling the attached tape on the MW-coated film at a constant speed (10 mm/min), with a steady increase until the coated film detached from the substrate with the attached adhesive tape. The resulting force was recorded during the process (Fig. 11). The R\textsubscript{d}/A\textsubscript{0} TiO\textsubscript{2} MW-coated film sample shows the highest adhesion force (15.2 N) among the three types of TiO\textsubscript{2} samples. This may be due to the ability of the R\textsubscript{d}/A\textsubscript{0} TiO\textsubscript{2} MW-coated film to retain a relatively better packing quality compared to the R\textsubscript{o}/A\textsubscript{d} TiO\textsubscript{2} film case (Figs. 5 and 8).

Normally, the crystalline phase will lose its regular lattice structure after transforming to the disordered amorphous state. In this work, even though the disordered TiO\textsubscript{2} phase is expected to form covalent bonds for maintaining film integrity and mechanical strength, a high portion of disordered phase may hinder the contact between TiO\textsubscript{2} particles and substrate for bond formation. In the pristine commercial P25 TiO\textsubscript{2}
powder, the composition is around 70% crystalline anatase and 30% crystalline rutile. Therefore, R_d/A_d and R_d/A_4 TiO_2 powder have about 30% and 70% disordered phase, respectively. Amorphous solid is known as that a solid which lacks long-range order, non-spherical and shape inhomogeneity. The irregularity stacking of disordered phases will result in random packing and less inter-particles connection [42]. Further, the disordered amorphous state TiO_2 region may reduce the covalent Ti–O–Ti interconnection formation. Therefore, due to a high proportion of amorphous anatase phase existence (70%), the loose stacking of the MW-coated R_d/A_3 TiO_2 film resulted with a 7.1 N adhesion force on the SiO_2 substrate. The above discussion can be supported by the Brunauer–Emmett–Teller (BET) measurements data [7, 14], as listed in the Supplementary Table 1. The BET specific surface area, total pore volume and mean pore size increased following P25 (0% amorphous), R_d/A_3 (30% amorphous rutile) and R_d/A_4 (70% amorphous anatase). Both R_d/A_4 and R_d/A_4 TiO_2 were synthesized from pristine P25. Therefore, the BET data indicated the TiO_2 particle irregularity is increased after the disordered amorphous phase generates by alkali-metal EDA solution. Besides, the R_d/A_4 and R_d/A_4 TiO_2 open-pore amount and pore size are also correlated with the amorphous TiO_2 portion. For forming condensation reaction and TiO_2 adhesion on the substrate, based on the Supplementary Fig. 6 and Supplementary Table 1, the hydroxylated TiO_2 powder (disordered portion) and BET including pore volume are supposed to have a linear relationship, which means that contact areas of R_d/A_4 TiO_2 film is larger than that of R_d/A_3 film. Finally, the more severe particle irregularity and elevated pore size and amount in R_d/A_4 are supposed to result in lower film adhesion force on the SiO_2 substrate than R_d/A_3 TiO_2. We prepared the model illustration of TiO_2 film particle interconnection of R_d/A_4 and R_d/A_4 for the understanding (Supplementary Fig. 6). Moreover, MW-coated P25 had the lowest value (0.9 N) adhesion forces due to the difficulty to form covalent bonding between TiO_2 particles with SiO_2 substrate, and TiO_2 particles themselves in the coated layer.

The covalent binding formation after microwave irradiation in the selectively reduced R_d/A_4 and R_d/A_4 TiO_2 MW-coated film can significantly enhance the adhesion ability and maintain better integrity of the coated film on the substrate. Interestingly, the remaining crystalline phases can act as an efficient charge separation site but also causes dense stacking in the MW-coated film to induce the covalent interconnection by condensation reactions.

### 3.6. Photocatalytic performance of the microwave coated R_d/A_4 TiO_2 film

To estimate the photocatalysis activity of the binder-free microwave coated TiO_2 film, the degradation of typical VOC compounds, acetaldehyde and toluene, have been performed under 420–680 nm visible light generated by a 100 W white LED lamp.

The microwave covalently coated R_d/A_4 TiO_2 film always shows a higher degradation percentage compared with the traditional dip-coating film sample (Fig. 12a). The acetaldehyde has degraded 20% and 40% by the MW R_d/A_4 film after 2 h and 4 h, respectively. The covalently coated R_d/A_4 TiO_2 film could maintain good integrity in the gas reaction chamber, while traditional dip-coating samples inevitably detached and lost catalytic activity. We use our group’s previous films in this setup, which provided a 3.46 mmol/g/h H_2 generation rate due to photocatalytic water splitting (higher than most of the previous works of literature) by R_d/A_4 TiO_2 and 4.0 μmol/g/h CH_4 production from CO_2 reduction (higher than current even metal-doped P25 TiO_2 by R_d/A_4 TiO_2 [8,14]. Besides, the R_d/A_4 TiO_2 film exhibited faster degradation speed than P25 MW TiO_2 film (Fig. 12b). To further confirm the versatile photodegradation strength, we collected the toluene gas degradation by the R_d/A_4 MW TiO_2 film under visible light. It can be seen that the R_d/A_4 MW TiO_2 film stepwise reduced the toluene amount under visible light irradiation and realized around 90% degradation after 9 h, as shown in Fig. 12c. To investigate the photodegradation active species, we conducted the EPR analysis to detect hydroxyl radical (•OH) reactive oxygen species. The R_d/A_4 MW TiO_2 film can generate more active •OH than P25 TiO_2 for participating in VOCs degradation reactions (Fig. 12d). Moreover, we determined the recycling test of R_d/A_4 MW TiO_2 film toluene degradation to examine photocatalytic stability. As presented in Fig. 12e, the toluene degradation amount of the R_d/A_4 MW TiO_2 film was around 80% after 7 h irradiation, which is confirmed with 5 recycling tests. By utilizing the scalable, efficient, and robust microwave covalent coating technique, a long-term good photocatalytic property will be realized. Furthermore, the microwave covalent binder-free coating strategy can be applied in other catalysts to maintain photocatalytic activity.
4. Conclusions

The binder-free and the visible-light-driven phase-selectively reduced TiO$_2$ (R$_x$/A$_y$ and R$_z$/A$_{3-y}$) films covalently bonded on the SiO$_2$ substrate were successfully prepared through a microwave irradiation method. This is the first known successful attachment of a phase-selectively reduced TiO$_2$ photocatalyst on the universal SiO$_2$ substrates through a rapid microwave coating method, showing a highly adhesive covalently coated film. The covalent bonding of Ti–O–Si between reduced TiO$_2$ and the hydroxylated SiO$_2$ substrate was formed through a condensation reaction between Ti–OH and Si–OH under microwave processing. Furthermore, similarly, Ti–O–Ti bonding between the disordered TiO$_2$ nanoparticles was formed to give a higher thickness packing film. By the condensation reaction strategy using the microwave, binder-free R$_x$/A$_y$ TiO$_2$ MW-coated film with a high thickness (38 μm) was achieved while maintaining surface integrity. The covalent bond formation of Ti–O–Si and Ti–O–Ti in R$_x$/A$_y$ TiO$_2$ MW-coated film produced the firm adhesion TiO$_2$ film on the SiO$_2$ substrate. Further, the VOC degradation performance using the MW-coated R$_x$/A$_y$ TiO$_2$ was realized with 40% removal efficiency within 4 h, which is faster to decompose acetaldehyde than normal dip-coating films. This microwave treated TiO$_2$ coating showed significant volatile organic compounds abilities under visible light irradiation. The microwave coated selectively reduced R$_x$/A$_y$ TiO$_2$ film realized around 75% acetaldehyde degradation within 12 h and almost 90% toluene degradation after 9 h, also retains stable photodegradation performance during the cycling test. This study proposes a scalable, cost-effective, and rapid method to manufacture good and long-term stable binder-free TiO$_2$ photocatalyst films, and also strengthens the application as a photocatalyst under severe conditions.

CRediT authorship contribution statement

Yongguang Luo: Conceptualization, Writing - review & editing, Project administration. Lingling Wang: Data curation, Formal analysis. Yosep Hwang: Data curation, Formal analysis. Jianmin Yu: Data curation, Formal analysis. Jinsun Lee: Data curation, Formal analysis. Yang Liu: Data curation, Formal analysis. Hongdan Wang: Data curation, Formal analysis. Joongsoo Kim: Data curation, Formal analysis. Hyun Yong Song: Data curation, Formal analysis. Hyoysung Lee: Conceptualization, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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