TiO$_x$N$_y$ Modified TiO$_2$ Powders Prepared by Plasma Enhanced Atomic Layer Deposition for Highly Visible Light Photocatalysis

Yan-Qiang Cao, Xi-Rui Zhao, Jun Chen, Wei Zhang, Min Li, Lin Zhu, Xue-Jin Zhang, Di Wu & Ai-Dong Li

In this work, TiN film deposited by plasma enhanced atomic layer deposition (PEALD) is adopted to modify the commercial anatase TiO$_2$ powders. A series of analyses indicate that the surface modification of 20, 50 and 100 cycles of TiN by PEALD does not change the morphology, crystal size, lattice parameters, and surface area of TiO$_2$ nano powders, but forms an ultrathin amorphous layer of nitrogen doped TiO$_2$ (TiO$_x$N$_y$) on the powder surfaces. This ultrathin TiO$_x$N$_y$ can facilitate the absorption of TiO$_2$ in visible light spectrum. As a result, TiO$_x$N$_y$ coated TiO$_2$ powders exhibit excellent photocatalytic degradation towards methyl orange under the visible light with good photocatalytic stability compared to pristine TiO$_2$ powders. TiO$_x$N$_y$ (100 cycles PEALD TiN) coated TiO$_2$ powders exhibit the excellent photocatalytic activity with the degradation efficiency of 96.5% in 2 hours, much higher than that of pristine TiO$_2$ powder of only 4.4%. These results clearly demonstrate that only an ultrathin surface modification layer can dramatically improve the visible light photocatalytic activity of commercial TiO$_2$ powders. Therefore, this surface modification using ALD is an extremely promising route to prepare visible light active photocatalysts.
prospects in various applications, such as lithium ion batteries\textsuperscript{27,28}, supercapacitors\textsuperscript{29–31}, catalysis\textsuperscript{32,33}, and solar energy conversions\textsuperscript{34}. Plasma enhanced ALD (PEALD), employing plasma as one precursor, has shown some merits over conventional thermal ALD (T-ALD), such as higher film density, lower impurity, higher growth rate, better electronic properties. Moreover, less energy is required to drive the surface reaction because of the high reactivity of plasma species, resulting in a lower deposition temperature\textsuperscript{35}.

Various N-doped TiO\textsubscript{2} nanomaterials, which exhibit highly visible light photocatalytic performance, have been successfully synthesized. However, the effect of ultrathin N-doped TiO\textsubscript{2} surface coating/modification on visible light photocatalysis of TiO\textsubscript{2} has not been well researched. Herein, PEALD was adopted to deposit ultrathin TiN film on TiO\textsubscript{2} powders. The deposited TiN film would be oxidized into TiO\textsubscript{x}N\textsubscript{y} (N doped TiO\textsubscript{2}) when exposed to the air, achieving TiO\textsubscript{x}N\textsubscript{y} coated TiO\textsubscript{2} after PEALD TiN coating. This ultrathin TiO\textsubscript{x}N\textsubscript{y} coating can facilitate the visible light absorption of TiO\textsubscript{2}. Correspondingly, the TiO\textsubscript{x}N\textsubscript{y} coated TiO\textsubscript{2} powders exhibit significantly enhanced visible light photocatalytic activity towards methyl orange (MO) and phenol degradation.

**Results**

Bui et al. have reported that the surface of deposited TiN film would be oxidized when exposed to the air\textsuperscript{26}. Therefore, the XPS spectra of the TiN film deposited by PEALD on silicon were firstly conducted to explore the surface chemistry of as-deposited TiN, as shown in Fig. S1. Both Ti-O and Ti-N bonding can be detected in Ti 2p spectra, confirming the formation of TiO\textsubscript{x}N\textsubscript{y} on the PEALD TiN surface, in consistent with reported literature\textsuperscript{36}. Therefore, it can be speculated that TiO\textsubscript{x}N\textsubscript{y} coated TiO\textsubscript{2} composite can be achieved here after coating ultrathin PEALD TiN on TiO\textsubscript{2} surface.

Next, the surface chemical nature of PEALD TiN coated TiO\textsubscript{2} catalyst was also characterized by XPS. XPS spectra were fitted with Gaussian-Lorentzian (G-L) functions after smart-type background subtraction. Figure 1a shows the N 1s spectra of pristine TiO\textsubscript{2} and TiO\textsubscript{x}N\textsubscript{y} coated TiO\textsubscript{2}. It can be found that pristine TiO\textsubscript{2} only exhibits a weak peak at ~400.1 eV, which can be assigned to absorptive nitrogen molecules\textsuperscript{37,38}. After PEALD TiN coating, there appears a new peak at 396.5 eV, corresponding to the formation of N-Ti bonds\textsuperscript{37,38}. And the intensity of N-Ti is enhanced with increasing the PEALD TiN cycles. In Ti 2p spectra of pristine TiO\textsubscript{2} (Fig. S2a), the doublet at 464.4 and 458.7 eV can be assigned to Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} peaks of Ti-O bonds with the spin orbit splitting energy of 5.7 eV, consistent with the value of TiO\textsubscript{2}\textsuperscript{31}. Besides, there are two weak doublet peaks at 462.9 eV and 457.2 eV can also be detected, which can be assigned to Ti\textsuperscript{3+} defects on the surface\textsuperscript{39}. More Ti\textsuperscript{3+} can be introduced onto the surface of TiO\textsubscript{2} after PEALD TiN coating. Therefore, the surface Ti\textsuperscript{3+}/Ti ratio increases with increasing PEALD deposition cycles, as shown in Fig. 1d. All the samples show the similar O 1s spectra with main O-Ti bonds of TiO\textsubscript{2} at 529.9 eV, as shown in Fig. 1c and Fig. S2, the peak at 532.4 eV related to the -OH
on the surface can also be detected. Figure 1d illustrates the plots of surface Ti$^{3+}$/Ti ratio and N content versus the PEALD TiN cycles, it can be seen that both surface Ti$^{3+}$ and N content increase with PEALD TiN coating. Combined with XPS data of PEALD TiN film on Si (Fig. S1), it can be concluded that TiO$_x$N$_y$ coating layer was formed on TiO$_2$ surface after ultrathin PEALD TiN coating. It has been proved in previous literatures that both Ti$^{3+}$ and N sites can narrow the band gap of TiO$_2$. Therefore, it can be speculated that a much smaller band gap can be achieved for the TiO$_x$N$_y$ layer, promoting the visible light absorption.

Figure 2 shows the Raman spectra of pristine TiO$_2$ and TiO$_2$@50TiN prepared by PEALD. According to the previously reported data, the anatase phase of TiO$_2$ has six Raman bands at 144 cm$^{-1}$ (E$_g$), 197 cm$^{-1}$ (E$_g$), 399 cm$^{-1}$ (A$_1g$), 513 cm$^{-1}$ (B$1g$) and 639 cm$^{-1}$ (E$_g$), and the rutile phase has four Raman bands at 143 cm$^{-1}$ (B$1g$), 447 cm$^{-1}$ (E$_g$), 612 cm$^{-1}$ (A$_1g$), and 826 cm$^{-1}$ (B$_2g$). Both samples here present Raman spectra the same as the pure anatase phase, with no peaks related to the rutile phase. More importantly, the most remarkable feature is that the predominant peak position (E$_g$) undergoes a blue shift from 141.1 cm$^{-1}$ to 144.0 cm$^{-1}$ after TiO$_x$N$_y$ modification. Previous literatures have demonstrated that the N doping in TiO$_2$ can result in the blue shift for E$_g$ mode. Therefore, the slight blue shift here can be ascribed to the small amount TiO$_x$N$_y$ formation on the TiO$_2$ surface.

FESEM was performed to observe the morphology and crystal size of TiO$_2$ and TiO$_x$N$_y$ coated TiO$_2$ powders, as shown in Fig. S3. It can be found that the pristine TiO$_2$ powders show well dispersed sphere of around 10–30 nm and aggregate together. After PEALD deposition, it can be seen that ultrathin TiO$_x$N$_y$ coating has no obvious effect on the morphology and crystal size of TiO$_2$. All the samples exhibit the similar morphology. In order to thoroughly characterize the microstructure change of TiO$_2$ after surface coating, high resolution transmission electron microscopy (HRTEM) was also applied to observe the microstructure of TiO$_2$ and TiO$_2$@50TiN. It can be found that pristine TiO$_2$ exhibits good crystallinity with a sharp well-ordered surface (Fig. 3a). After 50 cycles TiN coating, there is an amorphous layer formed on the TiO$_2$ surface of ~1 nm (Fig. 3b). It is supposed to be the ultrathin TiO$_x$N$_y$ coating formed after PEALD TiN deposition. Besides, both samples show a lattice spacing of 0.35 nm, which corresponds to the (101) planes of anatase TiO$_2$. Therefore, it can be concluded from XPS spectra, Raman spectra, and HRTEM images that an amorphous ultrathin TiO$_x$N$_y$ was formed on the TiO$_2$ surface.

The corresponding XRD patterns of pristine TiO$_2$ and TiO$_2$N$_x$ coated TiO$_2$ powders are shown in Fig. 4. All the samples exhibit the similar characteristic diffraction peaks at 25.4°, 37.9°, 48.0°, 54.1°, 63.0° etc., indicating good agreement with standard anatase TiO$_2$ (JCPDS No. 71-1168). Besides, there are no other peaks such as Ti-N detected in the samples. In addition, the average crystal size and lattice parameters of different samples can be determined by XRD using Scherrer equation, as listed in Table 1. It can be found that the crystal size of all the samples is estimated to be around 19 nm, in agreement with SEM images. In addition, all the samples show nearly the same lattice parameters, indicating that ultrathin TiO$_2$N$_x$ surface coating does not change the crystal size and average unit cell dimension. Moreover, Nitrogen adsorption-desorption isotherms were also performed to measure the surface area of TiO$_2$ powders, it can be found that all the samples exhibit nearly the same BET surface area of around 113 m$^2$/g (Table 1 and Fig. S4).

Therefore, it can be concluded that ultrathin TiO$_2$N$_x$ coating can be formed on the surface of TiO$_2$ powders. And this ultrathin surface coating doesn’t show obvious change in the morphology, crystal size, lattice parameters, and surface area of TiO$_2$ nano powders. However, it can be clearly seen that there is a vivid color change of TiO$_2$ powders from white to yellow after ultrathin TiO$_2$N$_x$ surface modification, as shown in Fig. 5a,b. Hence, UV-Vis diffuse reflectance spectra were conducted to explore the influence of ultrathin TiO$_2$N$_x$ surface coating on the visible light absorption of TiO$_2$ powders, as shown in Fig. 5c. For comparison, the spectrum of
pristine TiO₂ powder is also illustrated. The absorption edge of pristine TiO₂ is approximately 371 nm and does not show noticeable absorption in the visible region. However, all the TiOₓNᵧ coated TiO₂ samples exhibit distinct and meaningful absorption in the visible range from 390 to 500 nm, consistent with previous experimental results²⁰,⁴⁴. Furthermore, more TiOₓNᵧ coating can induce more visible light absorption. For the indirect bandgap semiconductor, the relation between the absorption edge and the photon energy (hν) can be written as follows: 
\[(\alpha h\nu)^{1/2} = A(h\nu - E_g)\]
where A is the absorption constant of the indirect band gap semiconductor material. The absorption coefficient (\(\alpha\)) is determined from the scattering and reflectance spectra according to Kubelka-Munk theory. The indirect bandgap energies estimated from the intercept of the tangents to the plots are presented in Fig. 5d. The bandgap of pristine TiO₂ powders is determined to be 3.24 eV. TiOₓNᵧ coated TiO₂ (100 cycles TiN) exhibits two bandgaps. The larger bandgap of 3.18 should be related to the TiO₂ supporters. Besides, a smaller

| Sample          | \(a_0\) (Å) | \(c_0\) (Å) | Crystallite size (nm) | BET surface area (m²/g) |
|-----------------|-------------|-------------|-----------------------|--------------------------|
| TiO₂            | 3.78        | 9.54        | 19.03                 | 112.6                    |
| TiO₂@20TiN      | 3.78        | 9.55        | 19.27                 | 112.6                    |
| TiO₂@50TiN      | 3.78        | 9.53        | 18.98                 | 111.7                    |
| TiO₂@100TiN     | 3.78        | 9.55        | 18.55                 | 115.2                    |

Table 1. Parameters of pristine TiO₂ and TiOₓNᵧ coated TiO₂ powders.

Figure 3. TEM images of (a) pristine TiO₂ and (b) TiOₓNᵧ coated TiO₂ (TiO₂@50TiN).

Figure 4. XRD patterns of (a) pristine TiO₂, (b) TiO₂@20TiN, (c) TiO₂@50TiN, and (d) TiO₂@100TiN.
band gap of 1.64 eV can be assigned to the band gap value of TiO$_x$N$_y$ coating layer. Therefore, it can be concluded that ultrathin TiO$_x$N$_y$ surface modification layer with smaller band gap can facilitate the visible light absorption of TiO$_2$ powders.

The photocatalytic activity of TiO$_x$N$_y$ coated TiO$_2$ has been investigated carefully through degrading methyl orange (MO) under visible light irradiation, as shown in Fig. 6. All the samples exhibit negligible adsorption capacity of MO, as shown in Fig. S5. Meanwhile, almost no degradation of MO is observed in the absence of catalyst, indicating that MO is stable under visible light irradiation. As shown in Fig. 6a, pristine TiO$_2$ shows very limited photocatalytic activity of ~4.4% in 120 min under visible light irradiation due to its large band gap. However, after ultrathin TiO$_x$N$_y$ coating with only 20 cycles PEALD TiN, a much-improved photocatalytic activity of ~57.3% is achieved. Moreover, the photocatalytic activity improves with increasing the TiN coating cycles, with the TiO$_2$@100TiN exhibiting the highest degradation efficiency of ~96.5%. The experimental results were also fitted to the pseudo-first-order kinetics. At low initial pollutant concentration, the rate constant $k$ was given by $\ln\left(C_t/C_0\right) = -kt$. Here, $k$ and $t$ represent the first-order rate constant (h$^{-1}$), and the irradiation time (h), respectively. $C_0$ is the initial concentration of MO, and $C_t$ is the concentration at reaction time of $t$. The corresponding plots of $-\ln(C_t/C_0)$ versus the irradiation time for photodegradation of MO are shown in Fig. 6b. A linear relation between $-\ln(C_t/C_0)$ and the irradiation time has verified that the photodegradation of MO using TiO$_x$N$_y$ coated TiO$_2$ catalyst follows the first-order kinetics. TiO$_x$N$_y$ coated TiO$_2$ exhibit the kinetic constants of 1.62 h$^{-1}$ (TiO$_2$@100 TiN), 0.82 h$^{-1}$ (TiO$_2$@50 TiN), and 0.45 h$^{-1}$ (TiO$_2$@20 TiN), which are much larger than pristine TiO$_2$ of 0.023 h$^{-1}$. Apparently, ultrathin TiO$_x$N$_y$ coating can greatly improve the visible light photodegradation efficiency of MO due to its absorption in visible light spectrum. In order to evaluate the stability of the photocatalyst, the recycling experiments about MO photodegradation were performed with TiO$_2$@50TiN catalyst. As shown in Fig. 6c, the photocatalytic activity of TiO$_2$@50TiN exhibits an extremely limited decline for three times. The degradation efficiency of MO solution is nearly the same for three recycling experiment under 120 min irradiation, exhibiting wonderful recycling ability.

Moreover, colorless phenol was also adopted to evaluate the visible photocatalytic performance of TiO$_2$@50TiN. As shown in Fig. 6d, it can be seen that both pure TiO$_2$ and TiO$_2$@50TiN exhibit negligible absorption for phenol molecule in the darkness. Pure TiO$_2$ powder shows no photocatalytic activity towards degrading phenol molecule. There is hardly any degradation of phenol for TiO$_2$ with 2 h visible irradiation. However, after modification with 50 cycles of TiN, the TiO$_2$@50TiN powders exhibit visible photocatalytic activity for phenol.
around 34.3% of phenol can degrade in 2 h. Therefore, it can also be demonstrated that surface modification with PEALD TiN can greatly improve the visible photocatalytic activity of TiO$_2$.

As reported previously, visible light active photocatalytic N-doped TiO$_2$ can be achieved by annealing TiO$_2$ under NH$_3$ flux at high temperature$^{17}$. Thus, a control experiment using TiO$_2$ photocatalyst treated by NH$_3$ plasma at 360 °C was also performed, as shown in Fig. 7. It can be seen that NH$_3$ plasma treatment can only slightly improve the photocatalytic activity of TiO$_2$, the photocatalytic activity is much lower than the TiO$_x$N$_y$. 

---

**Figure 6.** (a) Photocatalytic degradation of MO by using TiO$_2$ and TiO$_x$N$_y$ coated TiO$_2$ catalysts prepared by PEALD under visible-light irradiation, (b) the corresponding -ln(C$_t$/C$_0$) vs. time curves, (c) three cycles of MO degradation for TiO$_2$@50TiN in 120 min, (d) photocatalytic degradation of phenol by using TiO$_2$ and TiO$_2$@50TiN catalysts under visible-light irradiation.

**Figure 7.** Photocatalytic degradation of MO by using NH$_3$ plasma treated TiO$_2$ and TiO$_x$N$_y$ coated TiO$_2$ catalysts under visible-light irradiation.
coated sample. It can be concluded that, in order to achieve highly visible light active N-TiO2 based photocatalyst, it is easier and more effective to coat TiO\textsubscript{x}Ny thin film on TiO\textsubscript{2} than replacing O with N under NH\textsubscript{3} flux at high temperature.

The photocatalytic mechanism of TiO\textsubscript{x}Ny coated TiO\textsubscript{2} is also proposed. There are a large number of reports focusing on the photocatalytic activity mechanism of N-doped TiO\textsubscript{2}. It has been demonstrated that both N doping and Ti\textsuperscript{3+} can contribute to narrowing the band gap of TiO\textsubscript{2}\textsuperscript{21}, the band gap alignment and charge transfer of TiO\textsubscript{2}@TiO\textsubscript{x}Ny is shown in Fig. 8. It is widely accepted that N doping can form a new substitution N 2p band above the O 2p valance band. While the Ti\textsuperscript{3+} sites exhibit the 3d orbital in the band gap, which is found to below the bottom of the conduction band\textsuperscript{21}. Therefore, TiO\textsubscript{x}Ny coated TiO\textsubscript{2} exhibits a small band gap value of \approx 1.64 eV here, which can absorb the visible light. Upon visible light irradiation, electrons can transfer into the conduction band of TiO\textsubscript{2} and Ti\textsuperscript{3+} sites, reducing O\textsubscript{2} to form O\textsubscript{2} radical. Both radicals are responsible for the degradation of MO under visible light, as shown in Fig. 8. It should be noted that only an ultrathin TiO\textsubscript{x}Ny coating here can significantly improve the visible light photocatalytic activity of commercial TiO\textsubscript{2} powders. Therefore, maybe it's needless to synthesize the monolithic N-doped TiO\textsubscript{2} composites, adopting ultrathin TiO\textsubscript{x}Ny coating can be an effective approach to prepare visible light active photocatalysts. In addition, surface coating or modification using ALD technology can be easily extended to other supporters, such as porous materials, nanowires, and so on.

Conclusions
In summary, a novel and facile approach to prepare ultrathin TiO\textsubscript{x}Ny coated TiO\textsubscript{2} composite by PEALD has been developed to promote the application of TiO\textsubscript{2} photocatalyst under visible light. An ultrathin TiO\textsubscript{x}Ny film can be formed perfectly on the surface of TiO\textsubscript{2} powders using PEALD. Introducing ultrathin TiO\textsubscript{x}Ny coating with smaller bandgap of \approx 1.64 eV can facilitate the absorption of TiO\textsubscript{2} in visible light spectrum. As a result, this ultrathin TiO\textsubscript{x}Ny coating can extraordinarily improve the photocatalytic activity of commercial TiO\textsubscript{2} powders towards degrading both MO and phenol under visible light. TiO\textsubscript{2}@100TiN prepared by PEALD photocatalyst could nearly degrade MO completely (\approx 96.5%) in 120 min under visible light irradiation, while pristine TiO\textsubscript{2} shows very weak photoactivity of only 4.4%. Moreover, TiO\textsubscript{x}Ny coated TiO\textsubscript{2} photocatalyst is quite stable and reusable. Therefore, this surface modification using PEALD is an extremely promising route that could also be extended to other supporters to prepare visible light active photocatalysts. These results presented in this work could open a new window to the future design and synthesis of visible light photocatalysts.

Methods
Chemicals. In ALD process, Titanium tetrachloride (TiCl\textsubscript{4}) (5N, Suzhou Fornano Corporation Ltd.) and NH\textsubscript{3} plasma were used as Ti precursor and Nitrogen sources, respectively. High pure N\textsubscript{2} (5N) and Ar (5N) were used as carrier and purge gas. Commercial anatase TiO\textsubscript{2} powders (Nanjing Haitai nano materials Co) with diameter of \approx 20 nm were used as supporters. Methyl Orange (MO, C\textsubscript{14}H\textsubscript{14}N\textsubscript{3}NaO\textsubscript{3}S, J&K Scientific) and phenol was prepared into 4 mg L\textsuperscript{-1} with Milli-Q water.

Preparation of TiO\textsubscript{x}Ny modified TiO\textsubscript{2} powder. TiO\textsubscript{2} powders were loaded into a special powder container with porous mesh. The schematic diagram of coating TiO\textsubscript{2} powders by PEALD TiN is shown in Fig. S6. TiCl\textsubscript{4} and NH\textsubscript{3} plasma were used as precursors for TiN deposition. Plasma power and NH\textsubscript{3} gas flow rate were 2500 W and 160 sccm, respectively. And it is a remote plasma source. Pure N\textsubscript{2} (5N) and Ar (5N) were used as carrier/purge gas for TiCl\textsubscript{4} and NH\textsubscript{3} plasma, respectively. Various cycles of TiN were deposited onto TiO\textsubscript{2} surface at 360\degree C, where one cycle consisted of 2 s TiCl\textsubscript{4} injection, 10 s purging, 24 s NH\textsubscript{3} plasma injection, and 6 s purging. Long dosing/purging time was applied to gain conformal coating on nano powders. In this work, the samples coated by 20, 50, 100 cycles of TiN are termed as TiO\textsubscript{2}@20TiN, TiO\textsubscript{2}@50TiN and TiO\textsubscript{2}@100TiN, respectively. As a control experiment, TiO\textsubscript{2} powders were treated by NH\textsubscript{3} plasma at 360\degree C for 20 min, which is equal to the NH\textsubscript{3} plasma injection time of 50 cycles of PEALD TiN.

Characterization. The chemical feature was investigated by X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha) with standard Al K\textalpha (1486.7 eV) X-ray source. The binding energies were calibrated with respect...
to the signal from the adventitious carbon (binding energy = 284.6 eV). Raman spectra of TiO$_2$ were collected by a confocal Raman microscope (LabRAM HR Evolution, Horiba) with excitation laser wavelength of 632.8 nm. An objective lens is employed to focus the excitation laser on the substrate and collect the Raman signal. The microstructure and morphology were examined by field emission scanning electron microscopy (FESEM, Ultra55, ZEISS) and high-resolution transmission electron microscopy (HRTEM, Tecnai F20 S-Twin, FEI). Crystallinity and phase structures of powders were analyzed by a Rigaku-D/MAX 2000X-ray diffraction (XRD) system with Cu K$_\alpha$ radiation. The Brunauer-Emmett-Teller (BET) surface area was estimated by a surface area apparatus (TriStar-3000, Micromeritics). UV-visible absorption spectra were recorded by a UV-vis-NIR spectrophotometer (UV-3600, Shimadzu).

**Photocatalytic activity.** The photocatalytic activity of as-prepared photocatalysts was evaluated via the degradation of methyl orange (MO) or phenol in aqueous solution. A solar simulator (300 W Xe lamp, MircoSolar300, PerfectLight) with a 420 nm cut-off filter provides the visible-light irradiation. The lamp was located at 15 cm away from the reaction solution. 100 mg catalyst and 100 mL of aqueous solution containing 4 mg L$^{-1}$ MO or phenol were placed in a glass reactor with continuous stirring at 500 rpm. Prior to irradiation, the pollutant solutions suspended with photocatalysts were stirred in absence of light for 30 min (MO) or 2 h (phenol) to attain the equilibrium adsorption/desorption between photocatalyst powders and organic molecules. During the reaction, the temperature was maintained at 25 ± 1 °C using cooling water. For each given irradiation time, about 3 mL of the reacted solution was withdrawn and centrifuged at 10,000 rpm for 10 min to remove the photocatalyst. Then, the concentration of the centrifuged solution was determined by a UV-vis-NIR spectrophotometer, measuring the maximum absorption of MO at 464 nm and phenol at 270 nm.

**Stability test of photocatalysts.** In order to evaluate the stability of the photocatalysts, a recycled usage experiment was carried out. 100 mg TiO$_2$@50TN photocatalyst was suspended in a 100 mL of 4 mg L$^{-1}$ solution of MO and irradiated under Xe lamp for 120 min. The photocatalysts were collected and washed by distilled water and ethanol, then dried in the oven at 100 °C for 12 h. Finally, the photocatalyst was reused again for the second cycle of degradation with a fresh dye solution. This process was about to repeat up to 3 times of application.

**References**
1. Fujishima, A. Electrochemical photolysis of water at a semiconductor electrode. Nature 238, 37–38 (1972).
2. Chen, X. & Mao, S. S. Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. Chem. Rev. 107, 891–2959 (2007).
3. Pelaez, M. et al. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Appl. Catal. B Environ. 125, 331–349 (2012).
4. Linsebigler, A. L., Lu, G. & Yates, J. T. Jr. Photocatalysis on TiO$_2$ surfaces: principles, mechanisms, and selected results. Chem. Rev. 95, 735–758 (1995).
5. Ohno, T., Mitsui, T. & Matsumura, M. Photocatalytic activity of S-doped TiO$_2$ photocatalyst under visible light. Chem. Lett. 32, 364–365 (2003).
6. Diswald, O. et al. Photochemical activity of nitrogen-doped rutile TiO$_2$ (110) in visible light. J. Phys. Chem. B 108, 6004–6008 (2004).
7. Yan, X. et al. The interplay of sulfur doping and surface hydroxyl in band gap engineering: Mesoporous sulfur-doped TiO$_2$ coupled with magnetite as a recyclable, efficient, visible light active photocatalyst for water purification. Appl. Catal. B Environ. 218, 20–31 (2017).
8. Zhang, Z., Zhang, L., Hedhili, M. N., Zhang, H. & Wang, P. Plasmonic gold nanocrystals coupled with photonic crystal seamlessly on TiO$_2$ nanotube photoelectrodes for efficient visible light photocatalytic water splitting. Nano Lett. 13, 14–20 (2012).
9. Li, G.-S., Zhang, D.-Q. & Yu, J. C. A new visible-light photocatalyst: CdS quantum dots embedded mesoporous TiO$_2$. Environ. Sci. Technol. 43, 7079–7085 (2009).
10. Choi, T., Kim, J.-S. & Kim, J. H. Transparent nitrogen doped TiO$_2$/WO$_3$ composite films for self-cleaning glass applications with improved photodegradation activity. Adv. Powder Technol. 27, 347–353 (2016).
11. Guo, X. et al. Porous Ti$_3$B$_2$T$_4$O$_{16}$ heterostructures: Synthesis and enhanced photocatalytic properties from nanosheets to sweetrolled wafers. Appl. Catal. B Environ. 217, 12–20 (2017).
12. Fujishima, A., Zhang, X. & Tryk, D. A. TiO$_2$ photocatalysis and related surface phenomena. Surf. Sci. Rep. 63, 515–582 (2008).
13. Zhang, J., Wu, Y., Xing, M., Leghari, S. A. K. & Sajjad, S. Development of modified N doped TiO$_2$ photocatalyst with metals, nonmetals and metal oxides. Energ. Environ. Sci. 3, 715–728 (2010).
14. Burda, C. et al. Enhanced nitrogen doping in TiO$_2$ nanoparticles. Nano Lett 3, 1049–1051 (2003).
15. Chen, X., Lou, Y. B., Samia, A. C., Burda, C. & Gole, J. L. Formation of Oxynitride as the Photocatalytic Enhancing Site in Nitrogen-Doped Titania Nanocatalysts: Comparison to a Commercial Nanopowder. Adv. Funct. Mater. 15, 41–49 (2005).
16. Shibui, C., Lei, C., Shen, G. & Gengyu, C. The preparation of nitrogen-doped photocatalyst TiO$_2$-N$_x$, by ball milling. Chem. Phys. Lett. 413, 404–409 (2005).
17. Lai, Y.-K. et al. Nitrogen-doped TiO$_2$ nanotube array films with enhanced photocatalytic activity under various light sources. J. Hazard. Mater. 184, 855–863 (2010).
18. Martínez-Ferrero, E. et al. Nanostructured Titanium Oxynitride Porous Thin Films as Efficient Visible-Active Photocatalysts. Adv. Funct. Mater. 17, 3348–3354 (2007).
19. Quesada-Cabrera, R. et al. On the apparent visible-light and enhanced UV-light photocatalytic activity of nitrogen-doped TiO$_2$ thin films. J Photochem. Photobiol. A Chem 333, 49–55 (2017).
20. Lee, A. et al. Conformal Nitrogen-Doped TiO$_2$ Photocatalytic Coatings for Sunlight-Activated Membranes. Adv. Sustainable Syst. 1, 1600041 (2017).
21. Yang, G., Jiang, Z., Shi, H., Xiao, T. & Yan, Z. Preparation of highly visible-light active N-doped TiO$_2$ photocatalyst. J. Mater. Chem. 20, 5301–5309 (2010).
22. Luong, N. S. et al. Highly Visible Light Activity of Nitrogen Doped TiO$_2$ Prepared by Sol-Gel Approach. J. Electron. Mater. 46, 158–166 (2017).
23. Liu, M., Li, X., Karuturi, S. K., Tok, A. I. Y. & Fan, H. J. Atomic layer deposition for nanofabrication and interface engineering. Nanoscale 4, 1522–1528 (2012).
24. Knez, M., Nielsch, K. & Niinistö, L. Synthesis and surface engineering of complex nanostructures by atomic layer deposition. Adv. Mater. 19, 3425–3438 (2007).
25. Meng, X. et al. Atomic Layer Deposition for Nanomaterials Synthesis and Functionalization in Energy Technology. Mater. Horiz. 4, 133–154 (2017).
36. Van Bui, H.
35. Profijt, H., Potts, S., Van de Sanden, M. & Kessels, W. Plasma-assisted atomic layer deposition: Basics, opportunities, and challenges. Chem Electro Chem 3, 858–863 (2016).
34. Wang, T., Luo, Z., Li, C. & Gong, J. Controllable fabrication of nanostructured materials for photoelectrochemical water splitting via atomic layer deposition. Adv. Sci. 3, 1500405 (2016).
33. Livraghi, S.
32. Lu, J., Elam, J. W. & Stair, P. C. Atomic layer deposition—Sequential self-limiting surface reactions for advanced catalyst “bottom-up” synthesis. Surf. Sci. Rep 71, 410–472 (2016).
31. Cao, Y.-Q. Atomic layer deposition of Li₂Al,S Solid-State Electrolytes for Stabilizing Lithium–Metal Anodes. Chem Electro Chem 3, 858–863 (2016).
30. Ahmed, B., Xia, C. & Alshareef, H. N. Electrode surface engineering by atomic layer deposition: A promising pathway toward better energy storage. Nano Today 11, 250–271 (2016).
29. Guan, C. & Wang, J. Recent Development of Advanced Electrode Materials by Atomic Layer Deposition for Electrochemical Energy Storage. Adv. Sci. 3, 1500405 (2016).
28. Meng, X., Yang, X.-Q. & Sun, X. Emerging Applications of Atomic Layer Deposition for Lithium-Ion Battery Studies. Adv. Mater 24, 3589–3615 (2012).
27. Lu, J., Elam, J. W. & Stair, P. C. Atomic layer deposition—Sequential self-limiting surface reactions for advanced catalyst “bottom-up” synthesis. Surf. Sci. Rep 71, 410–472 (2016).
26. Cao, Y.-Q. et al. Atomic Layer Deposition Assisted Formation of Wafer Scale Double-Layer Metal Nanoparticles with Tunable Nanogap for Surface-Enhanced Raman Scattering. Sci. Rep 7, 5161 (2017).
25. Meng, X., Yang, X.-Q. & Sun, X. Emerging Applications of Atomic Layer Deposition for Lithium-Ion Battery Studies. Adv. Mater 24, 3589–3615 (2012).
24. Gong, J. Controllable fabrication of nanostructured materials for photoelectrochemical water splitting via atomic layer deposition. Chem. Soc. Rev 43, 7469–7484 (2014).
23. Wang, J., Zhu, W., Zhang, Y. & Liu, S. An efficient two-step technique for nitrogen-doped titanium dioxide synthesizing: visible-light-induced photodecomposition of methylene blue. J. Phys. Chem. C 111, 1010–1014 (2007).
22. Wang, J., Zhu, W., Zhang, Y. & Liu, S. An efficient two-step technique for nitrogen-doped titanium dioxide synthesizing: visible-light-induced photodecomposition of methylene blue. J. Phys. Chem. C 111, 1010–1014 (2007).
21. Irie, H., Watanabe, Y. & Hashimoto, K. Nitrogen-concentration dependence on photocatalytic activity of TiO₂. J. Phys. Chem. B 107, 5483–5486 (2003).

Acknowledgements
This work is supported by the Natural Science Foundation of China and Jiangsu Province (51571111, BK2016230, and BK20170645), a grant from the State Key Program for Basic Research of China (2015CB921203). Dr. Yan-Qiang Cao also thanks the support from the general grant from the China Postdoctoral Science Foundation (2017M611778) and the Fundamental Research Funds for the Central Universities (021314380075).

Author Contributions
Y.Q.C. and J.C. prepared samples, and X.R.Z. and J.C. performed the photocatalytic experiments. W.Z. conducted XPS analysis. Y.Q.C. and X.J.Z. performed Raman detection. X.R.Z. and J.C. prepared samples, and X.R.Z. and J.C. performed the photocatalytic experiments. W.Z. conducted in situ spectroscopic ellipsometry. Y.Q.C. and X.J.Z. performed Raman detection. X.R.Z. conducted the TEM characterization. L.Z. performed SE studies. Y.Q.C. and J.C. prepared samples, and X.R.Z. and J.C. performed the photocatalytic experiments. W.Z. conducted growth kinetics and oxidation mechanism of ALD TiN thin films monitored by in situ spectroscopic ellipsometry. J. Electrochem. Soc 158, H214–H220 (2011).

Saha, N. C. & Tompkins, H. G. Titanium nitride oxidation chemistry: An X-ray photoelectron spectroscopy study. J. Appl. Phys 72, 3072–3079 (1992).

Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. & Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. Science 293, 269–271 (2001).

Shultz, A. N. et al. Comparative second harmonic generation and X-ray photoelectron spectroscopy studies of the UV creation and O₂ healing of Ti³⁺ defects on (110) rutile TiO₂ surfaces. Surf. Sci. 339, 114–124 (1995).

Chen, Y. et al. Microwave-assisted ionic liquid synthesis of Ti³⁺ self-doped TiO₂ hollow nanocrystals with enhanced visible-light photoactivity. Appl. Catal. B Environ 191, 94–105 (2016).

Lavrigh, S. et al. Origin of photoactivity of nitrogen-doped titanium dioxide under visible light. J. Am. Chem. Soc 128, 15666–15671 (2006).

Nakagawa, K. & Ovenstone, J. Crystallization of anatase from amorphous titania using the hydrothermal technique: effects of starting material and temperature. J. Phys. Chem. B 103, 7781–7787 (1999).

Wang, J., Zhu, W., Zhang, Y. & Liu, S. An efficient two-step technique for nitrogen-doped titanium dioxide synthesizing: visible-light-induced photodecomposition of methylene blue. J. Phys. Chem. C 111, 1010–1014 (2007).

Irie, H., Watanabe, Y. & Hashimoto, K. Nitrogen-concentration dependence on photocatalytic activity of TiO₂–Nₓ powders. J. Phys. Chem. B 107, 5483–5486 (2003).

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-018-30726-w.

 Competing Interests: The authors declare no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2018