Synergistic effect between TiO$_2$ and ubiquitous metal oxides on photocatalytic activity of composite nanostructures

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We studied photocatalytic activity of highly porous nanotubular TiO$_2$ films modified with nanoclusters of ubiquitous metal (Ti, Al, Zn, Sn, Cu, W) oxides prepared by chemical bath deposition and atomic layer deposition as well as nanoclusters of metal rich suboxides and mixed titania suboxides prepared by atomic layer deposition by following decomposition of methylene blue under simulated solar light. The mixed titania suboxide clusters constructed on the surface of TiO$_2$ nanotubes by atomic layer deposition demonstrated significantly enhanced photocatalytic activity in comparison to the naked TiO$_2$ nanotubes attributed to the better absorption of visible light due to the upward shift of the valence band near the TiO$_2$ surface induced by the suboxide clusters that feature low valence states and metal-metal bonds.

Key-words : Photocatalysis, TiO$_2$ nanotubes, Suboxides, Nanoclusters, Atomic layer deposition

1. Introduction

Titanium dioxide has attracted extensive interest as a nontoxic, highly stable, and low-cost photocatalyst for the solar driven purification of water from toxic organic pollutants. Over the past decade, a variety of methods have been developed to synthesize anatase TiO$_2$ nanostructures with improved photocatalytic activity such as nanoparticles, nanotubes, nanostructured thin films and hierarchical brush nanostructures. Although these nanostructures indeed demonstrated an improved photocatalytic activity due to highly developed specific surface area, their photoresponse is fundamentally limited by the wide bandgap of anatase TiO$_2$ (3.2 eV) that is sensitive only to ultraviolet (UV) light. Since the portion of the UV light constitutes less than 5% of the solar energy spectrum there have been many efforts to reduce the bandgap of TiO$_2$ and make it sensitive to the visible (VIS) light. One of the most popular strategies to narrow the bandgap of TiO$_2$ is substitution doping with transition metals or non-metallic elements such as carbon or nitrogen. The introduction of foreign atoms into the Ti or O sublattice of TiO$_2$ creates new states in the bandgap. In the case of highly doped material these states can overlap and form impurity sub-bands. As a result, the energy of the interband electronic transition is reduced, which leads to a shift of the adsorption edge towards longer wavelengths. On the other hand, the high density of foreign atoms in the host lattice introduces structural imperfections and simultaneously leads to the formation of excessive number of recombination centers that in turn reduce the photocatalytic activity of the material.

An alternative approach to induce VIS response in TiO$_2$ by surface modification with dispersed metal oxide nanoclusters has been recently theoretically described by Nolan and demonstrated experimentally by Libera et al. and Tada et al. According to theoretical calculations of Nolan, the altering of TiO$_2$ surface with nanoclusters of certain metal oxides can induce an upward shift of the valence band (VB) of TiO$_2$ without affecting the conduction band. The calculations predict the upward shift of the VB near TiO$_2$ surface on 0.3, 0.4 and 0.6 eV by low valence FeOx, CrO$_2$ and MoO$_2$ clusters, respectively. It is necessary to emphasize that this approach is different from the construction of a heterojunction that requires suitable alignment of both conduction bands and valence bands of two materials to allow proper separation of photogenerated electrons and holes. Evidently, the low valence state of the metal ions in the oxide cluster plays an important role in the electronic interaction between the metal electron lone pairs and oxygen 2p states forming TiO$_2$ valence band. It was clearly demonstrated that in contrast to the Sn (II) oxo-clusters (i.e. SnO) that do induce the VIS photoresponse in TiO$_2$, the surface modification of TiO$_2$ by Sn (IV) oxo-clusters (i.e. SnO$_2$) does not lead to the photocatalytic activity of the composite under visible light.

From another perspective, Ye et al. demonstrated that the strong VIS photoresponse can originate from the formation of metal-to-metal electronic bonds at the non-stoichiometric interfaces between agglomerated TiO$_2$ nanoparticles. The excessive amount of Ti on the surface of TiO$_2$ nanoparticles corresponds to the shell of non-bonding Ti 3d electrons, which form Ti–Ti electronic bonds after interface formation upon agglomeration of the nanoparticles. The creation of non-stoichiometric interfaces is manifested in bright yellow color of agglomerated nanoparticles, which is in remarkable contrast to stabilized individual TiO$_2$ nanoparticles that are white. We would like to point out that in the both mentioned cases the sensitization of TiO$_2$ toward VIS light is realized by the utilization of the low valence state of the metal ions in the structure.

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novel functional materials by utilization of unusual electronic states of ubiquitous elements. This elemental strategy is viewed as a promising approach to overcome limitations of critical materials supply, which is especially important in the field of solar driven water purification where mass scale deployment of photocatalytic systems is envisioned.

Taking into account the ubiquitous elements approach, we explored photocatalytic activity of TiO$_2$ nanotubes modified with nanoclusters of ubiquitous metal (Ti, Al, Zn, Sn, Cu, W) oxides, nonstoichiometric metal rich suboxides and mixed titania suboxides prepared by chemical bath deposition (CBD) and atomic layer deposition (ALD).

2. Experimental procedure

TiO$_2$ nanotubes (NTs) were fabricated by the anodization of Ti foils in 0.3% NH$_4$F/ethylene glycol at 17°C under constant potential of 40 V. The Ti foils with the purity of >99.999% were purchased from Alpha Aesar. The potentiostatic anodization was conducted for 30 min. The schematic illustration of the electrochemical conversion of Ti into nanotubular TiO$_2$ is shown in the Fig. 1. The conversion of Ti into TiO$_2$ nanotubes proceeds through several transformation stages including formation of the barrier oxide layer, nucleation of nanotubes and stable nanotubular growth regime. The anodic TiO$_2$ acquires nanotubular morphology as a result of competing oxide dissolution at the TiO$_2$/electrolyte interface and new oxide formation at the Ti/TiO$_2$ interface. After the anodization, the TiO$_2$-NTs samples were thoroughly washed by deionized water and sintered by annealing in oxygen atmosphere at 450°C for 4.5 h in O$_2$ atmosphere with the O$_2$ flow rate of 6 SCCM. These annealing conditions correspond to the conversion of the as-grown amorphous TiO$_2$ nanotubes to crystalline anatase phase. The crystalline structure of the annealed TiO$_2$ nanotubes was analyzed by X-ray Diffraction (XRD) in Rigaku RINT-2500 (Cu K$_\alpha$, $\lambda = 1.540598\AA$, $U = 40$ kV, $I = 300$ mA). The morphology of the TiO$_2$-NTs was inspected in SEM (JEOL-7001F).

The nanoclusters of metal oxides were deposited into the TiO$_2$ nanotubes by two methods: chemical bath deposition (CBD) and atomic layer deposition (ALD). The chemical bath deposition of Al, Zn, Cu and Sn oxide clusters was conducted by soaking the TiO$_2$ nanotubes in 0.5 M NaOH solution for 1 h followed by soaking in 0.05 M solution of corresponding metal nitrate for 2 h. The Al (III), Zn (II), Cu (II), and Sn (IV) nitrates of >99.99% purity were purchased from Sigma Aldrich. In the case of W, the TiO$_2$ nanotubes were first soaked in 0.1 M H$_2$SO$_4$ solution for 1 h and then immersed into 0.05 M ammonium tungstate (Aldrich, >99%) for 2 h. In the case of Ti, the TiO$_2$ nanotubes were immersed into 0.1 M solution of titanium (IV) isopropoxide (Aldrich, >98%) for 2 h. After the CBD all samples were annealed in oxygen atmosphere at 450°C for 2 h.

The atomic layer deposition (ALD) was conducted at 250°C by using Al(me)$_3$ (trimethylaluminum), Zn(et)$_2$ (diethylzinc), Sn(me)$_3$ (tetramethylethyltin), TiCl$_4$ (titanium tetrachloride), Cu(thd)$_2$ (bis-2,2,6,6-tetramethyl-3,5-heptanedionato copper) and W(tba)$_2$ (bis-tert-butyliminobis-tert-butylamino tungsten) as metal precursors and H$_2$O as the oxygen source. Here we would like to introduce the abbreviation ML$_n$ for the metal precursors to simplify the
description of the ALD procedures in this manuscript. In the MLₙ abbreviation the M states for the metal atom (i.e. Al, Ti, Zn, Sn, Cu, W) and Ln states for coordinated ligands.

The oxide clusters were deposited by using conventional ALD cycles: -[MLₙ]-[H₂O]- where metal precursor and water were alternately injected into the reaction space while a purge/evacuation between the injection steps was used to remove excessive precursors and reaction byproducts. Each ALD cycle consisted of 100 s exposure to metal precursor, 150 s exposure to water and 200 s purge/evacuation between the exposure pulses. The purge step was conducted by flowing 100 SCCM of high purity 99.9999% Ar at the base pressure of 1 Torr. In total, six ALD cycles were conducted to deposit metal oxide clusters. The completeness of the ALD half reactions was followed by monitoring the concentration of the reaction byproducts with differentially pumped high-speed ion-trap mass spectrometer (ITMS) Brooks VQM-830.

The clusters of metal suboxides (MOₓ) were deposited by using atomic hydrogen [H] treatment between two [MLₙ] pulses: -[MLₙ]-[H]-[MLₙ]-[H₂O]-. The atomic hydrogen was introduced in the atomic hydrogen source by thermal cracking of hydrogen molecules over hot tungsten filament. The 600 s exposure to atomic hydrogen was maintained by flowing 10 SCCM of high purity hydrogen (99.9999%) through boron nitride tube with hot tungsten filament. The exposure time to [MLₙ] and [H₂O] were 100 and 150 s, respectively. The mixed titania suboxides (MTiOₓ) were prepared via the same procedure though TiCl₄ exposure pulse was used after the [H] step: -[MLₙ]-[H]-[TiCl₄]-[H₂O]-. In both cases, three full ALD cycles were conducted to deposit sub-oxide and mixed sub-oxide clusters.

The mechanism that leads to the formation of sub-oxides, i.e. metal rich oxide, upon treatment with atomic hydrogen is following. The [H] treatment strips the ligands (Lₙ) from the -MLₙ terminated surface liberating the HL molecules. This ALD half reaction leads to the reconfiguration of the metal-oxygen bonds in the subsurface monolayer and finally produce M-H terminated surface. The M-H terminated surface then reacts with the MLₙ again during the next [MLₙ] exposure step creating metal enriched layer with some portion of M-M bonds. This process is similar to the deposition of pure metallic films by ALD via alternating exposure of the sample to metalorganic precursor and hydrogen. In our case, the atomic hydrogen is used instead of molecular hydrogen to facilitate the ligand stripping half-reaction under relatively low temperature of 250°C. As a result the [MLₙ]-[H]-[MLₙ]-[H₂O] cycle results in the formation of sub-oxide under mild conditions due to increased reactivity of atomic hydrogen during the [H] treatment step. The formation of clusters is promoted by the steric hindrance of reaction sites by ligands and self-limited nature of the ALD half reactions. Although ALD is usually described as atomically smooth layer-by-layer growth technique, the large ligands linked to the M atom on the -MLₙ terminated surface hinder the adjacent reaction centers. The steric hindrance phenomenon typically results in the ALD deposition rate less than a monolayer promoting the growth of separated clusters during several first ALD cycles (typically 5–6) before their coalescence. The growth rate per cycle for the ALD of metal oxides is typically in the range of 1.5 angstrom per cycle. Therefore after 5 ALD cycles we can expect to have metal oxide clusters with the size of around 1 nm.

The photocatalytic properties of naked TiO₂-NTs and TiO₂-NTs modified with the nanoclusters of ubiquitous metal oxides were studied by following the transmittance of 0.05 mM methylene blue (C₁₆H₁₈N₃SCl) solution during its photocatalytic decom-

position under simulated AM1.5 solar light. The absorption of the methylene blue (MB) solutions at characteristic wavelength of 660 nm was sampled every 15 min by using USB-2000-FLG spectrometer (Ocean Optics Inc.).

3. Results and discussion

The SEM images of the top and side view of the anatase TiO₂-NTs are shown in the Figs. 2(a) and 2(b), respectively. The nanotubes have an average diameter of 95 nm and length of 7.5 μm. The XRD spectrum of the annealed TiO₂ nanotubes is shown in the Fig. 2(c) and confirms that TiO₂ nanotubes form crystalline anatase phase. Figures 3(a)–3(f) show the relative concentrations C/C₀ of methylene blue as a function of reaction time for all prepared samples. The photocatalytic decomposition of MB under AM1.5 simulated solar irradiation follows a first order reaction kinetics reasonably well. The reaction rate is described as r = kC₁, where k is the first order rate constant, C is reactant concentration and t the light intensity. In order to compare the photocatalytic activity of the samples relative to the naked TiO₂ nanotubes, the constant rate k was extracted from the experimental data for each sample. Figure 4 shows the ratio k/k_TNT, which is the ratio of the rate constant k of each sample to the k_TNT for naked TiO₂-NTs.

Apparently, there is no significant difference in the photocatalytic activity of TiO₂-NTs modified with nanoclusters of full oxides Al₂O₃, SnO₂, ZnO, CuO, WO₃, i.e. with the metal element in ground valence state, depending on the deposition method, CBD or ALD. Al₂O₃ and SnO₂ nanoclusters decrease the photocatalytic activity of TiO₂-NTs, while CuO and WO₃ slightly increase it. In contrast, SnO₂, TiO₂, and WO₃ suboxide clusters demonstrate significantly higher photocatalytic activity than naked TiO₂-NTs. The absence of this effect for Al, Zn and Cu indicates that suboxides of these elements were probably not formed due to the instability of their low valence state. On the other hand there is a clear synergistic effect in the mixed titania suboxide clusters. Several stable Ti-rich phases are known to exhibit absorption in the VIS region, i.e. 1-Ti₃O₅, β-Ti₃O₅ (410–535 nm). Also, the suboxide clusters are expected to retain a significant portion of metal-metal bonds which is given by their growth mechanism. The formation of metal to metal bonds can lead to significant enhancement of VIS absorption. While TiO₃ suboxide clusters demonstrate the highest photocatalytic activity in the MOₓ family, the mixed CuTiO₄ and WTiO₄ mixed
Fig. 3. Decomposition of methylene blue (MB) under simulated AM1.5 solar light by TiO$_2$-NTs modified with nanoclusters of ubiquitous metal oxides (MO) prepared by CBD (triangles) and by ALD (rectangles), and suboxides (MO$_x$, open rectangles) and mixed titania suboxides (MTiO$_x$, diamonds) prepared by ALD. The reference sample with naked TiO$_2$-NTs (circles) is included into each graph for comparison.

Fig. 4. Decomposition rate $k$ of each sample relative to the $k_{\text{TNT}}$ for naked TiO$_2$-NTs.
suboxide clusters possess superior photocatalytic activity in comparison to TiO$_x$. We did not observe significant difference between photocatalytic activity of the naked TiO$_2$-NTs and TiO$_2$-NTs modified with WO$_x$ and WTiO$_x$ nanoclusters under irradiation with UV light (<320 nm) and simulated AM1.5 light. This observation indicates that the enhanced photocatalytic activity of the TiO$_2$-NTs modified with suboxide and mixed suboxide clusters can be attributed to the enhanced absorption of the VIS light by the composite nanostructures, which is in good correspondence to the theoretical model of Nolan.[10], [11] The effect is attributed to the upward shift of the valence band near the TiO$_2$ surface induced by the suboxide cluster that features low valence states.

4. Conclusions

In conclusion, we explored photocatalytic activity of TiO$_2$ nanotubes (NTs) modified with nanoclusters of ubiquitous metal (Ti, Al, Zn, Sn, Cu, W) oxides, metal rich suboxides and mixed titania suboxides prepared by Chemical Bath Deposition (CBD) and Atomic Layer Deposition (ALD). The mixed titania suboxide clusters constructed on the surface of TiO$_2$-NTs by ALD demonstrate enhanced photocatalytic activity in comparison to the naked TiO$_2$-NTs. The effect is attributed to the upward shift of the valence band near the TiO$_2$ surface induced by the suboxide cluster that features low valence states and metal-metal bonds.

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