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Enhanced photocatalytic performances of n-TiO$_2$ nanotubes by uniform creation of p-n heterojunctions with p-Bi$_2$O$_3$ quantum dots

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An ultrasonication-assisted successive ionic layer adsorption and reaction (SILAR) strategy was developed to uniformly deposit high density p-type Bi$_2$O$_3$ quantum dots on n-type TiO$_2$ nanotube arrays (Bi$_2$O$_3$@TiO$_2$ NTAs), which were constructed by electrochemical anodizing in ethylene glycol containing electrolyte. Compared with pristine TiO$_2$ NTAs, the Bi$_2$O$_3$ quantum dots sensitized TiO$_2$ NTAs exhibited highly efficient photocatalytic degradation of methyl orange (MO). The kinetic constant of Bi$_2$O$_3$@TiO$_2$ NTAs prepared by an ultrasonication-assisted SILAR process of 4 cycles was 1.95 times higher than that of the pristine TiO$_2$ NTAs counterpart. The highly efficient photocatalytic activity is attributed to the synergistic effect between the formation of uniform p-n heterojunction with a high-density for enhancing light absorption and facilitating photogenerated electron-hole separation/transfer. The results suggest that Bi$_2$O$_3$/TiO$_2$ p-n heterojunction nanotube arrays are very promising for enhancing the photocatalytic activity and open up a promising strategy to design and construct high efficiency heterogeneous semiconductor photocatalysts.

Titanium dioxide (TiO$_2$), since discovered on water photolysis by Fujishima and Honda in 1972, has been paid much attention and widely used in photocatalytic degradation of organic pollutants, dye-sensitized solar cells, biomedical materials, sensor/detector and hydrogen production by splitting water because of its low cost, good mechanical properties and high biocompatibility. Compared to TiO$_2$ nanoparticles and nanowires, vertically aligned TiO$_2$ NTAs on Ti substrate by electrochemical anodizing have been paid more attention due to the oriented charge transfer channel, the large interfacial area, and especially lower recombination rate of photogenerated electrons and holes. However, associated with wide band gap (anatase: 3.2 eV, rutile: 3.0 eV) and the fast recombination of photogenerated electron-hole pairs, the wide application of TiO$_2$ NTAs was limited in some fields.

In recent years, in order to enhance the photocatalytic activity of TiO$_2$ NTAs, a lot of materials were used to modify TiO$_2$ NTAs by suppressing the recombination of photogenerated electrons-hole pairs and improving the transport of photocarriers, such as metal (Ag, Au, Pt and Pd), non-metal (N, C, F and S), semiconductor (CdS, Cu$_2$O and NiO). Especially, the formation of p-n heterojunctions is thought to be one of the most effective strategies to enhance the photocatalytic activity due to the existence of an external electric field in the interface. Therefore, it is urgent to search for novel heterostructured materials to couple with TiO$_2$ NTAs in material chemistry.

Bismuth oxide (Bi$_2$O$_3$), as a p-type semiconductor, has been extensively used in gas sensors, photoelectric coatings and catalysts because of high refractive index, high dielectric permittivity and photoluminescence properties. There are six polymorphs phase of Bi$_2$O$_3$: α-Bi$_2$O$_3$ (monoclinic), β-Bi$_2$O$_3$ (tetragonal), γ-Bi$_2$O$_3$ (b.c.c.), δ-Bi$_2$O$_3$ (f.c.c.), ε-Bi$_2$O$_3$ (orthorhombic) and w-Bi$_2$O$_3$ (triclinic). Among them, β-Bi$_2$O$_3$ has excellent advantages and demonstrates appreciable properties for decomposing pollutants. It has a narrower band gap of about 2.8 eV and can decrease the band gap of TiO$_2$. Since TiO$_2$ is a well-known n-type semiconductor, it is promising to decorate TiO$_2$ with p-Bi$_2$O$_3$ to enhance the photocatalytic efficiency because the formation of p-n junctions can markedly facilitate the separation of electron and hole. Recently, there are some reports about Bi$_2$O$_3$/TiO$_2$ composite nanotube arrays synthesized by an electrochemical method and electrophoretic deposition, but these techniques exhibit poor control over the particle size and distribution.

Herein, we present an ultrasonication-assisted successive ionic layer adsorption and reaction (SILAR) technique to uniformly deposit Bi$_2$O$_3$ quantum dots on vertically aligned TiO$_2$ NATs with a high density. The morphology, structure and photoelectrochemical
performance of TiO$_2$ NTAs with or without Bi$_2$O$_3$ quantum dots loading were systematically investigated and discussed. Compared to pristine TiO$_2$ NTAs, the Bi$_2$O$_3$@TiO$_2$ NTAs p-n heterojunction exhibited the synergistic effect between enhanced light adsorption capacity of specific composite structure and facilitated the photogenerated charges separation/transfer of novel p-n heterojunction. The photocatalytic activity of Bi$_2$O$_3$-TiO$_2$ NTAs p-n heterojunction was evaluated by the photocatalytic degradation of methyl orange aqueous solutions.

**Experimental**

**Preparation of anodized TiO$_2$ NTAs:** Prior to anodization, titanium foils were ultrasonically cleaned in acetone and ethanol for 30 minutes, respectively. Then cleaned Ti foils (3.0 $\pm$ 1.5 cm$^2$) was anodized at room temperature in a conventional two-electrode cell with Pt as counter electrode in ethylene glycol containing 0.5 wt% NH$_4$F and 2 vol% H$_2$O. Subsequently, the 50 V potential was applied for 2h for the growth of nanotube arrays. Rinsed with distilled water, the as anodized Ti foils was then ultrasonically rinsed in ethanol for 5 minutes. At last, the samples were rinsed in distilled water and dried in air. The as-prepared amorphous TiO$_2$ nanotube arrays were annealed in air at 400°C for 2 h with a heating rate and cooling rate of 5°C/min to convert to crystalline phases.

**Preparation of Bi$_2$O$_3$@TiO$_2$ NTAs:** Bi$_2$O$_3$ quantum dots were loaded onto the outer and inner walls of TiO$_2$ nanotubes by the ultrasonication-assisted successive ionic layer adsorption and reaction (SILAR) technique. Typically, the annealed TiO$_2$ NTAs were immersed successively in 5 mM Bi(NO$_3$)$_3$•5H$_2$O ethylene glycol solution and 0.1 M NaOH ethanol solution for 10 minutes, respectively, and simultaneously assisted with a ultrasound frequency of 40 kHz by using an ultrasonic generator (KQ100E, Kunshan Ultrasonic Instrument Co., Ltd). Between each immersion step, the samples were rinsed with ethanol adequately to remove excess ions. Such operation process was repeated for 1 to 7 cycles. The corresponding samples were marked as Bi$_2$O$_3$@TiO$_2$ NTAs-1 to Bi$_2$O$_3$@TiO$_2$ NTAs-7, respectively. The samples were rinsed with ethanol and dried in air, then annealed in air at 450°C for 2 h with a heating rate and cooling rate of 5°C/min. The procedures for the preparation of Bi$_2$O$_3$@TiO$_2$ NTAs are illustrated in Scheme 1.

**Characterization of Bi$_2$O$_3$@TiO$_2$ NTAs:** The structure and morphology of Bi$_2$O$_3$@TiO$_2$ NTAs were characterized by a field emission scanning electron microscope (SEM, Hitachi-S4800). The microstructures, compositions and the presence of Bi$_2$O$_3$ were further confirmed by using a transmission electron microscopy (TEM, FEI Tecnai G-20 operated at 200 kV). Energy dispersive X-ray (EDX) spectrometer fitted to the TEM was applied for elemental analysis. The crystal phases were identified by an X-ray diffractometer with Cu-Ka radiation (XRD, Philips, X’pert-Pro MRD). X-ray photoelectron spectroscopy (XPS, KRATOS, Axis Ultra HAS) was employed to analyze the chemical component and the concentration of atoms of Bi$_2$O$_3$@TiO$_2$ NTAs. The binding energies were normalized to the signal for adventitious C 1s at 284.5 eV. UV-Vis diffuse reflection spectroscopy (UV-DRS) was recorded in range of 250-800 nm at room temperature by using UV-3600 spectrophotometer. Photoluminescence (PL) measurements were carried out at room temperature by using fluorescence spectroscopy (made by HOKIBA JOBIN YVON, FM4P-TCSPC) with a Xenon lamp as excitation source ($\lambda_{ex}$ = 370 nm).

**Photoelectrochemical measurements:** The photocurrent measurement and electrochemical impedance spectroscopy (EIS) measures were carried out in a quartz beaker using an electrochemical workstation (CHI 660D) in a standard three-electrode configuration with TiO$_2$ NTAs, Bi$_2$O$_3$@TiO$_2$ NTAs electrode as the working electrode. The counter and reference electrodes were Pt wire and saturated calomel electrode (SCE), respectively. A 0.1 M Na$_2$SO$_4$ aqueous solution was used as the electrolyte. The area of working electrodes was 3.0 cm$^2$. The working electrode was irradiated with a GY-10 xenon lamp during the measurement. The distance between the window of the flask and light source was 15 cm. The focused incident light intensity on the flask was ca. 100 mW/cm$^2$. The EIS measurements were performed to scrutinize the interfacial properties between the electrode (i.e., TiO$_2$ NTAs, Bi$_2$O$_3$@TiO$_2$ NTAs) and the electrolyte over a frequency range from 1 $\times$ 10$^5$ Hz to 0.1 Hz with a low open circuit potential both in the dark and under solar light illumination.

**Photocatalytic measurements:** The photocatalytic activity of Bi$_2$O$_3$@TiO$_2$ NTAs was evaluated by the degradation of MO pollutant solution with an initial concentration of 10 mg/L (pH = 8.5). A 300 W mercury lamp was used as the simulated ultraviolet light source. The distance between the samples was 8 cm. Before light irradiation, the samples were immersed with 15 ml MO aqueous solution in quartz reactor at room temperature for 1 h to establish adsorption equilibrium. The reactor was equipped with a water jacket to control the reaction temperature. The concentration of MO was analyzed with a 30 min interval by using UV-Vis spectrophotometer (Hitachi, UV-1080, Japan) at wavelength of 463 nm.

**Results and discussion**

Figure 1a,b showed the FESEM images of TiO$_2$ NTAs. The TiO$_2$ NTAs demonstrated a high density, well-ordered and uniform tubular structure with a length of 4-6 µm and an average pore diameter of 90-100 nm. Figure 1c-f displayed the
SEM images of TiO$_2$ NTAs with ultrasonication-assisted SILAR deposition for 1, 4 and 7 cycles, respectively. A little amount of Bi$_2$O$_3$ quantum dots were deposited on the surface and inner walls of TiO$_2$ NTAs and were dispersed mainly around the nanotube entrance with one single cycle (Figure 1c). With the increase of SILAR cycles, the amount of Bi$_2$O$_3$ quantum dots on nanotube is also markedly increased. As SILAR processes were up to 4 cycles, the Bi$_2$O$_3$ quantum dots with an average size of about 10 nm were uniformly deposited on the top of TiO$_2$ nanotubes (Figure 1d). The corresponding cross-sectional SEM image (Figure 1e) showed that a lot of Bi$_2$O$_3$ quantum dots were well distributed on both outside and inside TiO$_2$ nanotube walls. When the SILAR process increases up to 7 cycles, the average size of Bi$_2$O$_3$ nanoparticles increases significantly to 25 nm, which leads to the obvious increase of wall thickness and decrease of nanotube inner diameter (Figure 1f).

The TEM image of the as-synthesized Bi$_2$O$_3$@TiO$_2$ NTAs sample showed that Bi$_2$O$_3$ quantum dots were uniformly deposited on and inside TiO$_2$ nanotubes (Figure 2a,b). Figure 2c presented a typical high resolution TEM image of the selected area marked in Figure 2a, which revealing a uniform distribution of Bi$_2$O$_3$ quantum dots on the nanotube with small particle size. The lattice fringes of 0.352 nm and 0.321 nm corresponded to the reflections from the (101) plane of anatase TiO$_2$ and (221) plane of β-Bi$_2$O$_3$, respectively. The EDX spectrum (Figure 2d) and corresponding element mapping (Figure 2e) of single nanotube demonstrate that the as-prepared Bi$_2$O$_3$ quantum dots is uniform and highly dispersed on TiO$_2$ nanotube. Except for Ti, O element, the Bi$_2$O$_3$@TiO$_2$ NTAs sample with 4 cycles of SILAR processes has an atomic percentage of Bi about 1.14%. In comparison to the uniform distribution of Ti and O sourced from TiO$_2$ substrate, the mapping of Bi exhibited an evenly distributed dot pattern, indicating that Bi$_2$O$_3$ quantum dots were uniformly anchored on and inside TiO$_2$ nanotubes. Figure S2† shows the TEM images of pristine TiO$_2$ nanotube arrays. After deposition Bi$_2$O$_3$ quantum dots, the wall thickness of Bi$_2$O$_3$@TiO$_2$ NTAs increased and the tubes become opaque.

Figure 1. Typical top-view (a) and side-view (b) SEM images of the pure TiO$_2$ NTAs, SEM images of Bi$_2$O$_3$@TiO$_2$ NTAs with SILAR processes for 1 cycle (c), top-view (e) and side-view (f) SEM images of Bi$_2$O$_3$@TiO$_2$ NTAs with multiple SILAR processes for 4 cycles, SEM images of Bi$_2$O$_3$@TiO$_2$ NTAs with multiple SILAR processes for 7 cycles (f).

Figure 2. (a,b) Low magnified TEM image of Bi$_2$O$_3$@TiO$_2$ NTAs fabricated by an ultrasonication-assisted SILAR process of 4 cycles; (c) The high resolution TEM image of the selected area marked in (a); (d) EDX spectrum of Bi$_2$O$_3$@TiO$_2$ NTAs sample; (e) EDX mapping of a single TiO$_2$ nanotube loaded with uniform Bi$_2$O$_3$ quantum dots.

Figure 3a presented the XRD patterns of the TiO$_2$ NTAs with or without the deposition of Bi$_2$O$_3$ quantum dots. The diffraction peaks at 25.3°, 37.9°, 48.0° and 53.9° of pristine...
TiO$_2$ NTAs could be well indexed to the (101), (004), (200) and (105) planes of TiO$_2$ anatase phase (JCPDS no. 21-1272). After Bi$_2$O$_3$ deposition, due to the well dispersed and small size Bi$_2$O$_3$ quantum dots, there is a low intensity peak at 27.9° and 31.8° in accordance with a standard diffraction of β-Bi$_2$O$_3$ (JCPDS no. 29-0236), corresponding to the (221) plane and (002) plane of β-Bi$_2$O$_3$, which is consistent with the results of TEM. The raman spectra of TiO$_2$ NTAs and Bi$_2$O$_3$@TiO$_2$ NTAs were showed in Figure 3b. The characteristics peaks of pristine TiO$_2$ NTAs at 144, 197, 395, 513 and 634 cm$^{-1}$ are attributed to Raman-active modes of anatase TiO$_2$.

When doping with Bi$_2$O$_3$ quantum dots, the obvious peaks of Bi$_2$O$_3$@TiO$_2$ NTAs appeared at 229, 307 cm$^{-1}$ because of internal stretching modes of Bi-O bonds with the various bond lengths, indicating that Bi-Bi$_2$O$_3$ quantum dots were deposited on TiO$_2$ NTAs successfully.

The chemical component of Bi$_2$O$_3$@TiO$_2$ NTAs was analyzed by XPS. Figure 4a,b showed XPS survey spectrum of TiO$_2$ NTAs and Bi$_2$O$_3$@TiO$_2$ NTAs, respectively. It can be seen that except for the O 1s (532.4 eV), Ti 2p (458.9 eV) and C 1s (284.5 eV) peaks, peaks such as Bi 4d and Bi 4f, emerged with strong relative intensities, indicating that TiO$_2$ NTAs were mainly coated with Bi$_2$O$_3$ quantum dots (Figure 4b). The C 1s peak is ascribed to adventitious hydrocarbon from the XPS instrument itself. The higher resolution XPS spectrum of the Bi 4f region is displayed in Fig. 4c. The Bi 4f XPS spectra were fitted into two peaks at 158.4 eV (Bi 4f$_{5/2}$) and 163.8 eV (Bi 4f$_{7/2}$). The binding energy between Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$ is approximately 5.4 eV, showing the +3 valence state of Bi element, which indicated the existence of Bi$_2$O$_3$. Figure 4d showed the high resolution XPS spectrum of O 1s. The oxygen on the sample surface existed in the form of the binding energies of 532.0, 530.2 and 529.5 eV. The main peaks at 530.0 eV and 529.5 eV could be ascribed to the O lattice of TiO$_2$ and Bi$_2$O$_3$ quantum dots, respectively. The peak at 532.2 eV is attributed to irreversibly adsorbed water molecules on the surface of the Bi$_2$O$_3$@TiO$_2$ NTAs sample.

Figure 4. Survey XPS spectrum of TiO$_2$ NTAs (a) Bi$_2$O$_3$/TiO$_2$ NTAs with a SILAR process of 4 cycles (b) and corresponding high resolution XPS spectra of Bi 4f (c) and O 1s (d) of Bi$_2$O$_3$@TiO$_2$ NTAs.

Figure 5a displayed the UV-Vis diffuse reflectance spectra (UV-DRS) of TiO$_2$ NTAs and Bi$_2$O$_3$@TiO$_2$ NTAs with different SILAR processes. The pristine TiO$_2$ NTAs showed an absorption band lower than 390 nm due to the charge from O 2p valance band to Ti 3d conduction band. Compared to pristine TiO$_2$ NTAs, the Bi$_2$O$_3$@TiO$_2$ NTAs-1, 4 and 7 exhibit a broader and stronger absorption in both UV and visible light regions. The band edges of the samples were approaching the visible-light region owing to the synergistic effect of Bi$_2$O$_3$ photosensitizing and the creation of p-n heterojunction. Moreover, the Bi orbit may be essential to decrease the energy gap between Ti and O orbitals of Ti oxide to enable the red shift. Usually, the higher absorption toward visible region verified the better photocatalytic activity of photocatalysis. Therefore, the Bi$_2$O$_3$@TiO$_2$ NTAs-4 possessed the strongest absorption among all samples, and thus the highest photocatalytic activity was expected. Figure 5b showed the PL spectra of TiO$_2$ NTAs and Bi$_2$O$_3$@TiO$_2$ NTAs with different SILAR processes. Due to the oxygen vacancy of TiO$_2$ NTAs, the peaks appeared at about 452 nm, 471 nm, 490 nm and 595 nm. The lower PL intensity signified that the separation and transfer efficiency of photogenerated electron-hole pairs was stronger and thus a higher photocatalytic activity yield. Compared with pristine TiO$_2$ NTAs, Bi$_2$O$_3$@TiO$_2$ NTAs displayed lower PL intensity. The increase in the order of Bi$_2$O$_3$@TiO$_2$ NTAs-4 < Bi$_2$O$_3$@TiO$_2$ NTAs-1 < Bi$_2$O$_3$@TiO$_2$ NTAs-7 < pure TiO$_2$ NTAs. The increase in the PL signal of the samples obtained with longer SILAR cycles (i.e., Bi$_2$O$_3$@TiO$_2$ NTAs-7) suggested that the larger Bi$_2$O$_3$ quantum dots and nanoclusters may act as the charge recombination center, rather than facilitate electron-hole separation, and partially block the channels of TiO$_2$ nanotubes. These results indicated that the presence of Bi$_2$O$_3$ quantum dots with optimized size and uniform distribution would decrease the recombination of electron-hole pairs to endow Bi$_2$O$_3$@TiO$_2$ NTAs-4 with the best photochemical activity. Figure S3† shows the time-resolved photoluminescence (TRPL) spectrum of TiO$_2$ NTAs and Bi$_2$O$_3$@TiO$_2$ NTAs with ultrasonication-assisted SILAR deposition for 1, 4 and 7 cycles. Compared to the pristine
TiO$_2$ NTAs, Bi$_2$O$_3$@TiO$_2$ NTAs displayed longer decay lifetime. Longer decay lifetime clearly indicates lower recombination and higher separation efficiency of electron-hole pairs.$^{31}$ What’s more, lower recombination of electron-hole pairs will lead to weaker photoluminescence and higher photocatalytic activity, which is consistent with the PL spectra. Bi$_2$O$_3$@TiO$_2$ NTAs with ultrasonication-assisted SILAR deposition for 4 cycles owns the longest decay lifetime and the highest photocatalytic activity.

The separation of photogenerated electron-hole pairs was evaluated by measuring the photocurrent. Figure 6 showed the current-time (I-t) characteristics of pure TiO$_2$ NTAs and Bi$_2$O$_3$@TiO$_2$ NTAs-1, 4 and 7 electrodes recorded in 0.1 M Na$_2$SO$_4$ under simulated solar irradiation. As shown in Figure 6, when the pristine TiO$_2$ NTAs electrode was under light irradiation, there was a photocurrent density with ca. 0.09 mA/cm$^2$. However, the photocurrent density of the Bi$_2$O$_3$@TiO$_2$ NTAs with different SILAR processes for 1, 4 and 7 cycles was 0.43 mA/cm$^2$, 0.51 mA/cm$^2$, 0.19 mA/cm$^2$, which was approximately 4.8 times, 5.8 times, 2.1 times higher than that of TiO$_2$ NTAs electrode, respectively. The enhanced photocurrent could be ascribed to the decoration of Bi$_2$O$_3$ quantum dots into the TiO$_2$ NTAs system, resulting in faster electron transport from the valence band to the conduction band of TiO$_2$ and higher separation efficiency of photogenerated electron-hole pairs.$^{32}$

The electrochemical impedance spectroscopy (EIS) measurements were an effective tool for scrutinizing the interfacial properties between the electrode (i.e., TiO$_2$ NTAs annealed at 450°C and Bi$_2$O$_3$@TiO$_2$ NTAs-4 at 450°C) and the electrolyte. The diameter of semicircle in the Nyquist plots at high frequency reflects the charge transfer process, and the smaller diameter of semicircle represents the lower charge transfer resistance.$^{33}$ As shown in Figure 7, the diameters of TiO$_2$ NTAs at 450°C were much larger than those of Bi$_2$O$_3$@TiO$_2$ NTAs-4 in the dark as well as under simulated solar light irradiation. This supported that the Bi$_2$O$_3$ quantum dots decoration considerably reduced the recombination of electron-hole pairs and enhanced photocatalytic activity. Figure S4† shows the Bode phase plots of TiO$_2$ NTAs and Bi$_2$O$_3$@TiO$_2$ NTAs-4 under simulated solar light irradiation. The electron lifetime in photodecomposition and corresponding kinetic rates of self-degradation cures and corresponding kinetic rates of self-degradation, pristine TiO$_2$ NTAs, Bi$_2$O$_3$@TiO$_2$ NTAs-4 displayed a little longer electron lifetimes. These results suggest the presence of Bi$_2$O$_3$ quantum dots can prolong the electron lifetimes and facilitate the charge transport.$^{14}$

Figure 6. Photocurrent responses of as-prepared pristine TiO$_2$ NTAs and Bi$_2$O$_3$@TiO$_2$ NTAs with different SILAR processes for 1, 4, and 7 cycles under UV irradiation in 0.1 M Na$_2$SO$_4$ solution recorded at 1.0 V. The illumination from a 150 W Xe lamp was interrupted every 60 s.

Figure 7. Electrochemical impedance spectra of TiO$_2$ NTAs at 450°C and Bi$_2$O$_3$@TiO$_2$ NTAs with repeated SILAR processes for 4 cycles in the dark and under solar light illumination, respectively.

The photocatalytic activity of the samples was evaluated by degradation of MO under UV irradiation. The decomposition of MO pollutant followed the first-order reaction kinetics, which could be defined as $\ln(C_0/C_t) = kt$, where $C_0$, $C_t$, $k$, $t$ was the initial MO concentration, concentration after certain reaction time, the rate constant and reaction time, respectively. The MO photodecomposition cures and corresponding kinetic rates of self-degradation, pristine TiO$_2$ NTAs, Bi$_2$O$_3$@TiO$_2$ NTAs with different repeated SILAR processes for 1, 4, and 7 cycles was depicted in Figure 8. When using the pure TiO$_2$ NTAs as the photocatalyst, the concentration of MO was reduced by 31.1% after 2 h irradiation. However, it was found that the Bi$_2$O$_3$@TiO$_2$ NTAs with different SILAR processes for 1, 4, and 7 cycles displayed that the concentration of MO was reduced by 43.4%, 51.2% and 40.1% respectively, indicating higher degradation rate than pure TiO$_2$ NTAs (Figure 8a). The reaction constants $k$ for the pristine TiO$_2$
NTAs and Bi$_2$O$_3$@TiO$_2$ NTAs with multiple SILAR processes for 1, 4, and 7 cycles were calculated 0.00302, 0.00462, 0.00590 and 0.00418 min$^{-1}$, respectively (Figure 8b). Evidently, the apparent reaction constant of the photocatalytic degradation of MO with the assistance of TiO$_2$ photocatalyst and the decoration of Bi$_2$O$_3$ quantum dots was significantly higher than that of MO self-degradation (0.00132 min$^{-1}$). The kinetic constants of the optimized Bi$_2$O$_3$@TiO$_2$ NTAs with a SILAR process of 4 cycles for MO degradation (0.00590 min$^{-1}$) was 1.95 times higher than the pure TiO$_2$ NTAs counterpart (0.00302 min$^{-1}$), indicating that the Bi$_2$O$_3$ quantum dots sensitized on the TiO$_2$ NTAs with p-n heterojunction significantly enhanced the photocatalytic activity.

Figure 8. Photodegradation rates of MO for pristine TiO$_2$ NTAs at 400°C, Bi$_2$O$_3$@TiO$_2$ NTAs with multiple SILAR processes for 1, 4, and 7 cycles.

In addition to the excellent photocatalytic degradation performance, the Bi$_2$O$_3$/TiO$_2$ NTAs with different SILAR processes also exhibited good stability of photocatalytic activity during the degradation process of MO solution. As shown in Figure 9, the MO removal rate of all Bi$_2$O$_3$@TiO$_2$ NTAs with different repeated SILAR processes had a little reduction within 5% after 10 photocatalytic recycling. This indicated that the Bi$_2$O$_3$/TiO$_2$ NTAs remained active for long-term service without obvious deactivation.

Figure 9. Recycling test of the Bi$_2$O$_3$@TiO$_2$ NTAs with different SILAR processes on the MO removal rate under 2 h of UV light irradiation.

It is believed that the enhanced photocatalytic activity of Bi$_2$O$_3$@TiO$_2$ NTAs is mainly attributed to the p-n heterojunction effect between p-type Bi$_2$O$_3$ and n-type TiO$_2$ heterojunction. In order to describe how Bi$_2$O$_3$@TiO$_2$ NTAs enhanced the photocatalytic activity, the degradation mechanism of MO was illustrated in Scheme 2. The Fermi energy level of n-type TiO$_2$ lies closer to the conduction band while the Fermi energy level of p-type Bi$_2$O$_3$ lies closer to the valence band. When the n-type TiO$_2$ and p-type Bi$_2$O$_3$ formed the p-n heterojunction, it would create the inner electric field between the surface of TiO$_2$ and Bi$_2$O$_3$. During the process, the electrons transfer from Bi$_2$O$_3$ to TiO$_2$ while the holes transfer from TiO$_2$ to Bi$_2$O$_3$ until the system attained equilibration due to the carrier diffusion between the TiO$_2$ and Bi$_2$O$_3$. Under UV irradiation, the photogenerated electron-hole pairs created on the n-type TiO$_2$ surface are drifted by the electric field in the opposite direction. The holes flow into the negative field and the electrons move to the positive field. Thus, the photoexcited electrons at the conduction band of Bi$_2$O$_3$ will move towards the conduction band of TiO$_2$, and conversely the holes transfer from the valance band of TiO$_2$ to the valance band of Bi$_2$O$_3$ because of the effect of the inner electric field. Therefore, photogenerated electron-hole pairs are separated efficiently and the resultant photocatalytic activity is enhanced. The photocatalytic degradation mechanism of MO is proposed as follows:

- $p$-Bi$_2$O$_3$ / $n$-TiO$_2$ + hv $\rightarrow$ Bi$_2$O$_3$(h$^+$) + TiO$_2$(e$^-$)
- TiO$_2$(e$^-$) + O$_2$ $\rightarrow$ O$_2^-$
- O$_2^-$ + H$_2$O $\rightarrow$ H$_2$O$_2$ + ·OH
- Bi$_2$O$_3$(h$^+$) + H$_2$O / ·OH $\rightarrow$ ·OH
- ·OH + MO $\rightarrow$ Degradation
Scheme 2. Schematic diagram showing the energy band structure and electron-hole pairs separation-transfer in the p-type Bi$_2$O$_3$/n-type TiO$_2$ heterojunction under UV irradiation.

Conclusions

In summary, we have developed a very promising strategy of ultrasonication-assisted SILAR processes to realize highly uniform Bi$_2$O$_3$ quantum dots dispersed on both inside and outside of the vertically aligned TiO$_2$ nanotubes. Such novel Bi$_2$O$_3$@TiO$_2$ NTAs p-n heterojunction substantially increased the photogenerated electron-hole separation-transfer, and notably improved photocatalytic activity (1.95 times over the pristine TiO$_2$ NTAs counterpart), indicating the synergistic effect between the specific nanotube array structure of TiO$_2$ and uniformly distributed Bi$_2$O$_3$ quantum dots facilitating the photoexcited electron transfer from p-type Bi$_2$O$_3$ to n-type TiO$_2$ NTAs for high-efficiency photocatalytic degradation of organic pollutants. Therefore, this study provides an effective synthetic strategy to uniformly synthesize nanoparticle-modified one-dimensional heterostructures which have promising applications in environmental reclamation and energy harvest.

Acknowledgements

The authors thank the Natural Science Foundation of Jiangsu Province of China (BK20130313; BK20140400), National Natural Science Foundation of China (91027039; 51373110), Deanship of Scientific Research at King Saud University (RGP-B089). We also acknowledge the funds from the project of the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Qing Lan Project for Excellent Scientific and Technological Innovation Team of Jiangsu Province (2012) and Project for Jiangsu Scientific and Technological Innovation Team (2013).

Notes and references


**Graphical Abstract:**

An ultrasonication-assisted successive ionic layer adsorption and reaction (SILAR) strategy was developed to uniformly deposit p-type Bi$_2$O$_3$ quantum dots on n-type TiO$_2$ nanotube arrays for greatly enhanced photocatalytic activity.