Photoelectrocatalytic degradation of organic pollutants via a CdS quantum dots enhanced TiO₂ nanotube array electrode under visible light irradiation†

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Ultra-fine CdS quantum dots modified TiO₂ nanotube arrays (TiO₂-NTs) with enhanced visible-light activity are fabricated via a cathodic electro-deposition combined with ion-exchange route (CEDIE). The as-formed CdS quantum dots were highly dispersed both outside and inside the TiO₂-NTs. The proposed CEDIE strategy results in the strong combination and heterojunctions between CdS and TiO₂ through Cd–O bonds. The crystal phases, chemical compositions and physicochemical properties of as-obtained CdS/ TiO₂-NTs have been investigated based on various characterizations. Compared to CdS/TiO₂-NTs prepared via a sequential chemical bath deposition method, the as-synthesized samples exhibit stronger visible-light absorption capability, higher photocurrent density, excellent stability, and greatly enhanced photoelectrocatalytic (PEC) activity toward degradation of methyl orange (MO) aqueous solutions under visible light irradiation (λ > 400 nm). Such enhanced PEC activity may be ascribed to the strong combination and heterojunctions between CdS and TiO₂, favorable for visible-light response and charge separation of TiO₂-NTs.

However, the practical application of pure TiO₂-NTs is still limited by its large band gap (3.2 eV for anatase) and a fast recombination rate of photo-generated electron–hole pairs. Many routes have been explored to overcome such an impediment, one of which is coupling TiO₂ with narrow band gap semiconductors, such as CdS,2–4 Cu₂O,5–8 BiOCl,9 ZnFe₂O₄,10–12 and CuInS.13 In particular, the band gap of CdS (Eg = 2.4 eV) and its relatively high absorption coefficient in the visible light region make it highly desirable for the utilization in photovoltaics and photoelectrochemistry in comparison with other semiconductors.14 CdS nanoparticles, usually, are deposited onto the surface of the TiO₂-NTs by the S-CBD method15–20 through immersing TiO₂-NTs in Cd²⁺ and S²⁻ solutions. Although such a method is convenient and simple, it shows a poor repeatability and weak bonding force between semiconductors. It should further be noted that the as-obtained CdS grains prefer to aggregate on the surface of TiO₂-NTs. Such aggregation of the CdS nanoparticles generally results in a significant decrease of the contact between CdS and TiO₂, leading to weak visible-light absorption capability and low charge separation and transfer rate. The aggregated CdS islands may also block the tube of the TiO₂-NTs. Thus, both the dispersion of CdS nanoparticles and the combination between CdS and TiO₂-NTs will significantly affect the visible-light-driven photocatalytic activity of the hybrid photocatalysts. It is highly required that the TiO₂-NTs be modified via ultrafine CdS quantum dots with a high degree of dispersion and strong combination between CdS and TiO₂-NTs for extending the photo-response to a longer wavelength region and accelerating...
the electron transfer from CdS to TiO2-NTs, while keeping the physicochemical properties of TiO2-NTs unchanged.

Herein, we have reported a novel, efficient and stable visible light driven TiO2-NT based photocatalyst in which highly dispersed ultrafine CdS quantum dots are incorporated within the pore walls of the TiO2 nanotubes. This is realized by two processes: (1) planting ultrafine CdO quantum dots as seeds into the pore walls of TiO2-NTs via Cd metal cathodic electrodeposition followed by calcination in air for converting Cd metal to CdO and (2) converting CdO to CdS via ion-exchange in Na2S solution. The electrodeposition route could allow homogeneous deposition of cadmium metal quantum dots with ultrafine size on the pore walls of the TiO2-NTs, supplying the seeds for the growth of CdO quantum dots. Based on ion-exchange, the as-formed CdS quantum dots were highly dispersed both outside and inside the TiO2-NTs. The proposed strategy resulted in the strong combination and heterojunctions between CdS and TiO2 through Cd–O bonds. The photo-response of TiO2-NTs was extended to the visible-light region and the electron transfer between CdS and TiO2-NTs was also accelerated without destroying the ordered porous structures. Therefore, enhanced visible-light photocatalytic performance is expected.

Recently, photoelectrocatalysis was proved as a feasible route to solving the tough problem of the recombination of photogenerated electron–hole pairs. In this process, an additional bias voltage between the working electrode (photocatalytic material) and counter electrode (Pt) was applied to promote photoelectron migration to the counter electrode through the outer circuit, thereby preventing the combination of electrons and holes and improving the efficiency of the photocatalytic reaction. Thus, the as-formed CdS quantum dots modified TiO2-NT film was utilized as the working electrode for the photoelectrocatalytic degradation of organic pollutants. Such an as-prepared CdS/TiO2-NT electrode exhibited excellent photocatalytic activity and photostability toward the degradation of methyl orange under visible light irradiation by applying a small bias voltage (0.8 V) owing to the strong combination and heterojunctions between CdS and TiO2-NTs.

**Experimental section**

**Chemicals**

Titanium sheets (0.3 mm thick, 99.5%) were purchased from Shanghai Right Titanium Industry Co., Ltd. Cadmium chloride, sodium sulfide, methyl orange, acetone and ethanol of analytical grade were obtained from Aladdin Company without further purification. All solutions were prepared with deionized water.

**Preparation of CdS-modified TiO2 nanotube array electrode**

A pure TiO2 nanotube electrode was fabricated by the electrochemical anodic oxidation technique. Prior to anodization, the titanium sheets were rinsed in an ultrasonic bath of acetone, ethanol and distilled water for 10 min successively. Then the cleaned titanium sheets were soaked in a mixture of 0.2 M NH4F and 0.1 M H3PO4 for 7 h at 20 °C. The as-anodized samples were crystallized by ambient annealing (500 °C) with a heating and cooling rate of 2 °C min⁻¹. CdS-modified TiO2 nanotubes were prepared by using a novel cathodic electrodeposition method followed by annealing and ion-exchange. A three-electrode setup was used for deposition by using a TiO2-NT electrode as the working electrode, Pt sheet as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The TiO2-NT electrode was immersed in CdCl2 solution for 6 min under ultrasonication. Then, the potentiostatic DC electrodeposition was carried out with a potential of 0.9 V for different times at room temperature. Upon electrodeposition, highly dispersed Cd metal quantum dots were homogeneously deposited onto the pore walls of the TiO2-NTs. The as-obtained films were further calcined at 500 °C in the atmosphere for 1 h for oxidizing Cd metal to CdO. Finally, CdO/TiO2-NT films were kept at 140 °C for 10 h in an autoclave containing 50 mL Na2S aqueous solution (0.2 M) for ion-exchange. For comparison, CdS/TiO2-NTs were also prepared by a conventional sequential chemical bath deposition (SCBD) route. Briefly, the TiO2-NT film was immersed in 0.2 M CdCl2 solution for 5 min. Upon being rinsed with DI water, the obtained film was further immersed in 0.2 M Na2S solution for 5 min and rinsed again with DI water. Repeating the above process two times resulted in the formation of CdS crystallites on the TiO2-NTs.

**Characterization**

Wide-angle X-ray diffraction measurements were carried out in parallel mode (ω = 0.5°, 2θ varied from 20° to 80°) using a Rigaku Dmax-3C Advance X-ray diffractometer (Cu Kz radiation, λ = 1.5406 Å). The morphologies of the products were observed and analyzed using a field emission scanning electron microscope (FESEM, S-4800). Transmission electronic microscopy (TEM) images were recorded on a JEM-2010. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000). All the binding energy values were calibrated by using C1s = 284.6 eV as a reference. The photoluminescence (PL) spectra were recorded on a Varian Cary-Eclipse 500. The diffuse reflectance spectra of the samples over a range of 200–800 nm were recorded by a Varian Cary 500 UV–vis system equipped with a Labsphere diffuse reflectance accessory using BaSO4 as a reference.

**Photoelectrochemical measurements**

Photoelectrochemical measurements were carried out in a conventional three-electrode, single-compartment quartz cell on an electrochemical station (CHI 660D). The CdS/TiO2-NT electrode and the TiO2-NT electrode with an active area of ca. 4 cm² served as working electrodes. The counter electrode and the reference electrode were a platinum sheet and saturated calomel electrode (SCE), respectively. A bias voltage of 0.5 V was utilized for driving the photo-generated electrons transfer from the working electrode to the platinum electrode. A 300 W Xe lamp with an ultraviolet filter (λ > 400 nm) was used as the visible light source and positioned 10 cm away from the
photocatalytic performance testing

The liquid-phase photocatalytic degradation of methyl orange was carried out at 303 K in an 80 mL self-designed quartz photochemical reactor containing 50 mL of aqueous solution (10 mg L\(^{-1}\)) under visible light (\(\lambda > 400\) nm) irradiation. Other reaction conditions are the same as those of the photoelectrochemical measurements. Upon being vigorously stirred for 1 h for reaching the adsorption–desorption equilibrium of MO on the catalyst, the photoelectrocatalytic reaction was initiated by irradiating the system with a 300 W xenon lamp with an ultraviolet filter (\(\lambda > 400\) nm) located at 10 cm away from the photoelectrochemical reaction cell. At given irradiation time intervals, ca. 3 mL of the reaction solution was sampled, and the residual MO concentration was analyzed using a UV spectrophotometer (UV 7504/PC) at its characteristic wavelength (\(\lambda_{\text{MO}} = 467\) nm). Preliminary tests exhibit a good linear relationship between the light absorbance and the pollutant concentration. No more than 2% pollutants degraded after reaction for 2 h under the same condition in the absence of either the working electrode or the light irradiation and, thus, could be neglected in comparison with the MO degraded via photoelectrocatalysis. The reproducibility was checked by repeating the results at least three times, and was found to be within acceptable limits (±5%).

Results and discussion

It has been reported that Fe, Zn and other metals can be successfully electro-deposited inside the pore channels of TiO\(_2\) by utilizing the resistance difference between the bottom and top of the nanotubes.\(^{13,23}\) Upon electrodeposition, highly dispersed metal quantum dots were homogeneously deposited onto the pore walls of TiO\(_2\)-NTs. Thus, a novel cathodic electrodeposition combined with ion-exchange (CEDIE) process was proposed for modifying TiO\(_2\) nanotube arrays with ultrafine CdS quantum dots. Scheme 1 illustrates the novel deposition procedure, which includes two steps: (1) Cd metal was firstly deposited onto the pore walls of TiO\(_2\)-NTs via cathodic electrodeposition and then converted to ultrafine CdO quantum dots by calcination in air and (2) CdO was converted into CdS via ion-exchange in Na\(_2\)S solution.

With the help of the capillary action (ultrasonication), the salt solution diffused through the nanochannels of TiO\(_2\). And then by electrochemical reduction, the first step allowed homogeneous deposition of cadmium metal quantum dots of ultrafine size on the pore walls of the TiO\(_2\)-NTs, supplying seeds for the growth of CdO quantum dots. Based on ion-exchange, the as-formed CdS quantum dots were highly dispersed both outside and inside the TiO\(_2\)-NTs. To investigate the effect of the electro-deposition time on the amount of CdS deposited and activity of CdS/TiO\(_2\)-NTs, the electrodeposition time was controlled at 2, 5, 15, 30, 60 seconds, respectively. The samples obtained correspondingly were denoted as 2 s-CdS/TiO\(_2\)-NTs, 5 s-CdS/TiO\(_2\)-NTs, 15 s-CdS/TiO\(_2\)-NTs, 30 s-CdS/TiO\(_2\)-NTs and 60 s-CdS/TiO\(_2\)-NTs. Based on the proposed method, CdS/TiO\(_2\)-NTs with enhanced visible-light activity could be anticipated because CdS quantum dots can be highly dispersed and intimate with TiO\(_2\)-NTs leading to more uniform heterojunctions and strong bond forces between CdS and TiO\(_2\)-NTs.

In order to identify the crystal phase of TiO\(_2\)-NTs and CdS/TiO\(_2\)-NTs, the X-ray diffraction (XRD) measurement was used with the results shown in Fig. 1. For pure TiO\(_2\)-NTs, all diffraction peaks can be indexed to the TiO\(_2\) anatase phase (JCPDS file no: 21-1272) and the Ti metal phase (JCPDS file no: 44-1294), respectively. There are no obvious differences between 2 s, 5 s, 15 s and 30 s-CdS/TiO\(_2\)-NTs and pure TiO\(_2\)-NTs, indicating that no CdS diffraction peak appeared, perhaps owing to its ultrafine size, high dispersity and low concentration. In the case of the 60 s-CdS/TiO\(_2\)-NT sample, there are two additional diffraction peaks at 2\(\theta\) values of 26.5° and 43.7°, which could be attributed to the (0 0 2) and (1 1 0) crystal planes of the hexagonal CdS phase (JCPDF 41-1049). The 60 s-CdS/TiO\(_2\)-NT sample also exhibits a new peak at ca. 29°, which may be ascribed to the crystal planes of Ti\(_8\)O\(_{15}\) (JCPDF 50-0790). The formation of the impurities could result from the excess electron-pulse deposition time. It should be pointed out that the other diffraction peaks of CdS were not clearly distinguished because they overlapped with those of anatase TiO\(_2\) and pure Ti metal. The XRD results indicate that the composite electrodes prepared by the
CEDIE approach are composed of CdS and TiO2 crystalline structures.

The morphologies of the TiO2-NT electrode were characterized by field emission scanning electron microscopy (FESEM). Fig. 2a and b display typical the top-view and side-view FESEM images of the pure TiO2-NTs. It can be seen that the pure TiO2-NTs possess a highly ordered structure and vertical orientation with an average outer pore diameter of ca. 100 nm, wall thickness of ca. 10 nm and tube length of ca. 1.0 μm. Fig. 2c and d show the FESEM images of 2 s-CdS/TiO2-NTs, which reveal that obtained ultrafine CdS quantum dots were highly dispersed on both outside and inside the TiO2-NTs. It was also observed that the size of CdS increased slowly upon prolonging the Cd metal deposition time in the first electrodeposition step, while the high dispersity can be maintained well. It is interesting that no aggregation of CdS particles can be found to block the tubes for all of the as-obtained CdS/TiO2-NT samples. Nevertheless, the sample of CdS/TiO2-NTs fabricated via S-CBD suffered from serious CdS aggregation on the surface of the TiO2 nanotubes and poor interaction between CdS and TiO2 as shown in Fig. 2i. These results suggest that the proposed CEDIE route is an excellent technique for homogeneous introduction of the semiconductor CdS on TiO2-NTs. The chemical composition of the 30 s-CdS/TiO2-NTs was further determined by energy-dispersive X-ray spectroscopy (EDX), as shown in Fig. S1.† The results confirm that the sample of 30 s-CdS/TiO2 is mainly composed of Ti, O, Cd, and S. Quantitative analysis shows that the atomic percentage of Cd and S is about 0.60 and 0.74, respectively, indicating that the content of CdS is very low.

In order to investigate the dispersion of CdS deposited in TiO2-NTs by CEDIE more thoroughly, transmission electronic microscopy (TEM) was explored to observe the samples of pure TiO2-NTs and 30 s-CdS/TiO2-NTs after ultrasonication. Fig. 3a shows the TEM image of broken fractals of the pure TiO2-NT sample obtained after ultrasonication. The outer pore diameter is about 100 nm, and the wall thickness of the TiO2 nanotubes is about 10 nm (Fig. 3b). It can also be noticed that the surface of pure TiO2 nanotubes is smooth and clean in accordance with the SEM image (Fig. 3a and b). As shown in Fig. 3c and d, ultrafine CdS quantum dots with an average diameter of ca. 3 nm are highly dispersed on the wall of the TiO2 tubes, with the formation of the heterojunctions between CdS and TiO2 justified by the HRTEM results. As shown in Fig. S2,† CdS QDs exhibit the typical lattice fringe spacing (0.316 nm) ascribed to the [101] plane. Close interaction between CdS and TiO2 could be clearly observed in the HRTEM images. These results are in agreement with those of FESEM. This indicates that the proposed fabrication route could avoid the aggregation of CdS nanoparticles and increase the intimate and effective contact between the two semiconductors.

X-ray photoelectron spectroscopy (XPS) was employed to investigate the valence states and chemical compositions of the obtained samples. As shown in Fig. 4a and b, the binding energy of Ti2p and O1s changed very little after CdS deposited on
TiO$_2$-NTs. For 30 s-Cds/TiO$_2$-NTs, two peaks of Cd3d in Fig. 4c were observed at 404.3 eV and 411.1 eV, assigned to Cd 3d5/2 and Cd 3d3/2, respectively. These data are in accordance with the results reported by Yu et al.$^{24}$ But for SCBD-Cds/TiO$_2$-NTs, the binding energies of Cd 3d are 405.3 eV and 411.9 eV, which are close to that of pure Cds.$^{25}$ In Fig. 4d, there is a doublet structure at 160.7 eV and 161.7 eV due to the presence of S 2p3/2 and S 2p1/2 for 30 s-Cds/TiO$_2$-NTs, while a broad peak appears in the XPS of the S element for SCBD-Cds/TiO$_2$-NTs. By analyzing the data of XPS, we may draw a conclusion that the combination between Cds and TiO$_2$ in the as-formed samples via CEDIE route is stronger than that in SCBD-Cds/TiO$_2$-NTs.

Fig. 5a depicts the UV-vis diffuse reflectance spectra of the pure TiO$_2$-NT and Cds/TiO$_2$-NT electrodes. It has been observed that the pure TiO$_2$-NT electrode exhibits photo-response in the UV region with a wavelength below 380 nm, which can be attributed to the intrinsic band gap of TiO$_2$. The weak absorption of pure TiO$_2$-NTs in the visible light region can be ascribed to the scattering of light caused by pores or cracks in the nanotube arrays.$^{1,3,13}$ Compared to the pure TiO$_2$-NTs, all the Cds/TiO$_2$-NT electrode shows strong absorption capability in the region ranging from 380 to 500 nm owing to the contribution of CdS. It indicates that the photo-response of TiO$_2$-NTs can be easily extended to visible light region by sensitizing with Cds quantum dots. It is worth noting that the absorbance in the visible region of 30 s-Cds/TiO$_2$-NT electrode prepared via the CEDIE route is stronger than that of the SCBD-Cds/TiO$_2$-NT electrode. Furthermore, by increasing the Cds amount via prolonging the electro-deposition time, the absorption intensity is improved. The photoluminescence (PL) technique is an effective way to investigate the efficiency of the charge carrier trapping, migration, and transfer due to the PL signals of semiconductor materials, resulting from the recombination of photo-induced charge carriers. It has been recognized that the lower the PL intensity, the lower the recombination rate of photo-induced electron–hole pairs.$^{26}$ As shown in Fig. 5b, all samples display PL peaks at around 560 nm. The PL intensity of pure TiO$_2$-NTs is much higher than that of the Cds modified TiO$_2$-NTs. These results demonstrate that the introduction of Cds into the pore walls of the TiO$_2$-NT samples effectively inhibits the charge carrier recombination. Compared to SCBD-Cds/TiO$_2$-NTs, the 30 s-Cds/TiO$_2$-NT sample exhibits a weaker PL absorption. It could be attributed to stronger combination and more uniform heterojunctions between Cds quantum dots and TiO$_2$ crystallites, supported by the FESEM and XPS results.

The photogenerated charge separations and transport properties on Cds/TiO$_2$-NTs could be investigated through electrochemical impedance spectroscopy (EIS). Fig. 6 shows the EIS response of pure TiO$_2$-NT electrode and Cds/TiO$_2$-NT electrode under visible light ($\lambda > 400$ nm) irradiation. The radius of the arc on the EIS Nynqust plot reflects the reaction rate occurring at the surface of electrode. The $x$ axis and $y$ axis represent the real part of the impedance ($Z'$) and the imaginary part of the impedance ($Z''$), respectively. The arc radius on the EIS Nynquist plot of Cds/TiO$_2$-NT electrode is smaller than that of the pure TiO$_2$-NT electrode, which suggests that a more effective separation of photogenerated electron–hole pairs and faster interfacial charge transfer occurred on the Cds/TiO$_2$-NT heterojunction.$^{27,28}$ Similarly to the PL results, the 30 s-Cds/TiO$_2$-NT electrode shows a lower recombination rate of photo-induced electron–hole pairs than the SCBD-Cds/TiO$_2$-NT electrode, according to the smaller radius of the arc on the EIS Nynquist plot in Fig. 6. This indicates that the CEDIE route employed here gives rise to a good interaction of the Cds particles with the TiO$_2$-NTs resulting in an efficient and faster charge transfer through the coupled semiconductor.

To test the photoelectrochemical response of as-prepared pure TiO$_2$-NTs and Cds/TiO$_2$-NTs under visible light irradiation, photocurrent densities were measured in the light on–off process with a pulse of 10 s by the potentiostatic technique.$^{29}$ As shown in Fig. 7, upon being irradiated with visible light ($\lambda > 400$ nm) at an applied potential of 0.5 V vs. SCE, all of the Cds/TiO$_2$-NT samples exhibited strong photocurrents. However, the photocurrent of pure TiO$_2$-NTs can be neglected compared with that of the Cds modified samples. For all Cds/TiO$_2$-NTs, the photocurrent value goes down to zero as soon as the light is turned off, and the photocurrent comes back to the original value as soon as the light is turned on again. Such a photocurrent response is highly reproducible for numerous on–off cycles. Among Cds/TiO$_2$-NTs fabricated by CEDIE, the photocurrent of 30 s-Cds/TiO$_2$-NTs reaches a maximum, while on
increasing the amount of CdS the photocurrent becomes lower. This phenomenon could be attributed to formation of charge recombination sites as a result of excess CdS grains. It is interesting to note that the 30 s-CdS/TiO2-NT sample exhibits a higher photocurrent density generation of ca. 0.8 mA cm⁻², which is greatly enhanced compared with that of the SCBD-CdS/TiO2-NTs (with a value of ca. 0.2 mA cm⁻²). These results demonstrate that the CdS-sensitized TiO2-NTs fabricated by the CEDIE technique could harvest visible light and separate electron–hole pairs more effectively than those prepared by the conventional SCBD approach, which has been verified by the characterization of DRS, PL and EIS above.

The photoelectrocatalytic (PEC), photocatalytic (PC), electrochemical (EC) process and direct photolysis (DP) of methyl orange (MO) in aqueous solutions were performed on the 30 s-CdS/TiO2-NT electrode under visible light illumination (Fig. 8a).

The results show that 89.8% of the MO removal rate was obtained after 180 min of the PEC process, while only 14.5% and 1.2% of MO removal in PC and EC process during the same illumination time. In the PEC process, an additional bias voltage between the working electrode (photocatalytic material) and counter electrode (Pt) was applied to promote photoelectrons to migrate to the counter electrode through the outer circuit, thereby preventing the combination of electrons and holes and improving the efficiency of the photocatalytic reaction. It demonstrates that photoelectrocatalysis is a feasible route to solve the tough problem of the electron recombination therefore providing the most effective way to degrade the MO aqueous solution. Furthermore, the degradation of MO in the PEC process was much higher than the summation of PC and PEC processes. Such synergetic effect between PC and EC has been reported by Zhang et al. and Xie et al. Fig. 8b demonstrates the kinetic behaviors of MO photoelectrocatalytic (PEC) degradation on the synthesized samples under visible light irradiation, applied a bias potential of 0.5 V vs. SCE. This process clearly obeys the first-order reaction kinetics, and its kinetics may be expressed as follows: ln(C0/C) = kt, where k is the apparent rate constant, while C0 and C are the initial concentration and the reaction concentration of MO, respectively. Evidently, the apparent rate constants of all the CdS/TiO2-NT samples are significantly higher than that of pure TiO2-NTs. The photoelectrochemical testing results could also support this conclusion. Upon illumination with visible light, CdS effectively excite electrons and holes. As the conduction band of the CdS is more negative than that of the TiO2, an internal local electric field is therefore generated. This makes the electrons quickly transfer to the conduction band of TiO2, and along aligned nanotubes be further transported to the external circuit, whereas the generated holes accumulate in the valence band of CdS. When the separated electrons and holes participate in reduction (cathode) and oxidation (anode) reaction, respectively, the photocurrent and PEC activity can be tested. Among CdS/TiO2-NTs fabricated by our novel method, the 30 s-CdS/TiO2-NT sample possesses the highest PEC activity (0.0129 min⁻¹). Upon increasing the amount of CdS via prolonging of the electro-deposition time to 60 s, the degradation rate goes down, which is in accordance with photocurrent results. As a comparison, the apparent rate constant of CdS/TiO2-NTs prepared by SCBD (0.0084 min⁻¹) is much lower than 30 s-CdS/TiO2-NTs, though the modified CdS amount of the latter can be neglected compared with that of the former based on EDS analysis.
From the FESEM images, one can see that the CdS prepared by SCBD just aggregated on the surface of TiO$_2$-NTs, which only facilitated excitation of near-to-surface CdS particles. This resulted in longer electron transportation pathways from the CdS to TiO$_2$-NTs, then through nanotube channels getting to the Ti substrate as shown in Scheme 2. In contrast, the high dispersity characteristic of CdS in 30 s-CdS/TiO$_2$-NTs, affords the sensitization of CdS located in the deeper level of TiO$_2$-NTs, allowing good usage of visible light. Furthermore, electron injection from CdS to TiO$_2$-NTs occurs more easily with this structure owing to uniform heterojunctions between two semiconductors. This indicates that the distribution of CdS nanoparticles and combination between CdS and TiO$_2$-NTs are very important factors for PEC activity under visible illumination. The preparation method recommended in this paper could improve the PEC activity. Such a nano-fabrication route provides a high photochemical stability of the CdS-modified TiO$_2$ nanotube systems because the hybrid nanostructure could greatly enhance the charge transfer to avoid charge build-up at the interfaces. As known, the charge built up in semiconductors has been demonstrated to be responsible for their corrosion in the photochemical system.

It should be noted that the concentration of the electrolyte can also affect the PEC degradation rate. As shown in Fig. 9a, changing the electrolyte concentration did not alter the order of the reaction kinetics. The optimal concentration of Na$_2$S aqueous solution is 0.2 M, producing the highest PEC reaction rate constant (0.0129 min$^{-1}$). As known, increasing the concentration of Na$_2$S aqueous solution can enhance the conductivity of the reaction solution, which can promote the separation of photo-induced electrons and holes. However, excess electrolyte, such as 0.5 M Na$_2$S, is not favorable for the enhanced PEC performance. This may be attributed to the ion adsorption on the electrode surface, occupying the reactive sites of the working electrode. The stability of the 30 s-CdS/TiO$_2$-NT electrode was investigated by repeating the photoelectrocatalytic degradation of MO under visible light irradiation 10 times. As shown in Fig. 9b, after 10 repeated experiments for PEC degradation of MO, the degradation yield can be retained to above 87.0%. It should be pointed out that the inductively coupled plasma (ICP) results indicated that almost no Cd$^{2+}$ cations can be observed in the residual reaction solution. These results indicate that the as-made CdS/TiO$_2$-NT electrode has an excellent photostability.

**Conclusions**

In summary, framework embedded CdS quantum dots sensitized TiO$_2$-nanotubes were fabricated via a cathodic electrodeposition combined with ion-exchange route. The as-obtained CdS/TiO$_2$-NT composites possess ultrathin CdS quantum dots with high dispersity, well crystallized anatase phases, large specific surface area, low band gap energy, and a close contact between CdS and TiO$_2$. The above merits produced both excellent visible-light photoelectrocatalytic activities and super strong photostabilities. The proposed route can also be extended to design other hybrid semiconductor based nanotube electrodes.

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Notes and references