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Toward efficient photocatalysts for light-driven CO₂ reduction: TiO₂ nanostructures decorated with perovskite quantum dots
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Abstract
Nanostructured TiO₂ is often used for photocatalytic CO₂ conversion due to its favorable electronic properties and stability, being coupled with large surface area and unique electrical properties. However, pure TiO₂, without any expensive cocatalysts, can not provide highly efficient CO₂ conversion because its bandgap and resulted limited numbers of photogenerated electrons and holes limit efficient energy conversion. Here, we demonstrate TiO₂ nanotube (TNT) photocatalysts equipped with two different perovskite quantum dots (PQDs) made of CH₃NH₃PbBr₃ and CH₃NH₃PbI₃. The fundamental properties of the PQDs and TNT/PQD photocatalysts are investigated and their potential for more efficient CO₂ conversion are discussed, to our best knowledge, for the first time. TNT/CH₃NH₃PbI₃ QD photocatalysts absorb a wider range of light energy and show superior charge transport characteristics due to less sensitivity against surface states at TNT/CH₃NH₃PbI₃ QD interface than the TNT/CH₃NH₃PbBr₃ photocatalysts.

1. Introduction
The conversion of CO₂ to useful fuels, driven by light energy, has been of great interest because the excess CO₂ gas in the atmosphere can used as an abundant and precious source of energy, simultaneously removing it and reducing its harmful environmental effects. Developing the efficient semiconductor photocatalysts for the CO₂ conversion would contribute the suppression of the global warming that is attributed to devastating CO₂ emission from the massive consumption of fossil fuels while also helping to meet the current energy demands in the world.

Two seminal publications for photocatalytic CO₂ conversion by semiconductor materials were those by M. Halmann in 1978 and T. Inoue et al in 1979 [1, 2]. Since these publications, TiO₂ has become highly popular material to study for photocatalytic CO₂ conversion due to its excellent stability and favorable alignment of energy level. However, innate and unmodified TiO₂ photocatalysts have some weaknesses when used to perform efficient conversion of CO₂ and one of those is its wide optical band gap (3.2 eV for anatase structure). The wide band gap of TiO₂ only allows about 5% of total incident light energy to be absorbed and this generates limited numbers of available electrons. In this context, unmodified TiO₂ cannot be considered as a promising material for efficient CO₂ conversion because all the CO₂ conversion reactions to fuels require multiple numbers of electrons and hydrogen ions. For example, the production of CO requires two electrons and cations while formation of CH₄ needs eight electrons and eight cations as listed in the equations below [3],

\[ \text{CO}_2 + 2e^- + 2H^+ \rightarrow \text{CO} + \text{H}_2\text{O} \]  \hspace{1cm} (1)

\[ \text{CO}_2 + 8e^- + 8H^+ \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \]  \hspace{1cm} (2)

To tackle this limitation of pure TiO₂ material, several attempts have been made to modify TiO₂ itself by adding additional materials. Various elements such as N, Se, or Pt have been doped in the TiO₂ to adjust its optical band gap and thereby, to achieve wider range of light energy harvest [4–6]. Hydrogenation of TiO₂ has
also been shown to modify its optical and electronic properties of TiO₂ for improved photocatalytic performance [7–9]. Low-dimensional structures such as nanotubes and nanowires have been made from TiO₂, providing high surface area and enhanced photocatalytic performance [10–12]. Smaller bandgap materials such as WO₃, Fe₂O₃, or CuO [12–14] or nanostructured metals such as Ag, Pd, Cu or Pt [10, 15, 16] form a heterojunction through decoration onto the surface or through deposition for more efficient charge separation or additional light absorption. However, in most cases, the fabrication of the efficient TiO₂-based photocatalysts requires expensive materials such as Pt, Au, or Ag and delicate control through complicated synthesis process. In addition, considering the limitation of elements in earth’s crust, the exploration on another more abundant and lower cost candidate materials should be considered for economical and efficient CO₂ conversion.

In this regard, metal halide perovskite quantum dots (PQDs) could be promising candidates owing to various advantages when they are coupled with TiO₂: Facile synthesis, low cost, excellent optical properties, and tunability of their properties depending on size and shape. In addition to these, metal halide perovskite materials themselves have a favorable energy band structure matching to TiO₂. All these valuable properties of the PQDs have led the excellent achievement in optoelectronic applications such as solar cells, light emitting diodes, and photodetectors [17–20].

In this work, facile fabrication and characterization for TiO₂ nanotubes (TNT) decorated with two different perovskite quantum dots, namely, CH₃NH₃PbBr₃ and CH₃NH₃PbI₃ are demonstrated. The unique material, optical, and electrical features of the TNT with PQDs are thoroughly investigated for their potential application for efficient CO₂ conversion.

2. Experimental section

2.1. Materials

For anodization, ammonium fluoride (NH₄F, Sigma) and ethylene glycol (99%, J.T. Baker) were used. For the synthesis of the perovskite quantum dots, CH₃NH₃Br (purity of 99+%, Sigma), PbBr₂ (99.999%, Sigma), Dimethylformamide (99%, J.T. Baker), Oleic acid (90%, Sigma), N-octylamine (99%, Alfa Aesar), Tert-butanol (99+, Uni-Onward company), Hexanes (98.5%, J.T. Baker), CH₃NH₃I (99+, Uni-Onward company), PbI₂ (99+%, Lumtecl company) Acetonitrile (99+%, HY BIOCARE CHEM), and Toluene (99.7%, J.T.Baker) were used. For synthesis of the CO₂-containing electrolyte, KHCO₃ (99.7%, Sigma) and CO₂ gas (99.999%, Jing De Gaseco CO., Ltd.) were used. All chemicals were used without further purification.

2.2. Preparation of TNTs

TNTs are fabricated by 2-step anodization process, following a published procedure [21]. 0.25-mm-thick titanium foils (99.5% purity, Alfa Aesar) are cut into 2 × 2 cm pieces and cleaned with DI water and acetone consecutively by ultrasonication for 10 min 400 ml of Ethylene Glycol was stirred overnight with 0.3 wt% of NH₄F and 2 vol% of DI water for the preparation of the anodization electrolyte at room temperature. Pt mesh served as counter electrode and the distance between Pt and Titanium foil was fixed by 1.5 cm during the anodization.

For the first anodization, 40 V is applied to the two-electrode system for 3 h to grow long nanotubes and, after the first anodization was finished, the firstly grown nanotubes were removed with vigorous sonication in DI water for 10 min, leaving a hexagonal footprint on the surface of the Ti foil. Then, 40 V is applied again for 20 min to grow highly ordered TNTs templated by the first growth. The ordered TNTs were subject to an annealing process in the furnace at 450 °C for 3 h with 1 °C min⁻¹ of a ramping rate under ambient conditions in order to attain the anatase phase.

2.3. Synthesis of CH₃NH₃PbBr₃ quantum dots

The synthesis of CH₃NH₃PbBr₃ quantum dots was accomplished following a published procedure [22]. A solution of 0.16 mmol of CH₃NH₃Br was dissolved in 0.3 ml of DMF (named as solution A). 0.2 mmol of PbBr₂ was dissolved in 0.5 ml of DMF (named as solution B). 10 ml of hexane was mixed with 0.5 ml of oleic acid and 20 μl of n-octylamine (named as solution C). A and B were added dropwise into solution C while under vigorous stirring. Then, 4 ml of tert-butanol was added into solution C and the solution was subsequently centrifugated at 6000 rpm for 5 min to obtain precipitates. The obtained precipitates were redissolved into 4 ml of hexane to extract the colloidal QDs solution and filtered out to remove larger particles in the solution. Then, another centrifugation of the solution was carried out at 5000 rpm for 5 min. The synthesized solution of the CH₃NH₃PbBr₃ quantum dots exhibits green color under UV light as shown in figure S1 (available online at stacks.iop.org/NANOX/2/020003/mmedia) in supplementary information and reported from referenced work [22].
2.4. Synthesis of CH$_3$NH$_3$PbI$_3$ quantum dots
The CH$_3$NH$_3$PbI$_3$ quantum dots were synthesized by following a published procedure [23]. A solution of 0.08 mmol of CH$_3$NH$_3$I and 0.1 mmol of PbI$_2$ were dissolved in the solution that consisted of 0.2 ml of oleic acid, 10 μl of n-octylamine, and 2 ml of acetonitrile. The mixed solution was sonicated for 15 min to obtain a clear precursor. The precursor solution was added dropwise to 10 ml of toluene while vigorously stirred. The solution was subsequently centrifugated at 6000 rpm for 10 min to remove the large precipitates. The synthesized solution of the CH$_3$NH$_3$PbI$_3$ quantum dots exhibits red color under UV light as shown in figure S1 in supplementary information and reported from referenced work [23].

| Sample name | Solvent | Volume of solvent (ml) | Volume of PQD solution (ml) |
|-------------|---------|------------------------|-----------------------------|
| TNT-Br$_3$  | Hexane  | 3                      | 0.1                         |
| TNT-Br$_5$  |         | 5                      | 0.1                         |
| TNT-Br$_7$  |         | 7                      | 0.1                         |
| TNT-I$_3$   | Toluene | 3                      | 0.1                         |
| TNT-I$_5$   |         | 5                      | 0.1                         |
| TNT-I$_7$   |         | 7                      | 0.1                         |

2.5. Decoration of PQDs onto the surface of TNTs
The decoration of PQDs onto TNTs was carried out by an immersion method. TNTs were treated with UV-ozone for 30 min to remove unwanted carbon contamination and to enhance the hydrophilicity of the surface. The TNT samples were immersed in a PQD solution with varied concentrations; the concentrations were adjusted by varying the volume ratio between the solvent and the PQD solution. The specifications of the
prepared solutions and the sample identifiers are listed in table 1. The immersion time for all samples was 10 min and a subsequent annealing process was performed at 40 °C for another 20 min in glove box. The fabricated samples were cooled down to room temperature for further characterization.

2.6. Characterization
The crystal structures and detailed morphologies of the PQDs and TNTs were analyzed by transmission electron microscopy (TEM, JEM-3010 from JEOL), operating with acceleration voltage of 300 kV under 10⁻⁵ Pa. The TNTs were characterized by Hitachi S-3000H Scanning Electron Microscope (SEM) at the acceleration voltage of 5 kV under the vacuum condition (5 × 10⁻³ Pa). The crystalline structure of TNTs was analyzed by X-ray diffraction machine (Bede D1). The scan range of 2θ is from 20° to 80° at a scanning rate of 0.03° min⁻¹ with X-ray tube operated at 40 mA and 40 kV at room temperature. The optical properties of PQDs were analyzed by Fluorescence Spectroscopy (Fluoromax-PLUS-C) with light source of 150 W Xenon lamp and 400 nm of the excitation wavelength. A diffuse reflectance measurement was implemented for evaluating absorption properties of the samples using a HITACHI Spectrophotometer U-3900H. The light source of the spectrophotometer is set up by diffraction grating-diffraction grating double monochromator with D₂ lamp (ultraviolet region) and W₁ lamp (visible light). The range of wavelength that was measured was 200 nm to 800 nm with an integrating sphere (Φ60 integrating sphere accessory). A solar simulator (LCS-100, 94011 A, purchase from Newport) was used for photocurrent measurement, simulating sunlight source, which provide AM1.5 G illumination (100 W cm⁻²) from ozone free Xenon lamp, (1.5-inch × 1.5-inch collimated beam). Photoresponse and electrochemical impedance measurements were conducted by CHI660E (CH instruments, Inc., USA). The measurement was carried out in CO₂-saturated electrolyte, containing 0.1 M KHCO₃. Photocurrent was scanned for 70 s with applied bias of 0.4 V and sensitivity of 10⁻⁵ A/W. The electrochemical impedance was measured with initial bias of 0.4 V and the frequency was ranged from 1 to 10⁵ Hz.

3. Results and discussion
Figure 1 shows the morphologies of the synthesized (a) CH₃NH₃PbBr₃ QDs and (b) CH₃NH₃PbI₃ QDs. The average sizes of the prepared PQDs are 17 nm and 16 nm for CH₃NH₃PbBr₃ and CH₃NH₃PbI₃, respectively. These synthesized PQDs was sporadically deposited both inside and outside surfaces of TNT figure 1(c). The
TiO2 NTs used here are \( \sim 2 \mu m \) of length and 70 nm of inner diameter as shown in figure 1(c) and are primarily anatase as shown in figure 1(d).

The synthesized PQDs exhibit their characteristic emission peaks at 650 nm and 525 nm of wavelengths for CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)NH\(_3\)PbBr\(_3\), respectively, as shown in figure 2(a). These peaks are well matched with previous works by others [22, 24], proving the material formation of CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)NH\(_3\)PbBr\(_3\) together with XRD results from CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)NH\(_3\)PbBr\(_3\) film in figure S2. Figure 2(b) shows absorption spectrum of two different PQDs. The range of light absorption is well matched to the results of PL, where CH\(_3\)NH\(_3\)PbI\(_3\) QDs and CH\(_3\)NH\(_3\)PbBr\(_3\) QDs absorb light energy from UV up to \( \sim 650 \) nm and \( \sim 525 \) nm, respectively. The light absorption spectrum of CH\(_3\)NH\(_3\)PbI\(_3\) QDs is broader than that of CH\(_3\)NH\(_3\)PbBr\(_3\) QDs and CH\(_3\)NH\(_3\)PbBr\(_3\) QDs only exhibit strong absorption at shorter wavelengths. Moreover, no additional absorption was observed from wavelengths above \( \sim 650 \) nm and \( \sim 525 \) nm for CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)NH\(_3\)PbBr\(_3\), respectively. To further determine the optical properties of the PQDs, Tauc equation has been applied as below [25, 26],

\[
\alpha h\nu = A(h\nu - E_g)^n
\]

where \( \alpha \) is the absorption coefficient, \( h\nu \) is the photon energy, \( A \) is a constant, \( E_g \) is the optical band gap, and \( n \) is the value for the modes of transitions that \( \frac{1}{2} \) is for allowed direct transition.

The extracted bandgaps of the PQDs are 2.38 eV and 2.13 eV for CH\(_3\)NH\(_3\)PbBr\(_3\) QDs and CH\(_3\)NH\(_3\)PbI\(_3\) QDs, respectively, and these bandgaps are larger than those of bulk materials (1.95 eV for bulk CH\(_3\)NH\(_3\)PbBr\(_3\) and \( \sim 1.6 \) eV for bulk CH\(_3\)NH\(_3\)PbI\(_3\), respectively) [27, 28]. This suggests that the synthesized PQDs are sufficiently small to exhibit quantum confinement characteristic of quantum dots.

Figure 3 exhibits the absorption characteristics after the PQDs deposition onto the surface of TNTs, for various concentrations. All concentrations of the PQDs applied to the TNTs result in remarkable increase in absorption. Moreover, relatively small differences in absorbance are observed in terms of concentrations. Even though figure 3 shows the small differences, through careful examination, there are two important findings here: (1) the samples with CH\(_3\)NH\(_3\)Br\(_3\) QDs show increased absorption differences only in shorter wavelengths (less
than 400 nm with varied concentrations while the samples with CH$_3$NH$_3$PbI$_3$ QDs exhibit the change of absorption through entire measured wavelengths (2) absorption is increased as the concentration of the PQDs become higher (TNT-Br$_7$ $\rightarrow$ TNT-Br$_3$). The lack of change at longer wavelengths for the CH$_3$NH$_3$PbBr$_3$ QDs
can be attributed to the fact that CH$_3$NH$_3$PbBr$_3$ QDs have a wider bandgap than that of CH$_3$NH$_3$PbI$_3$ QDs. Note that both PQDs have excellent absorption capability at shorter wavelengths. CH$_3$NH$_3$PbBr$_3$ QDs are more sensitive for the larger energy photons and the PQD allows deeper penetration from the surface of smaller energy photons while CH$_3$NH$_3$PbI$_3$ responds to a wider range of photon energies and has more total absorption.

Figure 4 shows photocurrent measurement of TNTs without/p PQDs in varied concentration in 0.1 M KHCO$_3$ aqueous solution saturated with CO$_2$ for the evaluation of photocatalytic CO$_2$ reduction. In this system, since the photocurrent in the electrochemical configuration can be carried by the redox species of in the 0.1 M KHCO$_3$ solution and dissolved CO$_2$ can act as more efficient redox species in the solution as shown in figure S3, the relative comparison can be interpreted as CO$_2$ reduction capability. All the decorated samples with PQDs prepared from lower concentration (TNT-Br$_7$ & TNT-I$_7$) are measured with the enhancement in photocurrent indicating the possibility of a higher rate of CO$_2$ reduction. In addition, thicker PQD decoration to TNT does not provide further improved performance, comparing to the ones with lower concentrations in spite of the fact that the sample with the thicker concentrations exhibited higher absorption as in figure 3. Rather, the photocurrent decreased as the concentration increased among the samples with PQDs (TNT-Br$_7$ → TNT-Br$_3$ & TNT-I$_7$ → TNT-I$_3$). In case of TNT-Br samples, their photocurrents are more reduced with the sample with thicker PQD decoration than that of bare TNT.

To explore the origin of the performance variation, electrochemical impedance spectroscopy was implemented in two electrode system in figure 5 and table 1. The diameter of the semicircle in Nyquist plots represents charge transfer resistance at the interface of catalyst/electrolyte and smaller diameter is interpreted as smaller charge transfer resistance. All charge transfer resistances of the PQD-decorated samples are improved in comparison with that from bare TNT. In semiconductor system, the resistance, $R$ can be described as below [29],

$$R = \rho \frac{L}{A} \quad (1a)$$

where $L$ is the length, $A$ is the area, and $\rho$ is resistivity. Again, the resistivity, $\rho$ can be expressed as [29],

$$\rho = \frac{1}{\epsilon \mu n} \quad (2a)$$

where $e$ is the electronic charge, $\mu$ is majority carrier mobility, and $n$ is majority carrier concentration.

Considering the two equations above (equation (1) & equation (2)) and our previous work relating to the interface and carrier accumulation in catalytic systems [16, 30], the decrease in $R_c$ found in the PQD-decorated samples can be interpreted as the presence of electron accumulation at the interface from PQD to TNT. These more conductive interfaces measured with the PQD-decorated samples imply that the PQDs decorated to the TNT contributed to additional charge injections toward the surface of the TNT. In both cases, the smallest charge transfer resistances are measured with the sample prepared with the smaller loading of PQDs (TNT-Br$_7$ & TNT-I$_7$) and the variation in $R_c$ coincide with the results from figure 4; $R_c$ decreased with the PQD decoration but no enhancement is observed with the thicker decoration of the PQDs in figure 5 and table 2.

Further analysis was carried out with photoluminescence measurements as shown in figure 6 for the investigation of the charge transport through the TNTs decorated with CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$ QDs photocatalytic system.

The TNT without the decoration of the PQDs emit the light around 400 nm, which is its unique wavelengths that corresponds to the optical bandgap of anatase TiO$_2$ (3.2 eV). With the incorporation of CH$_3$NH$_3$PbBr$_3$ QDs to the surfaces of the TNTs, the PL intensity at ~400 nm decreases and no remarkable variations are detected with varied QD solution concentration, exhibiting quenching effect as in figure 6(a). This quenching behavior suggests that the presence of CH$_3$NH$_3$PbBr$_3$ QDs on the surface of TNTs induces strong charge transfer from the conduction band edge of the TNT to the valence band edge of the PQD as described in figures 6(b) and (d).

The heterointerface made of two different semiconductor materials as in the case of the PQD/TNT interface possesses innate band offset between conduction band edges ($\Delta E_c$) or/and valence band edge ($\Delta E_v$) [29]. These offsets are not favorable for efficient injected carrier transport with the presence of surface states because the surface states located at the heterointerface resulted in severe recombination of the injected carriers [31]. Moreover, this recombination, $U$, becomes more deteriorative with the density of traps, following the equation below [32],

| Sample | TNT | TNT-Br$_3$ | TNT-Br$_5$ | TNT-Br$_7$ |
|--------|-----|------------|------------|------------|
| $R_c$(Ω) | 6811 | 5328 | 5355 | 4715 |
| $R_c$(Ω) | 7693 | 6120 | 2688 | 1316 |

**Table 2.** Charge transfer resistances of TNT/PQD photocatalysts by electrochemical impedance spectroscopy.
where $B_n$ is the coefficient, $n$ is the electron concentration, $N_t$ is the trap density, and $f_t$ is the probability that the trap is occupied. In other words, the recombination is stronger with higher density of traps, $N_t$. In case of CH$_3$NH$_3$PbBr$_3$ QDs, it is reported that the heterointerface made with the QDs exhibits the presence of the surface states at the interface and the charge transport is affected by the surface states [33]. Therefore, through the surface states, the possibility of nonradiative recombination becomes larger and this is possibly what leads to the decreased PL intensity. Contrary to this, TNT/CH$_3$NH$_3$PbI$_3$ QD samples exhibit improved PL intensity in comparison with bare TNT as shown in figure 6(c). This means that the decoration of CH$_3$NH$_3$PbI$_3$ QDs helps to make the conduction band of TNT more populated by electrons, without severe recombination. It is speculated that this is because CH$_3$NH$_3$PbI$_3$ QDs have more favorable energy band alignment to TNT than CH$_3$NH$_3$PbBr$_3$, and less surface states at the interface. $E_C$ of Bulk CH$_3$NH$_3$PbI$_3$ is closer by 90 mV to $E_C$ of TNT [34] and this smaller $\Delta E_C$ possibly suppress the recombination at the heterointerface more efficiently, increasing the PL intensity as described in figure 6(d). However, TNT/CH$_3$NH$_3$PbBr$_3$ QD samples also exhibit a similar trend in terms of the concentration of the PQD solution as in figure 6(c). As in the case of TNT/CH$_3$NH$_3$PbBr$_3$ QD, large amount of the decoration causes severe charge transfer to PQDs through the surface states, it is that the charge transport through TNT/CH$_3$NH$_3$PbI$_3$ QD samples also affected by the surface states and this is not helpful for the enhancement of photocurrent for efficient CO$_2$ reduction. However, all these findings prove that the CH$_3$NH$_3$PbI$_3$ QDs play an important role in injecting additional carriers much to TNT. Moreover, after the charge injection to TNT, the charge transport is less sensitive against the presence of surface states at TNT/CH$_3$NH$_3$PbI$_3$ QD interface than that of TNT/CH$_3$NH$_3$PbBr$_3$ QD interface as described in figure 6. In summary, TNT/CH$_3$NH$_3$PbI$_3$ QD combination is more favorable for obtaining additional photocarriers as seen in figure 4 than the TNT/CH$_3$NH$_3$PbBr$_3$ QD combination because CH$_3$NH$_3$PbI$_3$ PQDs can harvest wider range of light energy and more efficient charge transport is possible through the TNT after charge injection.

4. Conclusion

TNT photocatalysts incorporating two different kinds of PQDs were demonstrated for possible use in light-driven CO$_2$ conversion applications. The diameters of the synthesized PQDs were 17 nm and 16 nm for CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$, respectively, showing quantum confinement effect evidenced by the widened optical bandgaps. The TNTs were decorated with different concentrations of these two different kinds of the PQDs. All PQD-decorated samples showed additional photocarrier injection into the TNT which is favorable for the improvement of the photocatalytic performance. However, the CH$_3$NH$_3$PbI$_3$ QDs contribute more to the photoresponse of TNT/PQD than CH$_3$NH$_3$PbBr$_3$ PQDs. This can be attributed to the fact that CH$_3$NH$_3$PbBr$_3$ PQDs can harvest a wider range of light energy and have more efficient charge transport through TNT after charge injection owing to less nonradiative recombination. In spite of possible long-term stability issue of the PQD materials, this work proposes the extended availability of TNT/PQD structure and would be a stepping stone for further development of efficient PQD-based nanostructured photocatalysts in the field of light-driven CO$_2$ conversion.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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