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A Stable Perovskite Sensitized Photonic Crystal P–N Junction with Enhanced Photoelectrochemical Hydrogen Production

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The slow photon effect in inverse opal photonic crystals represents a promising approach to manipulate the interactions between light and matter through the design of material structures. This study introduces a novel ordered inverse opal photonic crystal (IOPC) sensitized with perovskite quantum dots (PQDs), demonstrating its efficacy for efficient visible-light-driven H₂ generation via water splitting. The rational structural design contributes to enhanced light harvesting. The sensitiza-

Introduction

In recent decades, there has been a growing concern about the global energy crisis and the greenhouse effect resulting from carbon dioxide emissions. Consequently, the scientific and industrial communities have been actively pursuing the development of clean and sustainable energy solutions as alternatives to traditional fossil fuels.^[1,2]

Hydrogen stands out as one of the most promising alternative fuel sources due to its zero-carbon emissions, ease of recyclability, and high energy conversion efficiency.^[3] A costeffective strategy for large-scale hydrogen production in the near future involves photoelectrochemical water splitting (PEC) driven by sunlight. Various nanostructures have been explored as photoelectrodes for hydrogen production, aiming to address

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tion of the IOPC with PQDs improves optical response performance and enhances photocatalytic H₂ generation under visible light irradiation compared to the IOPC alone. The designed photoanode exhibits a photocurrent density of 3.42 mA cm⁻² at 1.23 V vs RHE. This work advances the rational design of visible light-responsive photocatalytic heterostructure materials based on wide band gap metal oxides for photoelectrochemical applications.

challenges such as light harvesting, charge separation, carrier mobility, and photostability. $^{\left[4-8\right] }$

In the realm of photocatalysts for PEC water cleavage into hydrogen and oxygen, titanium dioxide (TiO₂) takes a prominent position. This is attributed to its abundance, low cost, low toxicity, superior photostability, and high intrinsic catalytic activity under ultraviolet (UV) illumination.[9-11] However, the use of TiO₂ in photocatalysis has been hindered by its low quantum efficiency resulting from the recombination of photogenerated carriers (electrons and holes) and poor solar light harvesting caused by the wide band gap (3.0-3.2 eV) in most polymorphic phases of titania.^[12,13] This wide band gap allows absorption only in the ultraviolet region, which accounts for just 4% of solar irradiation. Although various research efforts have successfully reduced the band gap through intragap states, the reactivity of the photocatalysts and the associated process efficiency were compromised due to the decreased thermodynamic driving force between the photogenerated charge carriers.[15-17]

A novel approach to enhancing the light harvesting efficiency of TiO₂ involves the utilization of a photonic crystal, which is a periodic structure with a photonic stop band (PGB). The photonic crystal (PC) exhibits the slow photon effect, characterized by photons propagating with a reduced group velocity, particularly at frequencies close to the edges of the PGB. This effect arises from the enhanced interaction of light with the periodic dielectric structure.^[18-20] The inherent potential of the slow photon effect lies in its ability to increase the length of the optical path, leading to a delay and storage of light within the $\text{PC.}^{\scriptscriptstyle[19]}$ Tuning the PGB of a specific PC can be achieved by altering the structural repeat unit size according to Bragg's law,^[18] allowing for manipulation of the interaction between light and matter by adjusting the structural parameters of the PC. Various research endeavors have focused on enhancing solar-to-energy efficiency by manipulating the

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optical interaction within photonic crystal (PC)-based materials. Often, the improvement in light conversion efficiencies arises from a delicate balance between Bragg's reflectance and the slow photon effect of PCs when interacting with incident light.^[21-23]

Inorganic perovskite materials have garnered significant research attention due to their unique tunable optical response coupled with charge transfer capabilities.^[24] Perovskite QDs and other inorganic QDs materials have found applications in diverse fields such as solar energy conversion,^[25] light-emitting diodes, photodetectors,[26-28] and photocatalysts for hydrogen production,^[29-32] Perovskites, characterized by outstanding optoelectronic properties, have been extensively studied for use in photovoltaic solar cells, achieving high power conversion efficiencies (PCE) of up to 25.2%. This success is attributed to their high light absorption coefficient, tunable band gaps, and efficient carrier extraction.^[33] However, the primary challenge in hydrogen production using perovskites lies in severe charge recombination and poor stability.^[34] Therefore, a rational approach involving surface modification is crucial to enhance hydrogen production in perovskite-based materials.

In this study, we present a novel electrode design by combining a TiO₂ inverse opal photonic crystal (IOPC) with sensitization using methylammonium lead bromide quantum dots (PQDs) to create a p-n junction photoanode (Figure 1). This design is employed for photoelectrochemical (PEC) hydrogen production through water splitting. The percolated periodic pores of the IOPC, offering a high surface area, were effectively utilized for loading PQDs, providing an excellent electron transport path and intimate contact with the electrolyte. The PQDs exhibited enhanced stability within the hybrid system and functioned as "light antennas" for efficient visible light harvesting. Additionally, the TiO₂ acted as a hole-blocking layer and formed a type II p-n heterojunction with PQDs to facilitate interfacial charge transfer and separation efficiency. As a result, the fabricated photoanode material demonstrated outstanding PEC performance, achieving a maximum photocurrent density of 3.48 mA cm⁻² at 1.23 V vs. RHE. This performance can be attributed to the synergistic effect of the slow light effect from the IOPC and the light harvesting efficiency of PQDs. To the best of our knowledge, this study represents the first report on perovskite QDs sensitized TiO₂ inverse opals for photocatalytic water splitting.

Result and Discussion

In Figure 2a, the SEM image of the PMMA opal photonic crystal (OPC) reveals an ordered face-centered cubic (FCC) lattice arrangement of PMMA particles, with the top layer exhibiting spherical PMMA spheres in point contact, as expected from the (111) planar geometry.^[35] This OPC, referred to as OPC_{262} , displays a narrow size distribution of 262 nm. Following the infiltration of OPC_{262} with TiO₂ precursor (titanium isopropoxide) and subsequent calcination, the SEM image in Figure 2b depicts the formation of an ordered microporous inverse opal photonic crystal (IOPC) structure, resulting from the inversion of the planar (111) PMMA opal crystal plane. The mean void spherical diameter for the IOPC is measured at 189 nm.

The mercaptohexadecanoic acid modified PQDs bind to the TiO_2 surface through the carboxylate moiety.^[36] The SEM images of the hybrid IOPC-PQDs (Figure 2c, d) maintain the ordered structure, and the EDX spectra, along with elemental mapping (Figure S1), confirm the uniform distribution of the expected elements, hence affirming the incorporation of PQDs into the crystal.

The high-resolution TEM (HRTEM) image of IOPC-PQDs (Figure 3b) and the corresponding fast-Fourier transforms (FFTs) and inverse FFTs obtained using Gatan digital micrograph software (Figure 3a–c) show lattice fringes with interplanar distances of 0.30 nm (Figure 3a) and 0.35 nm (Figure 3c), corresponding to the (200) and (101) lattice planes of PQDs and anatase TiO2, respectively.^[37,38]

The XRD patterns of the IOPC reveal a vastly dominant anatase phase of TiO₂, with intensity peaks of (101), (004), (200), (105), and (211) appearing at 25.39°, 37.89°, 48.1°, 54.005°, and 55.18° (Figure 3a). Similarly, PQDs exhibit the cubic phase, with measured diffraction peak positions at 15.0°, 21.21°, 30.12°, 33.78°, 37.15°, 43.18°, 45.93°, and 48.63° corresponding to interplanar spacings of (100), (110), (111), (200), (210), (211), (220), (300), and (310) crystal planes, respectively. The highly intense PQDs dominate the XRD peak in the hybrid IOPC-PQDs, with a visible presence of IOPC but with weakened intensity.

The specific surface composition of the prepared materials was analyzed by X-ray photoelectron spectroscopy (XPS) to obtain basic information about the interaction of the PQDs with TiO_2 . The XPS survey spectra (Figure S2) showed the expected elements at their respective binding energies.

The Pb4f electron binding energy peaks at 144.8 and 138.3 eV in the high resolution XPS spectra of PQDs (Figure 3e) can be assigned to the spin orbit coupling of Pb4f_{5/2} and



Figure 1. Schematic illustration of synthetic route for the photoanode materials.

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Figure 2. SEM images of the prepared materials (a) PMMA opals, (b) TiO₂ inverse opal, (c) PQDs modified TiO₂ inverse opal and (d) the corresponding high magnification image with yellow arrow showing PQDs spots.

Pb4f_{7/2}.^[39] Similarly, the characteristic peaks for Br3d were observed at 69.40 eV and 68.40 eV (Figure 3f). The spin orbit coupling electron binding energy for Ti 2p in the perovskite modified IOPC were observed at 458.32 and 464.65 eV. Furthermore, a slight positive shift of the Ti $2p_{3/2}$ after perovskite loading reveals feasibility of the electron transfer between the PQDs and TiO₂ (Figure 3g, insert).

The absorption spectra of the OPC_{262} , IOPC, IOPC-PQDs, PQDs and TiNC are shown in Figure 4a. The excitonic peak of PQDs at 475 nm is blue shifted from the stopband of IOPC. A stopband centered at 510 nm was observed for the IOPC replicated from PMMA opals assembled from 262 nm spheres (OPC_{262}). This stopband also shows a significant blue-shift from

561 nm for the OPC_{262} , which can be ascribed to the bending of the photonic bands associated with decreasing size.^[40]

The stopband of the hybrid IOPC-PQDs show a blue-shift and red-shift to the stopband of OPC₂₅₂ and IOPC respectively. The red-shifting of the stop-band peak position following sensitization with PQDs is due to the increased refractive index ($n_{PQDs} \approx 1.98$, $n_{TIO_2} = 2.2 - 2.4$, $n_{air} = 1.33$) while the blue shift is associated with decreasing size after removal of the PMMA templates.

Forming high quality TiO_2 periodic structures would prevent certain wavelengths of light from passing through, depending on the size of the cavity and the refractive index of the surrounding medium. Bragg's law relates the position of stopband to diameter of assembled colloids.^[41] The diameter of

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Figure 3. Structure and surface characterization (a) XRD pattern of the anode materials (c) HRTEM and (b, d) corresponding Fourier transformed of the highlighted areas, (e–g) XPS high resolution spectra of Pb 4f, Br 3d and Ti 2p, insert in fig. 2e is expanded Ti 2p1/2 in IOPC and IOPC-PQDs.

the spheres after the assembly can be determined from the Bragg equation (eq. 1) prior to infiltration of the void as follows:

$$\lambda = 2 \times 0.817 D \sqrt{\left(0.74 n_s^2\right) + \left(0.26 n_v^2\right)}$$
 (1)

Where λ is the stopband wavelength, n_s is the refractive index of the PMMA spheres (1.49), n_v is the refractive index of the material filling the voids (air in this case, $n\!=\!1.33$), and D is the measured diameter of PMMA spheres. The diameter of OPC using this relation is 235.2 nm, indicating a 10.3% shrinkage

relative to the 262 nm measured size, which can be attributed to solvent evaporation.

Similarly, taking the refractive index of TiO_2 as 2.44 after filling the opal and calcination, the diameter of the void in the IOPC calculated from Eqn. (1) is 141.5 nm indicating 25.3% shrinkage relative to the measured 189 nm. This shrinkage can be explained by the fact that the TiO_2 initially formed by hydrolysis inside the polymeric opal is mainly amorphous. The calcination step required to crystallize it into the anatase structure is accompanied by volume contraction, hence the

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Figure 4. Optical study (a) UV-Vis, (b) PL, (c) decay lifetime for the prepared photo-electrocatalyst. (d) Band alignment and electron transfer in the IOPC-PQDs heterostructure.

observed size reduction. The TiNC shows an absorption peak at 383 nm indicating low light harvesting efficiency.

The charge carrier separation property of the prepared catalysts was investigated using photoluminescence (PL) study (Figure 4b), since the PL intensity reflects the charge recombination of free carriers.

We prepared a disordered titanium dioxide sensitized peroxide (Figure S3) to investigate if the ordered IOPC sensitized with PQDs possessed any photocatalytic advantage arising from charge separation. A lower PL intensity suggests lower rate of charge recombination. It is evident from Figure 4b that the PQDs show a strong PL intensity peak, which indicates a fast charge recombination of photo-induced carriers. In comparison, the PQDs modified bulk TiO₂ (TiNC-PQDs) show a significant decrease in PL intensity indicating de-activation of charge carrier recombination. Similarly, the IOPC-PQDs show the lowest PL intensity, suggesting enhanced charge carrier separation, which is expected to boost the photocatalysis performance. We synthesized PQDs sensitized non inverted TiO₂ nanostructure (TiNC-PQDs) to prove that formation of the TiO₂ into photonic crystal indeed possess photocatalytic advantage. The PL peak red-shifted for TiNC-PQDs and IOPC-PQDs in comparison to PQDs, which could be attributed to strong interaction of the materials^[42] arising from migration of PQDs into the IOPC.

The time resolved (TRPL) analysis was carried out to validate the charge carrier transport observed from the PL study. The TRPL decay curve (Figure 4c) was fitted to bi-exponential function in Eqn. (2) and Eqn. (3) can be used to calculate the average carrier lifetime.

$$y(\tau) = A_1 e^{1/\tau_1} + A_2 e^{1/\tau_2}$$
(2)

$$\tau_{av} = \frac{A_1 \times \tau_1^2 + A_2 \times \tau_2^2}{A_1 \times \tau_1 + A_2 \times \tau_2} \tag{3}$$

where A_1 and A_2 are the amplitudes constant and the τ_1 and τ_2 represent the fluorescence lifetimes component.

The two-decay lifetime can be attributed to the existence of fast and slow decay components within the structure.^[9,10] The fast decay lifetime (τ_1) can be associated to the radiative process arising from initial exciton generated in the PQDs, while the slow decay component is related to the radiative recombination resulting from the surface defects or trapping sites.^[43,44] A glance at values of lifetime obtained from the decay curve (Table S1) show a shorter τ_1 of 2.45 and 5.91 ns respectively for IOPC-PQDs and TiNC-PQDs compared to 11.23 ns for PQDs alone. This can be explained based on the redistribution of the photonic density of state (DOS). In a typical 3D photonic crystal (PC), the DOS in the band edge of the photonic stop band

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(PBG) is higher compared to other range within the $PC^{[45]}$ and DOS is related to the rate of radiative emission (ρ_R) according to Eqn. (4)^{[46]}

$$\rho_{R} = \frac{2\pi}{\hbar M_{T}(E_{21})^{2}\rho_{r}(E_{21})\rho_{0}(v_{21})}$$
(4)

Where $M_T(E_{21})$ is the transition matrix element of the electronic wavefunctions, the second factor ρ_r (E_{21}) is the reduced electronic density of states (DOS) and the third factor ρ_0 (ν_{21}) is the photonic DOS, i.e. the number of photonic states available for recombination. Thus, the observed reduced τ_1 in the hybrid catalysts can be linked to redistribution of the photonic DOS within the PC. On the contrary, the second decay lifetime (τ_2) of 5.30 and 7.82 ns respectively for IOPC-PQDs and TiNC-PQDs is longer than 2.64 ns observed for PQDs. This could be explained by the fact that nonradiative process is related to the surface states of the PQDs, such as point defects, dislocations, and impurities.^[47] The second decay lifetime arises from unquenched PQDs with less defect site and elongated lifetime.

To effectively enhance the extraction of photogenerated carriers with concomitant suppressing of non-radiative recombination, it becomes crucial to optimize the band alignment. The band edge of PQDs and IOPC-PQDs as a representative were obtained from the Tauc plot and valence band XPS measurement as shown in Figure S4. From the band alignment profile in Figure 4d, it can be clearly seen that the valence band (VB) edge of PQDs (-5.60 eV) was higher than that of IOPC (-7.6 eV), which is well positioned to eliminate the formation of large Schottky barrier from the IOPC junction, hence enhanced the extraction hole capability. Furthermore, the higher conduction band edge (-2.7 eV) for the PQDs will provide easy access to electron injection into the conduction band of IOPC resulting in enhanced charge carrier separation. It is pertinent to mention that incorporation of PQDs in the IOPC pores provides strong photostability (83% photoluminescence retention) after 15 weeks compared to less than 4% retention for PQDs alone within 9 weeks (Figure S5). It has been shown that ionic and electronic defects produced by environmental factors such as oxygen, moisture or light adversely affect the stability and durability of perovskites QDs^[48] and this result not only in chemical reactions that disintegrate the structure and properties of perovskites but also induce undesired photoluminescence blinking to perovskite guantum dots. Thus, the enhanced stability of PQDs in the porous IOPC could be due to the protection of the PQDs from adverse environmental effects.

The photoelectrochemical performance of the photoanodes materials were evaluated by measuring the current density versus potential under dark and simulated sunlight illumination (AM 1.5 at 100 mW cm⁻²) using three-electrode cell configuration. As shown in the photo-response J–V curve profile (Figure 5a), the photoanodes show negligible photocurrent density under dark conditions. A pronounced photocurrent density was observed under light illumination, suggesting efficient harvesting of light with corresponding charge carrier separation at the photoanode/electrolyte interface. The IOPC-

PQDs exhibit superior photocurrent density of 3.48 mA cm^{-2} at 1.23 V vs. RHE compared to photocurrent density of 1.98 and 1.02 mA cm^{-2} observed for TiNC-PQDs and IOPC.

The enhanced photoactivity for the perovskite synthesized IOPC could be attributed to the slow photon effect on the edges of the photonic band gaps which enhances the absorption at the edge of PQDs as has been reported by Nishimura et.al in dye sensitized TiO₂ photonic crystal.^[49] Furthermore, we measured the chronoamperometric I–t curves (Figure 5b) under illumination of visible light ($\lambda \ge 420$ nm) with a constant potential of 1.23 V vs RHE, which is the most widely used potential for evaluation of performance of photoanodes since it corresponds to the potential for water oxidation. It can be clearly seen that that the photocurrent density following sensitization of the IOPC with PQDs was significantly enhanced by ≈ 2 and 4 times respectively compared to TiNC-PQD and IOPC.

This indicates that efficient PQDs sensitization combined with the slow photon effect in the IOPC can significantly improve the light harvesting efficiency, which is aided by the effective surface decoration on the accessible voids of the inverse structure.

The incident photon-to-electron conversion efficiency (IPCE) measurement were performed from 400 to 700 nm under a constant potential of 1.23 V vs RHE (Figure 5c) to estimate the correlation between light absorption and photocurrent density on the photoanodes materials. A strong photo-response was observed in the IPCE spectra from 400-750 nm, which correlates with the absorption edge characteristics of IOPC and PQDs. The perovskite sensitized IOPC-PQDs showed enhanced IPCE value of \approx 5% compared to 4 and 3.2% observed for TiNC-PQDs and IOPC respectively, which is consistent with the corresponding J-V curve performance. In addition, the PEC performance of the photoelectrodes was also investigated under entire solar light irradiation (AM 1.5G, intensity: 100 mW cm²) and presented in Figure 5d. The linear sweep voltammograms (LSV) under illumination of chopped light (frequency of 0.2 Hz) within the potential range of 0 to 2 V vs RHE clearly show that the photoelectrodes possess fast light response, which can be ascribed to efficient charge transport through 3-Dimensional nanoplatform. The PQDs sensitized **IOPC-PQDs** showed superior photocurrent density (2.17 mA cm⁻²), higher than TiNC-PQDs (1.02 mA cm⁻²) and IOPC (0.51 mA cm⁻²), indicating the important of sensitization of photonic structure in light harvesting and charge separation enhancement.

The photon-to-hydrogen (photoconversion) efficiencies (η) was calculated using Eqn. (5)

$$\eta = I(E_{rev}^0 - V)/J_{light}$$
⁽⁵⁾

where I is the measured photocurrent density (mA cm⁻²), J_{iight} is the incident light irradiance (mW cm⁻²), E_{rev} is the standard reversible potential (1.23 V vs RHE) and V is the applied bias potential vs RHE (V). The plot of photoconversion efficiencies against applied bias potential (Figure 5e) indicates enhanced Research Article doi.org/10.1002/cssc.202400395



Figure 5. Photoelectrochemical study. (a) photocurrent densities of the photoanode materials under simulated light (100 mW cm⁻²), (b) Amperometric I-t curves at an applied potential of 1.23 V vs RHE under illumination of visible light with wavelength \geq 420 nm with 50 s light on/off cycles, (c) Plots of IPCE in the range of 400–750 nm at 1.23 V vs RHE, (d) linear-sweep voltammograms under chopped illumination, collected at a scan rate of 5 mV s⁻¹, (e) corresponding photoconversion efficiency as a function of applied potential and (f) Calculated and experimental amounts of H₂ and O₂ gases evolved during the PEC water splitting reaction using the photoanodes materials.

conversion efficiency of 1.04 for IOPC-PQDs, much higher than 0.47 and 0.24 observed for TiNC-PQDs and IOPC respectively.

The simultaneous evolution of H_2 and O_2 is a prerequisite for photocatalyst meant for overall PEC water-splitting. The measurement of evolved H_2 and O_2 gases were studied under simulated sunlight. A simultaneous evolution of H_2 and O_2 from the photoanodes and Pt counter electrode at a stoichiometric ratio of approximately 2:1 was observed (Figure 5f, using IOPC-PQDs as representative), which indicates complete overall water splitting The H_2 and O_2 evolution rate were 770.0 and 376.5 µmol cm⁻² respectively and the amounts of experimental evolved H_2 and O_2 were slightly less than the theoretical amount, which could be probably due to gas leakage or dissolution in the electrolyte solution. The IOPC-PQDs anode still show more than 86% water splitting efficiency after three cycle test (Figure S6) indicating robust durability of the material. The comparative analysis of the rate of hydrogen and oxygen generation in the IOPC-PQD (Table S2) indicates superior or comparable performance to similar materials reported in literature.

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Experimental Section

The synthesis and self-assembly of monodispersed PMMA template were carried out following a modified emulsifier-free emulsion polymerization technique as reported in literature method.^[50]

Preparation of 3-Dimensional Ordered TiO₂ Inverse Opal Photonic Crystals

The precursor solution was prepared by stirring a mixture of 5.0 mL of ethanol, 1.0 mL of HCl, 5.0 mL of titanium (IV) isopropoxide, and 2.0 mL of water for 30 minutes in a 20 mL vial. This precursor was then used to fill the PMMA colloidal crystals in a 50 mL beaker and placed in an oven at 50 °C to dry. The template PMMA was removed by calcination in an air/nitrogen mixture. During the calcination, the temperature was raised from room temperature at a rate of 2 °C/min and allowed to stabilize at 300 °C for 2 hours, then increased at a rate of 2 °C/min and allowed to stabilize at 500 °C for 8 hours, and finally cooled down to room temperature at a rate of 20 °C/min.

Synthesis of MAPbBr₃ Perovskite Quantum Dots (PQDs)

For the synthesis of MAPbBr₃ PQDs, the precursor solution was prepared by dissolving 0.1 mol CH3NH3Br (0.0112 g) and 0.1 mol PbBr₂ (0.036 g) in 1 mL DMF, followed by ultrasonication for 10 minutes at 25 °C. Then, 200 μ L of mercaptohexadecanoic acid and 18 μ L of oleyamine were added to the homogeneous solution and further sonicated for 5 minutes. In a separate vial, 21 mL of toluene was maintained at 75 °C, and 0.7 mL of the perovskite precursor solution was injected, followed by ultrasonication for 2 minutes. A yellowish colloidal solution was observed, and the formed PQDs were collected by centrifugation at 7000 rpm for 15 minutes and stored in a sealed vial.

Synthesis Perovskite Modified $\mathrm{TiO}_{\mathrm{2}}$ Inverse Opal Photonic Crystals

 $\rm TiO_2$ inverse opal photonic crystals were dissolved in 21 mL of toluene and the temperature was raised to 75 °C. Then 0.7 mL of the perovskite precursor described above was injected into the solution followed with ultrasonication for 10 min to disperse the PQDs inside the photonic crystals. The formed heterostructure was collected by centrifugation 7000 rpm for 15 min and washed three times with toluene.

Synthesis of Disordered Titanium Nanocrystal (TiNC) and the Perovskite Synthesized Analogue

A mixture of 3 ml titanium isopropoxide, 30 ml hydrochloric acid and 30 ml deionized water was stirred at room temperature for 30 min and the solution was transferred to 100 mL Teflon beaker, sealed with stainless steel autoclave. The hydrothermal process conducted at 140 °C for 12 hr. and the formed product was collected by centrifugation, washed several times with acetone and deionized water.

The perovskite sensitized $\rm TiO_2$ nanocrystals (TiNC-PQDs) follow the same procedure as IOPC-PQDs with only substitution of IOPC with TiNC.

Characterizations

Field-emission scanning electron microscopy (FE-SEM) images were acquired using a FE-SEM Merlin Compact instrument from Carl Zeiss, Germany. Transmission electron microscopy (TEM) was conducted with a Tecnai G2 F30 S-TWIN instrument from FEI company, United States, while high-resolution transmission electron microscopy (HR-TEM) utilized a JEM-3010 instrument from JEOL, Tokyo, Japan. Energy dispersive x-ray spectroscopy (EDS or EDX) was performed using an AZtech Energy_X-MaxN instrument from OXFORD, UK.

Material composition and surface electronic characterization were carried out through X-ray photoelectron spectroscopy (XPS) using a MultiLab 2000 instrument from Thermo Scientific, MA, USA. X-ray diffraction spectroscopy (XRD) analysis utilized a MiniFlex II instrument from Rigaku, Tokyo, Japan, with a Cu target (λ =1.540598 Å), operated at a generator voltage of 30 kV and a scanning rate of 0.05° per minute.

Absorbance spectra were measured using a diffuse reflectance UV-VIS-NIR spectrophotometer (DRS) from Shimadzu, Kyoto, Japan, with a SolidSpec-3700 instrument.

PEC Evaluation

A three-electrode cell system consisting of photoanodes materials as working electrode, Pt wire counter electrode and Ag/AgCl as reference electrode was used to evaluate the PEC performance using an electrochemical workstation ((Ivium Technologies, Eindhoven, Netherlands)) at room temperature. A solar simulator equipped with an AM 1.5G filter and 150 W Xe lamp (Abet Technologies) was used as the light source to produce one sun illumination (100 mW/cm²). The photoanodes materials were spin coated on conducting side of fluorine-doped tin oxide (FTO) and dried in vacuum oven at 80°C. A copper wire was secured on the exposed electric conductive parts of the FTO with a silver conducting paste and subsequently sealed on all edges with epoxy resin, with only active working areas (0.5 cm²) exposed. 1 M KOH aqueous solution (pH=13.5) was used as the electrolyte. Time dependent transient photocurrent performance of the photoelectrodes were obtained during on-off (50 s) cycling of the solar simulator shutter at an applied potential of 1.23 V vs RHE. The measurement of evolved gases was obtained using a gas chromatograph (Young Lin Autochro-3000, model 4900) equipped with thermal conductivity detector and a 5 Å molecular sieve column with nitrogen (5.0 grade) as the carrier gas (flow rate 5.0 mL/min). Silicon septum was used to seal the top part of the reactor to enable sampling of the gaseous headspace by gas tight syringes. The system was kept inert through bubbling with argon for 30 min to remove the air inside before irradiation. After specific reaction time, 0.5 mL gas was injected into GC-TCD for quantification. Different volumes of standard 1.2% H₂-in-N₂ gas was injected into the GC to create a calibration curve relating the chromatogram peak area units to the amount of hydrogen produced (in micromoles).

Conclusions

In summary, a TiO_2 inverse opal photocatalyst sensitized with MAPbBr₃ quantum dots (QDs) was prepared using a simple and mild vacuum thermal treatment for TiO_2 inverse opal. This process was followed by the in-situ generation of QDs within the voids of the inverse opals. The resulting photocatalyst

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exhibited a synergistic enhancement of visible light harvesting ability, attributed to the slow light effect and perovskite nano antenna. This fabricated photocatalyst demonstrated excellent performance, owing to the combined highly porous network and efficient light harvesting capability. We anticipate that our research has the potential to serve as a promising model and design approach for the development of highly efficient solar light-driven photocatalysts.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Hydrogen production · inverse opals · perovskite quantum dots · photocatalyst · Photonic crystal

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RESEARCH ARTICLE



This study introduces a novel ordered inverse opal photonic crystal (IOPC) sensitized with perovskite quantum dots (PQDs), demonstrating its efficacy for efficient visible-lightdriven H_2 generation via water splitting. Dr. N. Nwaji^{*}, M.Sc. H. Kang, Dr. B. Bayissa Gicha, Dr. M. Osial, Prof. Dr. J. Vapaavuori, Prof. J. Lee, Prof. Dr. M. Giersig

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A Stable Perovskite Sensitized Photonic Crystal P—N Junction with Enhanced Photoelectrochemical Hydrogen Production