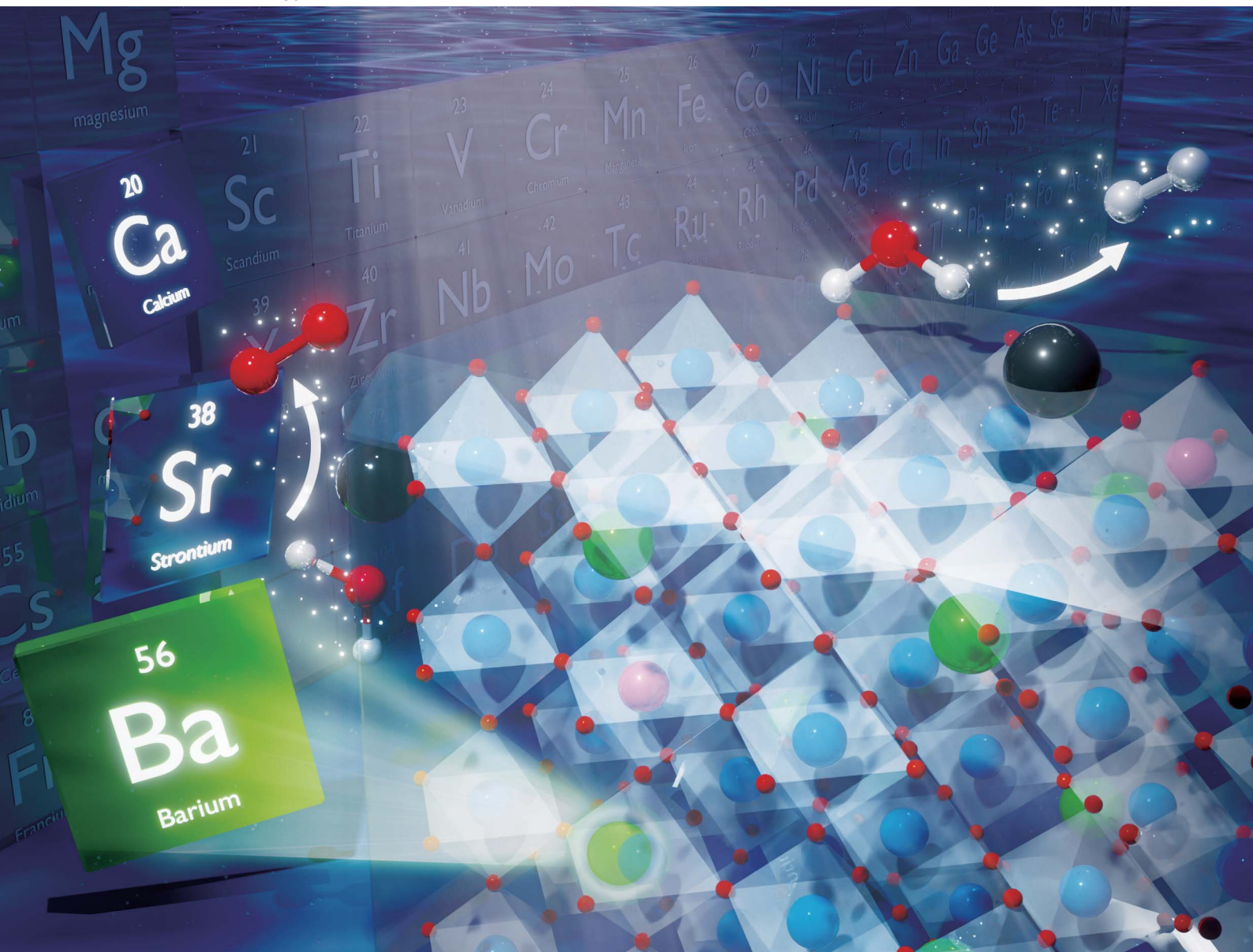


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Activation of barium titanate for photocatalytic overall water splitting *via* low-valence cation codoping

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Barium titanate (BaTiO₃) has long been regarded as inactive for photocatalytic overall water splitting, in stark contrast to its perovskite counterparts SrTiO₃ and CaTiO₃. Here we report that BaTiO₃ codoped with Al³⁺ and Sc³⁺ at Ti⁴⁺ sites under flux synthesis conditions is activated as a robust photocatalyst for overall water splitting. This material achieves apparent quantum yields of 29.8% at 310 nm and 27.5% at 365 nm, representing the first demonstration of efficient overall water splitting on BaTiO₃. Comparative analyses show that BaTiO₃ doped only with Al³⁺ suffers from severe band-edge disorder, whereas BaTiO₃ codoped with Al³⁺ and Mg²⁺ exhibits clear activation with moderate efficiency. In contrast, BaTiO₃ codoped with Al³⁺ and Sc³⁺ achieves the critical defect and structural control required to push the material across the threshold from inactive to highly active. These findings overturn the long-standing perception of BaTiO₃ as unsuitable for water splitting and establish a general design principle for activating previously inactive perovskite oxides, thereby expanding the materials palette for solar-to-hydrogen energy conversion.

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Introduction

Photocatalytic overall water splitting using semiconductor oxides has long been studied as a promising route for sustainable hydrogen (H₂) production from sunlight.¹ Among perovskite-type oxides, strontium titanate (SrTiO₃) has been the most extensively investigated and has emerged as a benchmark photocatalyst.² Recent studies have demonstrated that SrTiO₃ can achieve an apparent quantum yield (AQY) approaching unity under monochromatic ultraviolet (UV) irradiation at 365 nm, enabled by a bulk structural modification through flux treatment and Al³⁺ doping, together with optimized cocatalyst loading.³ Moreover, SrTiO₃ photocatalysts have been scaled up to 100 m²-class modules for pilot demonstrations of solar H₂ production.⁴ Al³⁺ has been regarded as an essential dopant, acting both as a p-type dopant to compensate surplus electrons generated by oxygen vacancies and as a promoter of specific crystal facets critical for overall water splitting.^{3,5} More recently, we demonstrated that

highly active SrTiO₃ photocatalysts can also be realized without Al³⁺, by employing codoping with Mg²⁺ and Sc³⁺ in place of Al³⁺.⁶ In addition, visible-light-responsive SrTiO₃-based photocatalysts have also been achieved by doping transition-metal cations such as Cr³⁺, Ir³⁺, and Rh³⁺,⁷ and their application in Z-scheme two-step water splitting systems has enabled solar-to-H₂ (STH) efficiencies as high as 1%, a value still unattainable in one-step photocatalyst systems.⁸

Another perovskite oxide, calcium titanate (CaTiO₃), with Ca²⁺ occupying the A-site, has also been studied for photocatalytic reactions including overall water splitting.⁹ Although its application dates back several decades, the activity had long remained modest compared with SrTiO₃. By applying our codoping strategy, however, we significantly improved its photocatalytic activity and achieved an AQY exceeding 70% at 310 nm.¹⁰ Visible-light response was further realized by Rh³⁺ doping,¹¹ expanding the scope of CaTiO₃ photocatalysts.

In contrast, barium titanate (BaTiO₃), another perovskite titanate with Ba²⁺ at the A-site, is well known for its ferroelectric, dielectric, and piezoelectric properties,¹² but has been regarded as unsuitable for overall water splitting. Only a limited number of studies have examined BaTiO₃ in this context,¹³ and the material has consistently shown negligible activity. Inoue *et al.*, in their early studies on related titanates in the 1990s, explicitly noted BaTiO₃ as inactive, while reporting that BaTi₄O₉, a phase composed of the same elements, exhibited water-splitting activity.¹⁴ Subsequent optimization of BaTi₄O₉, moreover, achieved an AQY of 41% at 313 nm.¹⁵ To date, however, no report

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has demonstrated efficient overall water splitting using BaTiO₃, which has fundamentally hindered its consideration as a viable photocatalyst.

Herein, we demonstrate for the first time that BaTiO₃ can be activated as an efficient photocatalyst for overall water splitting through low-valence cation codoping under flux conditions. While Al³⁺ doping alone, which is effective in SrTiO₃ and CaTiO₃, proved insufficient in BaTiO₃, codoping with Al³⁺ and Sc³⁺ or with Al³⁺ and Mg²⁺ led to a significant enhancement in photocatalytic activity. Among these, the BaTiO₃ sample codoped with Al³⁺ and Sc³⁺ exhibited the highest performance, achieving AQYs of 29.8% at 310 nm and 27.5% at 365 nm. These results overturn the long-standing perception of BaTiO₃ as an inactive material and establish a design principle for activating previously unsuitable perovskite oxides, thereby expanding the materials palette for solar-driven H₂ production.

Experimental

Materials

All chemicals were reagent grade (≥99%) or higher and used without further purification.

Synthesis of BaTiO₃ powders

Non-doped BaTiO₃ powder was prepared *via* a conventional solid-state reaction (SSR). A stoichiometric mixture of BaCO₃ and TiO₂ was ground in an agate mortar and heated at 1000 °C for 10 h in air. Doped BaTiO₃ powders were synthesized by flux treatment of the obtained BaTiO₃ powder together with dopant source oxides (Al₂O₃, Sc₂O₃, or MgO) in molten BaCl₂ (1000 mol% relative to BaTiO₃) at 1050 °C for 10 h in an alumina crucible (Nikkato, 99.6%). The nominal contents of dopant cations (Al³⁺, Sc³⁺, or Mg²⁺) were fixed at 1.0 mol% relative to Ti⁴⁺. After the reaction, the resulting powders were washed repeatedly with deionized water until no Cl⁻ was detected (confirmed by AgNO₃ test) and dried at 70 °C in a convection oven. For comparison, flux treatment of non-doped BaTiO₃ powder without intentional dopant addition was performed; this yielded BaTiO₃ powder containing trace Al³⁺ due to elution from the alumina crucible.

Cocatalyst loading

For loading of Rh/Cr₂O₃ and CoOOH cocatalysts, 100 mg of the doped BaTiO₃ powder was dispersed in 100 mL of distilled water in a cylindrical glass vessel (diameter 50 mm, height 70 mm) with a quartz window. The suspension was stirred magnetically during irradiation with a 300 W Xe lamp (CERMAX PE300BF) positioned at a distance of 15 cm from the liquid surface. Aqueous precursor solutions of RhCl₃·3H₂O, K₂CrO₄, and Co(NO₃)₂·6H₂O were sequentially added to deposit 0.1 wt% Rh, 0.05 wt% Cr, and 0.05 wt% Co, respectively. The deposition times were 10 min for Rh, and 5 min each for Cr₂O₃ and CoOOH, all under continuous light irradiation.

Alternatively, loading of mixed Rh–Cr oxide ((Rh,Cr)₂O₃) was carried out by the impregnation method.⁴ Precursor solutions of RhCl₃·3H₂O and K₂CrO₄ were added to 100 mg of each BaTiO₃

sample, followed by drying at 70 °C and subsequent mild heating at 300 °C for 1 h in air to form (Rh,Cr)₂O₃.

Photocatalytic overall water splitting

Photocatalytic reactions were carried out in the same quartz-windowed vessel connected to a closed, air-free gas circulation and analysis system. The reaction suspension (100 mg photocatalyst in 100 mL pure water) was thoroughly degassed by evacuation and backfilled with argon (Ar, 99.999%) to *ca.* 20 kPa prior to irradiation. The photocatalyst was irradiated using a 300 W Xe lamp (CERMAX PE300BF) through a cold mirror that mainly reflects UV light, thereby providing UV/near-UV irradiation (<500 nm) to the suspension. Evolved H₂ and molecular oxygen (O₂) were analyzed using a GL Sciences GC3210 gas chromatograph equipped with a thermal conductivity detector (TCD) and an MS-5A column, with Ar as the carrier gas.

Characterization

The actual molar compositions of the samples were determined by inductively coupled plasma (ICP) analysis (Shimadzu ICPS-8100). Crystallographic structures were determined by powder X-ray diffraction (XRD, PANalytical X'Pert PRO Alpha-1 diffractometer) equipped with a Johansson-type curved Ge(111) monochromator, using monochromatic Cu Kα₁ radiation (λ = 0.15406 nm). Raman spectra were measured using a JASCO NRS-3100 laser Raman spectrometer with an excitation wavelength of 532 nm. Particle morphologies were observed using a JEOL JSM-IT800 scanning electron microscope (SEM). UV-vis diffuse reflectance spectra (DRS) were obtained with a Shimadzu UV-2600i spectrophotometer equipped with an ISR-2600Plus integrating sphere. The specific surface areas of the samples were measured using a BELSORP MAX X gas adsorption-desorption analyzer at 77 K with Kr as the adsorbate gas. Samples were degassed under vacuum at 150 °C for 5 h prior to measurement.

AQY measurements

AQY was estimated from the H₂ evolution rate and the incident photon flux per unit time using the following equation:

$$\text{AQY (\%)} = \{(N_{\text{H}_2} \times 2)/N_{\text{p}}\} \times 100 \quad (1)$$

where N_{H_2} is the number of evolved H₂ and N_{p} is the number of incident photons that reached the surface of the reaction solution. The factor of 2 accounts for the two electrons required to generate one H₂ molecule. Monochromatic irradiation for this measurement was performed using a Hamamatsu Photonics LC8 high-pressure mercury (Hg) lamp equipped with bandpass filters (Asahi Spectra, 310 ± 5 nm or 365 ± 5 nm). The incident photon flux was determined using a calibrated silicon photodiode power meter.

Results and discussion

Photocatalytic activity of BaTiO₃-based samples

BaTiO₃-based photocatalysts with different dopant compositions were examined for overall water splitting. In this study, the



samples are denoted as follows: BaTiO₃:Al (flux-treated BaTiO₃ containing Al³⁺ eluted from the alumina crucible), BaTiO₃:Al,Al (intentionally Al³⁺-doped BaTiO₃ further containing crucible-derived Al³⁺), BaTiO₃:Al,Sc (codoped with crucible-derived Al³⁺ and intentionally added Sc³⁺), and BaTiO₃:Al,Mg (codoped with crucible-derived Al³⁺ and intentionally added Mg²⁺). All samples were loaded with Rh/Cr₂O₃ and CoOOH cocatalysts *via* photo-deposition method, and their activities for H₂ and O₂ evolution were evaluated under UV irradiation. Fig. 1a summarizes the photocatalytic activities of these BaTiO₃-based samples, presented as the rates of H₂ and O₂ evolution (μmol h⁻¹). As in previous reports,¹⁴ BaTiO₃ prepared by solid-state reaction (SSR) exhibited only slight H₂ evolution with no detectable O₂ generation, even when loaded with highly active cocatalysts, confirming that pristine BaTiO₃ is below the threshold for overall water splitting. Unlike SrTiO₃, where Al³⁺ doping under flux conditions markedly enhances activity, the BaTiO₃:Al and BaTiO₃:Al,Al samples showed no improvement; their H₂ evolution rates were even lower than those of pristine BaTiO₃, suggesting that Al³⁺ addition alone introduces unfavourable structural and electronic effects that hinder efficient carrier utilization.

When Sc³⁺ or Mg²⁺ was introduced together with crucible-derived Al³⁺ during flux treatment, a significant enhancement in photocatalytic activity was achieved. In particular, BaTiO₃:Al,Sc exhibited the highest activity, with H₂ and O₂ evolution

rates approaching stoichiometric ratios. BaTiO₃:Al,Mg also showed clear activation, though with somewhat lower efficiency. These results demonstrate that codoping allows BaTiO₃ to overcome its long-standing activity threshold, providing the first clear evidence that this material can function as an efficient photocatalyst for overall water splitting. The time course of H₂ and O₂ evolution for BaTiO₃:Al,Sc under continuous UV irradiation is shown in Fig. 1b. Over at least five runs, corresponding to 15 h of irradiation, the gas evolution rates remained essentially unchanged, demonstrating the durability and steady-state performance of the BaTiO₃:Al,Sc photocatalyst.

To verify that these differences in activity do not arise from the cocatalyst deposition method, (Rh,Cr)₂O₃ was also deposited by an impregnation method,⁴ and photocatalytic tests were performed under identical conditions. As shown in Fig. S1, the same relative trend was reproduced, confirming that the observed activity enhancement originates from the intrinsic bulk and surface properties of the BaTiO₃ host materials. Notably, in these comparative tests, CoOOH was not deposited as an O₂-evolution cocatalyst. As a result, BaTiO₃:Al,Mg exhibited detectable H₂ evolution, whereas O₂ remained below the detection limit. This deviation from stoichiometric gas evolution therefore arises primarily from the absence of CoOOH, which limits the kinetics of water oxidation, rather than from any intrinsic inactivity of the BaTiO₃:Al,Mg sample itself.

Structural, optical, and morphological properties

The dopant concentrations determined by ICP analysis are summarized in Table 1. In line with previous reports on SrTiO₃ and CaTiO₃,^{3–6,10} appreciable amounts of Al³⁺ (*ca.* 0.4–0.7%) originating from the dissolution of the alumina crucible were detected in all samples. However, the Al³⁺ content in intentionally doped samples was nearly identical to that in BaTiO₃:Al, which contained only crucible-derived Al³⁺. This result indicates that, unlike SrTiO₃ and CaTiO₃, substitution of Al³⁺ (0.0535 nm, CN = 6) for Ti⁴⁺ (0.0605 nm, CN = 6) is strongly hindered in BaTiO₃,¹⁶ likely due to its relatively large lattice constant and the resulting size mismatch that prevents effective incorporation at the B-site. In contrast, dopants with larger ionic radii than Ti⁴⁺, such as Mg²⁺ (0.0720 nm, CN = 6) and Sc³⁺ (0.0745 nm, CN = 6),¹⁶ were incorporated at significant levels, with Sc³⁺ showing nearly quantitative incorporation, highlighting its high compatibility with the BaTiO₃ lattice.

X-ray diffraction (XRD) patterns of the BaTiO₃-based samples exhibited sharp reflections characteristic of tetragonal BaTiO₃ with no detectable impurity phases, as shown in Fig. 2. All values deviated by at most 0.2% from those of the ICDD PDF04-013-5890 reference (*a* = *b* = 0.3995 nm, *c* = 0.4039 nm), indicating that the lattice constants of the doped samples were essentially unchanged from undoped BaTiO₃. This suggests that, within the present doping range, the incorporated ions did not significantly affect the average lattice dimensions. Nevertheless, the tetragonal structure was preserved in all cases, and no phase transition to cubic or hexagonal polymorphs was observed. Taken together with the above ICP results, these findings imply that the differences in photocatalytic activity

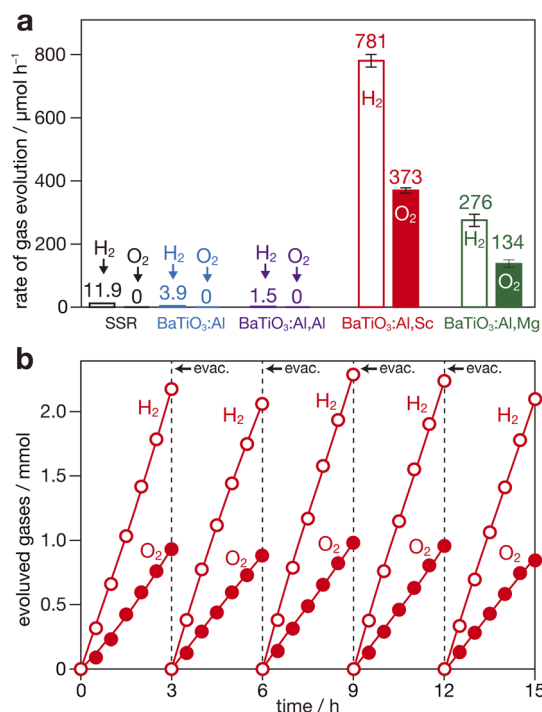


Fig. 1 (a) H₂ and O₂ evolution rates of photocatalysts based on BaTiO₃ prepared by solid-state reaction (SSR), BaTiO₃:Al, BaTiO₃:Al,Al, BaTiO₃:Al,Sc, and BaTiO₃:Al,Mg under UV irradiation (<500 nm, 300 W Xe lamp). Error bars represent the standard deviation from at least three independent runs. (b) Time course of H₂ and O₂ evolution over BaTiO₃:Al,Sc-based photocatalyst. The reaction system was evacuated every 3 h.



Table 1 Structural, compositional, spectroscopic, and surface properties of flux-treated BaTiO₃-based samples

Sample	Dopant content ^a /mol%		Lattice constant ^b /nm			FWHM ^c /cm ⁻¹	SA ^d /m ² g ⁻¹
	Al	Sc	Mg	<i>a</i> , <i>b</i>	<i>c</i>		
BaTiO ₃ :Al	0.46	Trace ^e	Trace ^e	3.988	4.032	10.4	1.1
BaTiO ₃ :Al,Al	0.43	Trace ^e	Trace ^e	3.991	4.035	10.7	1.6
BaTiO ₃ :Al,Sc	0.55	0.94	Trace ^e	3.990	4.030	9.3	4.0
BaTiO ₃ :Al,Mg	0.67	Trace ^e	0.46	3.990	4.032	11.4	1.2

^a Dopant concentrations (mol% relative to Ba²⁺) determined by ICP analysis. ^b Lattice parameters estimated from 111, 002, and 200 reflections in XRD patterns. ^c Full width at half maximum (FWHM) values of the 312 cm⁻¹ Raman band obtained by double-Gaussian fitting. ^d Specific surface area (SA) measured by Kr adsorption using the BET method. ^e Not detected (below the detection limit).

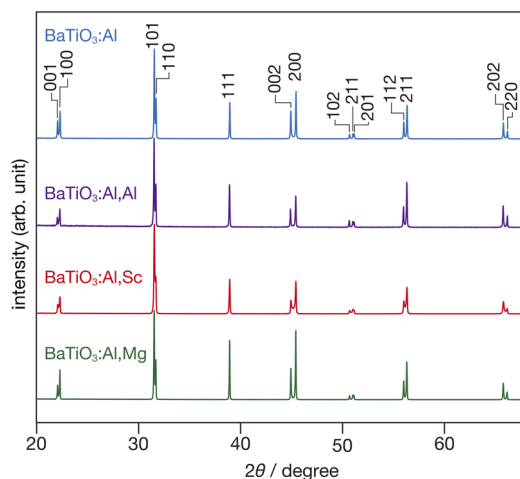


Fig. 2 X-ray diffraction (XRD) patterns of BaTiO₃:Al, BaTiO₃:Al,Al, BaTiO₃:Al,Sc, and BaTiO₃:Al,Mg powders.

among the BaTiO₃-based samples cannot be attributed to macroscopic lattice distortion. Instead, the observed activity enhancement upon Sc³⁺ and Mg²⁺ doping is more likely related to local structural perturbations, defect formation, and electronic effects associated with the dopant ions, rather than changes in the average crystal lattice constants. Such effects may include modification of carrier generation and separation efficiencies, as well as suppression or activation of defect-mediated recombination pathways.

Fig. 3 shows diffuse reflectance (DR) spectra of the flux-treated samples. All the samples exhibited a sharp absorption edge near 400 nm. However, BaTiO₃:Al and BaTiO₃:Al,Al displayed pronounced Urbach tails extending into the visible region, indicative of band-edge disorder and high defect densities. For comparison, the DR spectrum of BaTiO₃ prepared by the SSR method (Fig. S1) showed a clean band edge without tailing, confirming that the Urbach tail observed in the Al-doped samples originates from Al-induced lattice disorder rather than from the intrinsic electronic structure of BaTiO₃. The absorption edge of BaTiO₃:Al,Sc was further analysed using Tauc plot analysis,¹⁷ assuming an indirect allowed transition, as commonly applied in previous optical studies (inset in Fig. 3). The estimated optical band gap of 3.16 eV, determined from the

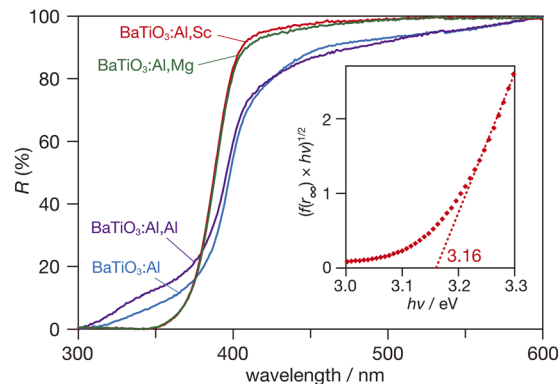


Fig. 3 Diffuse reflectance (DR) spectra of BaTiO₃:Al, BaTiO₃:Al,Al, BaTiO₃:Al,Sc, and BaTiO₃:Al,Mg samples. Inset: Tauc plot for the BaTiO₃:Al,Sc sample assuming an indirect allowed transitions.

x-axis intercept of the linear region, is in good agreement with the reported value for tetragonal BaTiO₃ at room temperature.¹⁸

Raman spectra of the samples (Fig. 4) exhibited a broad band centered at *ca.* 260 cm⁻¹, a sharp peak at *ca.* 312 cm⁻¹, representative of tetragonality strength in BaTiO₃, an asymmetric broad band near 510 cm⁻¹, and a weak broad band around 715 cm⁻¹, consistent with reported spectra for BaTiO₃.¹⁹ While the overall spectral shapes were similar, the 312 cm⁻¹ peak

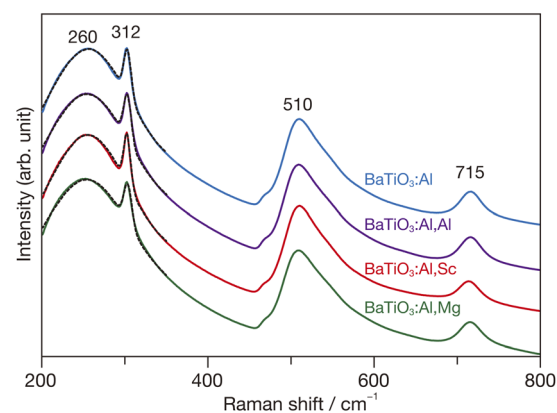


Fig. 4 Raman spectra of BaTiO₃:Al, BaTiO₃:Al,Al, BaTiO₃:Al,Sc, and BaTiO₃:Al,Mg samples. Dotted lines in 200–350 cm⁻¹ range denote fitting curves obtained by double-Gaussian fitting.



appeared relatively sharper for the BaTiO₃:Al,Sc sample compared with the others. To verify this observation, the spectra in the 200–350 cm⁻¹ range were fitted using a double-Gaussian function, and the FWHM values of the 312 cm⁻¹ peak were extracted and are summarized in Table 1. The results confirmed that the BaTiO₃:Al,Sc sample exhibited the smallest FWHM, while the BaTiO₃:Al,Mg sample showed a comparatively large FWHM. As reported previously,^{19b} Raman band width is inversely correlated with phonon lifetime, and accordingly, the observed sharpening indicates an increased phonon coherence length. Longer coherence lengths are generally associated with lower local defect densities, suggesting that BaTiO₃:Al,Sc contains fewer defects relative to the other samples. In contrast, the broader peak of BaTiO₃:Al,Mg reflects a shorter coherence length and thus a higher defect density. Although BaTiO₃:Al,Mg exhibits a broader Raman band, indicating a higher overall defect density, its relatively weak Urbach tail (Fig. 3) suggests that many of these defects are shallow and less detrimental to carrier transport. Therefore, partial defect tolerance likely contributes to the moderate yet distinct photocatalytic activity of BaTiO₃:Al,Mg compared with BaTiO₃:Al and BaTiO₃:Al,Al.

As shown in Fig. 5, FE-SEM images of the flux-treated samples revealed clear morphology-dependent trends. BaTiO₃:Al consisted of highly inhomogeneous particles with irregular shapes and rough surfaces. BaTiO₃:Al,Al contained predominantly large grains (*ca.* 10 μm) but also an admixture of smaller particles, and the large grains exhibited notably rough,

pitted surfaces. In contrast, the codoped samples were more uniform and generally smaller in size. Particularly, BaTiO₃:Al,Sc showed an order-of-magnitude reduction in particle size relative to BaTiO₃:Al and smooth, well-crystallized facets. Although BaTiO₃:Al,Mg became more uniform than BaTiO₃:Al or BaTiO₃:Al,Al, its size suppression was less pronounced than in BaTiO₃:Al,Sc. Such Sc³⁺-induced suppression of particle growth is consistent with observations in SrTiO₃ and CaTiO₃.^{6,10}

BET surface area measurements (Table 1) supported these tendencies while also reflecting surface texture and size distributions: the surface areas followed the order BaTiO₃:Al,Sc > BaTiO₃:Al,Al > BaTiO₃:Al,Mg > BaTiO₃:Al. The appreciably large value for BaTiO₃:Al,Sc reflects its pronounced particle-size suppression, leading to an increased external surface area. Although BaTiO₃:Al,Al has larger average particles than BaTiO₃:Al,Mg, its BET area is slightly higher, which can be rationalized by the rough, bumpy surfaces of the large grains and the coexistence of smaller particles that together raise the accessible external area. Conversely, the more uniform but less size-suppressed BaTiO₃:Al,Mg exhibits a smaller value than that for BaTiO₃:Al,Sc. These SEM/BET results indicate that Sc³⁺ codoping most effectively suppresses grain growth and improves surface quality, thereby increasing the density of accessible active sites, whereas Mg²⁺ codoping primarily homogenizes the particle size distribution but provides a weaker inhibition of crystal growth.

Furthermore, several diffraction peaks of the BaTiO₃:Al,Sc sample (Fig. 2) exhibited slightly weaker relative intensities than those of the other samples, although all reflections remained sharp. This attenuation likely reflects the smaller crystallite size of BaTiO₃:Al,Sc rather than reduced crystallinity. The smaller, more uniform particles observed by SEM and the increased surface area determined by BET analysis (Table 1) both support this interpretation. Such microstructural refinement, *i.e.*, fine, well-crystallized particles with enlarged surface area, provides more active sites and facilitates carrier separation, thereby accounting for the markedly enhanced photocatalytic activity of BaTiO₃:Al,Sc.

Apparent quantum yield performance and mechanistic considerations

The apparent quantum yields (AQYs) of the most active photocatalyst (*i.e.*, BaTiO₃:Al,Sc loaded with Rh/Cr₂O₃ and CoOOH cocatalysts) reached 29.8% at 310 nm and 27.5% at 365 nm, marking the first report of significant AQY values for a BaTiO₃-based photocatalyst. Table 2 compares these results with benchmark SrTiO₃- and CaTiO₃-based systems. While the AQYs of BaTiO₃:Al,Sc remain lower than those of optimized SrTiO₃ (>90% at 365 nm) and CaTiO₃ (>70% at 310 nm), they represent a major advance given that BaTiO₃ has long been considered inactive. By contrast, BaTiO₃:Al alone exhibited essentially zero AQY, underscoring the critical role of codoping in surpassing the intrinsic activity threshold. The relatively lower AQY of BaTiO₃:Al,Sc compared with SrTiO₃ and CaTiO₃ can be attributed to the absence of well-developed crystal facets (Fig. 5d), which are known to promote anisotropic charge separation and

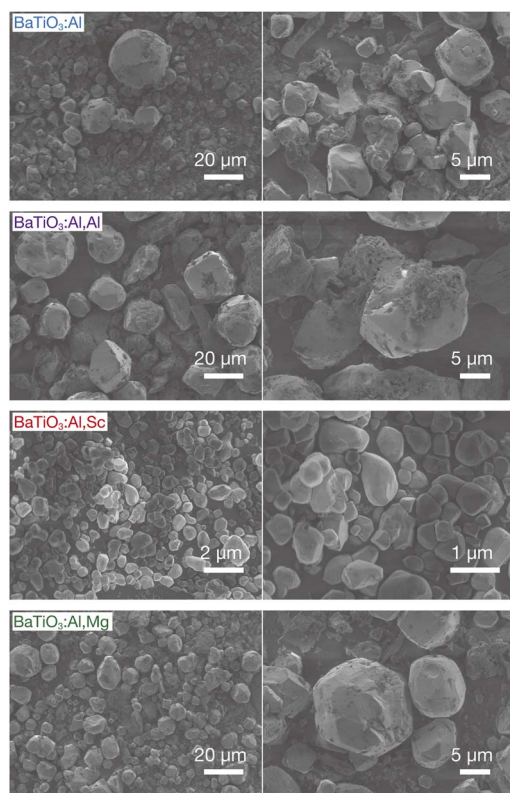


Fig. 5 SEM images of BaTiO₃:Al, BaTiO₃:Al,Al, BaTiO₃:Al,Sc, and BaTiO₃:Al,Mg samples.



Table 2 Comparison of AQYs for overall water splitting over several benchmark titanate-perovskite photocatalysts under monochromatic UV irradiation^a

Sample	AQY (%)	Wavelength/nm	Reference
SrTiO ₃ :Al ^b	>96	365	3
SrTiO ₃ :Sc,Mg ^b	66	365	6
CaTiO ₃ :Al,Sc,Mg ^b	73.8	310	10
BaTiO ₃ :Al,Sc	29.8	310	(This work)
BaTiO ₃ :Al,Sc	27.5	365	(This work)

^a AQY measurements were performed after loading Rh/Cr₂O₃ and CoOOH cocatalysts for H₂ and O₂ evolution, respectively. ^b Titanate perovskites doped with various elements were obtained by high-temperature flux treatments.

accelerate surface redox processes. In addition, the present codoping strategy has not yet been optimized in terms of dopant ratios or flux treatment conditions. These factors indicate substantial room for further improvement, and ongoing efforts in our laboratory focus on morphology control, dopant optimization, and cocatalyst engineering.

Mechanistically, the activation of BaTiO₃ by Sc³⁺ codoping can be attributed to suppression of recombination-active defects and the resulting extension of carrier lifetimes. In Al³⁺-only samples, limited substitution and charge imbalance promote oxygen vacancy formation, which acts as recombination centres and accounts for their negligible activity. In contrast, BaTiO₃:Al,Sc exhibits markedly different behaviour. In SrTiO₃, Al³⁺ doping is known to enhance photocatalytic activity, suggesting that oxygen vacancies generated for charge compensation behave as shallow or electronically benign defects that do not significantly promote carrier recombination. By analogy, the lack of activity in Al-doped BaTiO₃ can be rationalized by considering its much larger lattice constant: the size mismatch between Ti⁴⁺ (0.0605 nm, CN = 6) and Al³⁺ (0.0535 nm, CN = 6) produces substantial local strain, which drives the formation of deep-level oxygen vacancies acting as non-radiative recombination centres. Codoping with Sc³⁺ (0.0745 nm, CN = 6) mitigates this lattice strain and provides local charge compensation, thereby suppressing the generation of deep-level vacancies and stabilizing the surrounding lattice. These effects manifest themselves in the narrower Raman peaks, reduced Urbach tails, smoother particle surfaces, and larger BET surface areas observed for BaTiO₃:Al,Sc compared with BaTiO₃:Al or BaTiO₃:Al,Mg. The stabilization of the local structure leads to prolonged carrier lifetimes, more efficient charge separation, and the highest photocatalytic activity among all BaTiO₃-based samples. Mg²⁺ codoping also improves activity, though less effectively, owing to less favourable charge balance and size mismatch. Further optimization of the codoping composition and detailed analyses of carrier lifetimes are currently underway to refine and extend these mechanistic insights.

Conclusions

This study demonstrates, for the first time, that BaTiO₃ can be activated as an efficient photocatalyst for overall water splitting through a codoping strategy. While BaTiO₃ doped only with Al³⁺

remained essentially inactive, codoping with Sc³⁺ together with crucible-derived Al³⁺ under flux conditions enabled significant activity, achieving apparent quantum yields of 29.8% at 310 nm and 27.5% at 365 nm, the highest values reported to date for BaTiO₃-based photocatalysts. These results overturn the long-standing perception of BaTiO₃ as unsuitable for photocatalytic water splitting. The enhanced performance originates from defect suppression and improved carrier dynamics induced by Sc³⁺ incorporation, which provides effective charge compensation and lattice stabilization. Mg²⁺ codoping also activated BaTiO₃, though less effectively, highlighting the critical role of ionic size and charge balance.

Overall, this work establishes codoping as a general design principle for unlocking latent activity in perovskite oxides, thereby broadening the family of viable photocatalysts for solar-driven H₂ production.

Author contributions

S. I. directed and led the research. K. T. performed photocatalytic experiments. K. T., R. T., A. Y. and Y. N. performed structural analyses. R. T., T. N., and K. H. performed compositional analyses. All the authors discussed the results. S. I. wrote the manuscript. All authors have given approval to the final version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

All data supporting the findings of this study are available within the article and/or its supplementary materials (SI). Additional datasets are available from the corresponding author upon reasonable request. Supplementary information: includes additional photocatalytic reaction data (time courses of H₂ and O₂ evolution) and diffuse reflectance spectra used for comparison of optical properties. See DOI: <https://doi.org/10.1039/d5se01323b>.

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