

SOLAR CELLS

Electron-hole diffusion lengths > 175 μm in solution-grown $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals

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Long, balanced electron and hole diffusion lengths greater than 100 nanometers in the polycrystalline organolead trihalide compound $\text{CH}_3\text{NH}_3\text{PbI}_3$ are critical for highly efficient perovskite solar cells. We found that the diffusion lengths in $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals grown by a solution-growth method can exceed 175 micrometers under 1 sun (100 mW cm^{-2}) illumination and exceed 3 millimeters under weak light for both electrons and holes. The internal quantum efficiencies approach 100% in 3-millimeter-thick single-crystal perovskite solar cells under weak light. These long diffusion lengths result from greater carrier mobility, longer lifetime, and much smaller trap densities in the single crystals than in polycrystalline thin films. The long carrier diffusion lengths enabled the use of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in radiation sensing and energy harvesting through the gammavoltaic effect, with an efficiency of 3.9% measured with an intense cesium-137 source.

Demonstrated optoelectronic applications of organolead trihalide perovskites include high-efficiency photovoltaic cells (1–3), lasers (4), light-emitting diodes (5), and high-gain photodetectors (6), but the understanding of their fundamental properties, such as carrier diffusion length, has lagged behind. The carrier diffusion length in $\text{CH}_3\text{NH}_3\text{PbI}_3$ (henceforth MAPbI_3) should be sensitive to defects. Point defects in MAPbI_3 do not constitute midgap trap states (7), but a large density of charge traps has been broadly observed at the grain boundaries and surfaces of MAPbI_3 polycrystalline (MPC) films (8, 9). We showed that the carrier diffusion length of MPC films increased to 1 μm when solvent annealing was used to enlarge the grain size to the thickness of the film (10). Determining the limit of carrier diffusion length requires larger MAPbI_3 single crystals (MSCs). We grew millimeter-sized MSCs using a low-temperature solution approach and characterized their fundamental electronic properties. Both electrons and holes were found to have diffusion lengths of >175 μm under 1 sun illumination and >3 mm in MSCs under weak illumination (0.003% sun).

Large-sized MSC growth from a supersaturated MAPbI_3 solution used a top-seeded solution-growth (TSSG) method (fig. S1) with a temperature gradient. Small-sized MSCs at the bottom of the container maintained the MA^+ , Pb^{2+} , and Γ^- ion concentration for a saturated solution; the cooler top half of the solution was supersaturated. The large MSCs were grown by the

consumption of small MSCs in the bottom. The small temperature difference between the bottom and the top of the solution induced sufficient convection to transport the material to the large MSCs. The as-grown MSCs had an average size of 3.3 mm and a largest size of ~10 mm (Fig. 1A); powder x-ray diffraction (XRD) (Fig. 1B) confirmed the tetragonal structure. Single-crystal XRD was best fit with an $I4/m$ space group, in agreement with the results of Baikie *et al.* (11). The goodness of fit was 1.154, and the crystal data are summarized in tables S1 and S2.

We fabricated MSC photovoltaic devices by depositing 25-nm gold (Au) layers on one crys-

tal facet as anodes and contacting gallium (Ga) with the opposite facet as cathodes (Fig. 2A). Thin MSCs with a thickness of 100 to 200 μm were peeled off from the large MSCs to fabricate MSC devices with thicknesses of either >3 mm or 200 μm . The optical and electrical properties of MSCs were compared with those of the 600-nm-thick solvent-annealed MPC thin films formed by the interdiffusion method (10). The MSCs displayed an extended absorption band to 850 nm, whereas regular MPC thin films had an absorption cutoff at 800 nm (Fig. 2B), which is consistent with the external quantum efficiency (EQE) of devices made of these two types of materials (Fig. 2C). These MSC devices differed from other MPC thin-film devices in that they exhibited a strong exciton absorption at 790 nm that was more intense in the thicker devices. The red shift of the EQE cutoff by 50 nm to 850 nm in the MSCs increased the upper limit of short-circuit current density (J_{SC}) in MAPbI_3 -based solar cells from 27.5 mA cm^{-2} to 33.0 mA cm^{-2} . The photoluminescence (PL) peak of the MSCs, 770 nm, had a shorter wavelength than the exciton peak (Fig. 2C), which indicates that all of the excitons generated in MSCs dissociate to free charges at room temperature; and the band gap of the MSCs should be 1.61 eV. The blue-shifted and narrower PL peak indicates a lower trap density in MSCs.

The EQE of a 3-mm-thick MSC solar cell (Fig. 2D) ranged from 12.6 to 15.8% for wavelengths from 520 to 810 nm. The EQE of the MSC device decreased for shorter wavelengths, which suggests that the Au-MSC interface contains a large defect density (shorter wavelengths generate carriers closer to the MSC surface). These defects are most likely from the Pb^{2+} clusters formed by partial loss of the more soluble methylammonium iodide (MAI) when the single crystal

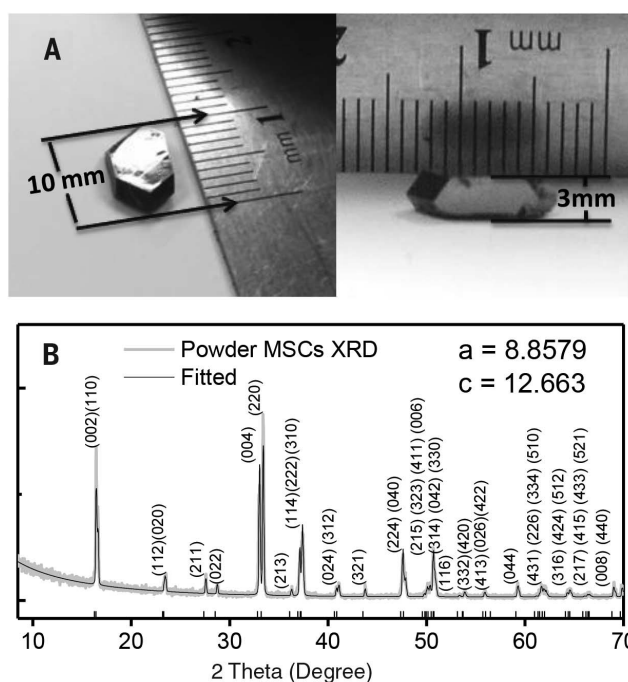


Fig. 1. MSC structure characterization. (A) Images of a piece of as-prepared MAPbI_3 single crystal. (B) X-ray diffraction pattern of the ground powder of a single crystal (gray line) and fitted patterns (black line).

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is removed from solution. Our recent density functional theory calculation verified that the Pb^{2+} clusters on the MAPbI_3 surface tend to form charge traps (6). The internal quantum efficiency (IQE) of the 3-mm MSC device (derived by dividing EQE by the transmittance of the Au electrode; see Fig. 2D and fig. S2) was near unity ($95 \pm 7\%$).

The electrons generated in the very thin perovskite layer near the Au anode must traverse the whole crystal to be collected by the Ga cathode, indicating that the electron diffusion length in MSCs is greater than the crystal thickness (~ 3 mm). We also replaced Ga by a semi-transparent Au (25 nm)/ C_{60} (25 nm) layer as the cathode so that photogenerated charges would be located at the cathode side. Again, the value of J_{SC} measured at 0.1% sun was comparable with incident light from both sides, which indicates that the hole diffusion length in MSCs is also longer than the MSC thickness.

The dependence of responsivity (R) and J_{SC} on light intensity (I_L) for thick devices is summarized in Fig. 2, E and F, respectively [see fig. S3 for photocurrent density-voltage ($J_{\text{ph}}-V$) curves]. Under 1 sun, the open-circuit voltage V_{oc} was 0.62 V, versus -1.00 V in optimized MPC thin-film devices, again indicating a strong charge recombination in the MSC devices under strong illumination. For thick MSC devices, R decreased from 35 mA W^{-1} to 0.19 mA W^{-1} when the intensity of white illuminated light increased from 0.003 mW cm^{-2} to 100 mW cm^{-2} because of increased charge recombination for higher I_L . Fitting of J_{sc} with I_L as $J_{\text{sc}} \propto I_L^\beta$ gave a value of β (recombination parameter) of 0.5 ± 0.01 , which suggests that second-order charge recombination dominated in the thick MSC devices for $I_L > 0.003 \text{ mW cm}^{-2}$, as seen previously (12, 13). Reducing the MSC thickness to 200 μm recovered large R (Fig. 2E) at 1 sun and increased β to 0.88, which indicates that the carrier diffusion length of MSCs is near 200 μm for 1 sun illumination.

We could characterize the carrier mobility μ and carrier lifetime τ_r because the carrier diffusion length L_D is determined by $L_D = (k_B T \mu \tau_r / e)^{1/2}$, where k_B , T , and e are the Boltzmann constant, absolute temperature, and elementary charge, respectively. The device dark current (J_D) was measured to derive the trap density and carrier mobilities. The MSCs were sandwiched by two Au electrodes deposited by thermal evaporation to form hole-only devices. As shown in Fig. 3A, the linear J_D-V relation (green line) indicates an ohmic response at the low bias (< 2.1 V). A trap-filling process was identified by the marked increase of the current injection at a bias range of 2.1 to 10.7 V. The voltage at which all the traps are filled (trap-filled limit voltage V_{TFL}) was determined by the trap density (14):

$$V_{\text{TFL}} = \frac{en_t L^2}{2\epsilon\epsilon_0} \quad (1)$$

where L is the thickness of the MSCs, ϵ ($= 32$) is relative dielectric constant of MAPbI_3 , and ϵ_0 is the vacuum permittivity. The trap density n_t in MSCs was calculated to be $3.6 \times 10^{10} \text{ cm}^{-3}$. For

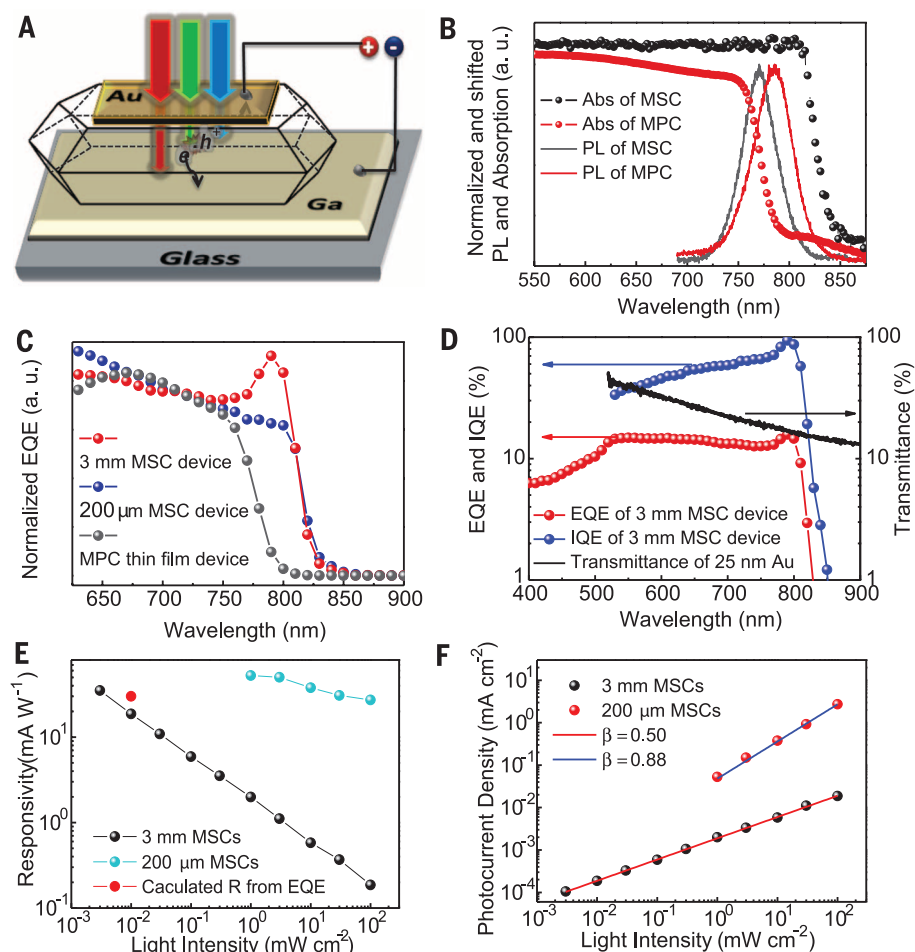


Fig. 2. Device structure and electrical and optical characterization of the MSC devices and MPC thin films. (A) Schematic device structure of the MAPbI_3 single-crystal devices. (B) Normalized PL and absorption spectra of the MSCs and MPC thin films. (C) Normalized EQEs of 3-mm-thick and 200- μm -thick MSC photovoltaic devices and a MPC thin-film device. (D) EQE of a 3-mm-thick MSC device, average transmittance of a 25-nm Au electrode, and calculated average IQE of the same MSC device. (E) Responsivity of the 3-mm-thick and 200- μm -thick MSC devices and responsivity calculated from the EQE of the 3-mm-thick MSC device. (F) Current density J_{sc} versus light intensity I_L fitted by $J_{\text{sc}} \propto I_L^\beta$ for the 3-mm-thick and 200- μm -thick MSC devices.

comparison, the hole-only devices with MPC thin films were also fabricated with PEDOT:PSS and Au as the hole injection electrodes (fig. S4). The calculated hole trap density in the MPC thin films was $2.0 \times 10^{15} \text{ cm}^{-3}$, which is almost five orders of magnitude greater than in the MSCs. Thermal admittance spectroscopy (fig. S5) confirmed the reduction in trap density by two to three orders of magnitude in MSCs. Thus, the extraordinary carrier diffusion length in the MSCs is the result of largely suppressed trap density. When operating in the trap-free space charge limit current (SCLC) regime above 10.7 V, the dark current of the MSC was well fitted (Fig. 3A, green line) by the Mott-Gurney law:

$$J_D = \frac{9\epsilon\epsilon_0\mu V_b^2}{8L^3} \quad (2)$$

where V_b is applied voltage. A large hole mobility of $164 \pm 25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was derived from the curve fitting. The uncertainties we reported

represent a single standard deviation in the measurements on 10 nominally identical devices. Hall effect measurements revealed that the MSC was slightly p-doped, with a low free hole concentration of $9 (\pm 2) \times 10^9 \text{ cm}^{-3}$ (see supplementary materials). The hole mobility from Hall effect measurement was $105 \pm 35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, in agreement with the SCLC results. Similarly, the electron trap density and electron mobility of MSCs were measured with the electron-only devices, which had phenyl- C_{61} -butyric acid methyl (PCBM): C_{60} /Ga as both electrodes. A low electron trap density of $4.5 \times 10^{10} \text{ cm}^{-3}$ was derived (Fig. 3B), comparable to the hole trap density, and the electron mobility was $24.8 \pm 4.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Finally, we used time-of-flight (ToF) to verify the high electron mobilities of $24.0 \pm 6.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Fig. 3, C and D). The electron and hole mobilities in MSCs are several times the intrinsic band transport mobility in MPC thin films (10) and polycrystals (15) measured by the Hall effect method

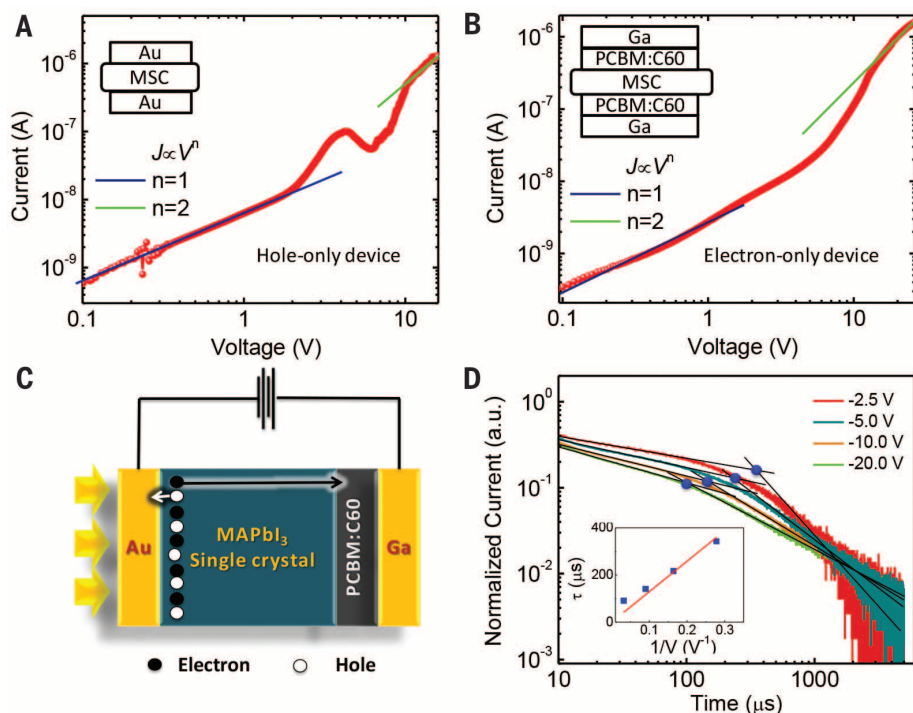


Fig. 3. Carrier mobility characterization of MSCs. (A and B) Current-voltage curve for a hole-only MSC device (A) and an electron-only MSC device (B). The insets show the device structure of hole-only and electron-only MSC devices, respectively. Three regions can be identified according to different values of the exponent n : $n = 1$ is the ohmic region, $n = 2$ is the SCLC region, and in between is the trap-filled limited region. (C) Schematic illustration of the device for the time-of-flight measurement. (D) The transient current curves of the MSC device show the normalized transient photocurrent under various reverse biases. The carrier transit time is determined by the intercept of the pretransit and posttransit asymptotes of the photocurrent, marked by solid blue circles. Inset shows the charge transit time versus the reciprocal of bias; the solid line is a linear fit to the data.

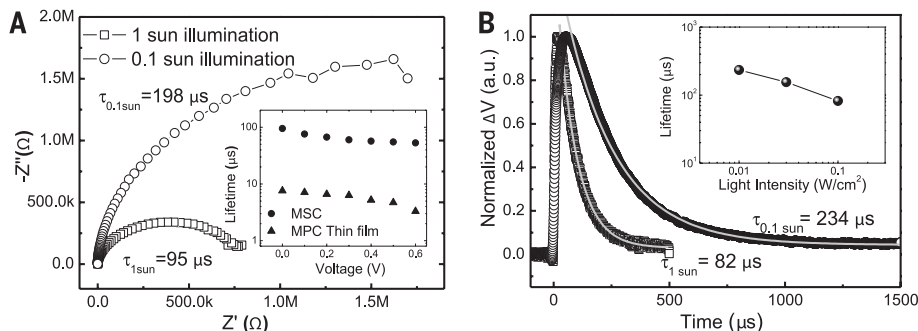


Fig. 4. Carrier recombination lifetime characterization of MSCs. (A and B) Impedance spectroscopies (A) and transient photovoltaic curves (B) of the MSC devices under 1 sun and 0.1 sun illumination, respectively, with incident light from the semitransparent Au anode. The TPV decay curves were fitted by a single-exponential decay function. The inset of (A) is the extracted charge recombination lifetime from IS measurement of the MSC device and the MPC thin film at various applied voltage biases under 1 sun illumination. The inset of (B) is the extracted charge recombination lifetime from TPV measurement of the MSC device under various light bias intensities.

and those measured by transient terahertz spectroscopy (16), both of which measure band transport mobility. However, ToF and SCLC mobilities are sensitive to the presence of charge traps in the materials. The excellent agreement of Hall mobility with ToF and SCLC mobilities in the single-crystal MAPbI₃ devices indicates that the band-tail states in the organolead trihalide perovskite single crystals are negligible.

We measured τ_r in MSCs with transient photovoltaic (TPV) and impedance spectroscopy (IS) at different values of I_L (Fig. 4); at 1 sun, the TPV and IS values of τ_r were $82 \pm 5 \mu\text{s}$ and $95 \pm 8 \mu\text{s}$, respectively, more than 10 times the τ_r values in the best thin-film devices with sophisticated surface passivation (10). Combining the measured mobility and lifetime of MSCs, the hole diffusion length is $175 \pm 25 \mu\text{m}$ under 1 sun.

The measured bulk carrier lifetime can be underestimated because of the presence of surface charge recombination, so the bulk carrier diffusion length should exceed this value. Reducing the bias light intensity to 0.1 sun increased τ_r to 234 and 198 μs by TPV and IS measurements, respectively, indicating a longer carrier diffusion length under weaker light intensity.

The long carrier diffusion length of MAPbI₃ can find direct application in x-ray and gamma-ray sensing and in radiation energy harvesting. Radiation is generally much weaker than 1 sun but should penetrate the entire device. Details pertaining to the carrier diffusion length extrapolation under weak light, radiation measurement, simulation, and estimation of gammavoltaic efficiency can be found in the supplementary materials. We extrapolated a carrier recombination lifetime of 2.6 ± 0.2 s and carrier diffusion length sum of 33 ± 5 mm under a light intensity of 0.003 mW cm^{-2} from our 1 sun data. The presence of surface recombination should reduce the carrier diffusion length, and the measured >3 mm electron and hole diffusion length under weak light is thus reasonable. We exposed the 3-mm MSC device to intense gamma radiation and measured the electric current generation. A cesium-137 gamma irradiator of 102 Ci yielded a persistent current of $36.3 \pm 0.3 \text{ nA}$, which corresponds to a photon-to-electron conversion efficiency of 3.9% and agrees with the theoretic estimation.

The demonstrated high carrier mobility, carrier lifetime, and diffusion length of the MSCs described above point to several new directions for the application of MAPbI₃ materials in printable electronics, lasers, and solar cells (4). The high PL quantum yield of MAPbI₃ and the excellent overlap of the PL spectra with the absorption spectrum of the single crystal allow photon recycling in thick perovskite crystals by reabsorbing the emission (4, 5). The demonstration of a charge diffusion length that greatly exceeds the absorption depth of photons with energy larger than the band gap of perovskites implies that IQEs of essentially 100% can be achieved under the low internal electric fields at device working condition.

REFERENCES AND NOTES

- S. D. Stranks *et al.*, *Science* **342**, 341–344 (2013).
- M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, H. J. Snaith, *Science* **338**, 643–647 (2012).
- A. Mei *et al.*, *Science* **345**, 295–298 (2014).
- G. Xing *et al.*, *Nat. Mater.* **13**, 476–480 (2014).
- Z. K. Tan *et al.*, *Nat. Nanotechnol.* **9**, 687–692 (2014).
- R. Dong *et al.*, *Adv. Mater.* 10.1002/adma.201405116 (2015).
- J. Kim, S. H. Lee, J. H. Lee, K. H. Hong, *J. Phys. Chem. Lett.* **5**, 1312–1317 (2014).
- N. K. Noel *et al.*, *ACS Nano* **8**, 9815–9821 (2014).
- I. A. Shkrob, T. W. Marin, *J. Phys. Chem. Lett.* **5**, 1066–1071 (2014).
- Z. Xiao *et al.*, *Adv. Mater.* **26**, 6503–6509 (2014).
- T. Baikie *et al.*, *J. Mater. Chem. A* **1**, 5628–5641 (2013).
- J. S. Manser, P. V. Kamat, *Nat. Photonics* **8**, 737–743 (2014).
- S. D. Stranks *et al.*, *Phys. Rev. A* **2**, 034007 (2014).
- R. H. Bube, *J. Appl. Phys.* **33**, 1733–1737 (1962).
- C. S. Stoumpos, C. D. Malliakas, M. G. Kanatzidis, *Inorg. Chem.* **52**, 9019–9038 (2013).
- C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith, L. M. Herz, *Adv. Mater.* **26**, 1584–1589 (2014).

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P.M., J.Q., and L.C. measured the devices under gamma ray irradiation and did the simulation; and J.H. wrote the paper.

SUPPLEMENTARY MATERIALS

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Materials and Methods

Figs. S1 to S11
Tables S1 and S2
References (17–21)

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WATER SPLITTING

Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway

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The use of solar energy to produce molecular hydrogen and oxygen (H₂ and O₂) from overall water splitting is a promising means of renewable energy storage. In the past 40 years, various inorganic and organic systems have been developed as photocatalysts for water splitting driven by visible light. These photocatalysts, however, still suffer from low quantum efficiency and/or poor stability. We report the design and fabrication of a metal-free carbon nanodot–carbon nitride (C₃N₄) nanocomposite and demonstrate its impressive performance for photocatalytic solar water splitting. We measured quantum efficiencies of 16% for wavelength $\lambda = 420 \pm 20$ nanometers, 6.29% for $\lambda = 580 \pm 15$ nanometers, and 4.42% for $\lambda = 600 \pm 10$ nanometers, and determined an overall solar energy conversion efficiency of 2.0%. The catalyst comprises low-cost, Earth-abundant, environmentally friendly materials and shows excellent stability.

Production of hydrogen and oxygen from water is a promising means of storing solar energy in a way that compensates for the intermittency of sunlight as a primary source of power (1, 2). It can be realized by applying a hybrid system in which a solar cell powers an electrolyzer [photovoltaic (PV) electrolysis]. Photoelectrolysis (PE) uses photocatalyst electrodes with additional electrical power provided by a photovoltaic element. Photocatalysis (PC) involves light-irradiated catalysts (typically catalyst powders suspended in water) for water splitting (3). Recently reported “solar-to-hydrogen” (STH) efficiencies for PV electrolysis systems exceed 10% (4–6). State-of-the-art PE systems yield STH values of 2 to 3% (7) but are believed to provide a cheaper solution for H₂ production. PC is the simplest water-splitting approach, more amenable to cheap, large-scale applications of H₂ generation. Unfortunately, despite intense efforts during the past 40 years (8–15), current direct photocatalysts for water splitting still face several challenging issues: (i) Currently reported catalysts suffer from low quantum efficiency (QE) in the visible range, with STH efficiencies less than

0.1% (16–18); (ii) many photocatalysts are made of rare and expensive materials; (iii) various photocatalysts show poor stability [e.g., inorganic sulfide and (oxy)nitride-based photocatalysts are less stable and more susceptible to oxidation than water]; (iv) O₂ release from semiconductor catalysts is difficult, so that the use of sacrificial reagents is required; (v) the overall four-electron water oxidation to O₂ encounters a large overpotential; and (vi) the kinetically competing two-electron reaction to H₂O₂ often poisons the photocatalysts (19).

Overall water splitting to H₂ and O₂ requires a high free energy of 113.38 kcal/mol (20, 21). The challenge lies mainly in the release of diatomic O₂, which involves four electron and four proton transfers for the eventual formation of an O–O bond. The concerted four-electron process for oxygen evolution (1.23 eV) is thermodynamically more favorable than the two-electron process for H₂O₂ formation (1.78 eV). However, detailed analysis (see supplementary text) shows that a higher reaction rate may be achieved in a system where water is first oxidized via a two-electron reaction to H₂O₂ and H₂, followed by H₂O₂ decomposition to O₂ and H₂O. For this stepwise two-electron/two-electron water splitting to H₂ and O₂ to be viable and practical, the photocatalyst applied should be capable of promoting generation as well as subsequent decomposition of H₂O₂ with high efficiencies and low overpotentials, so as to allow considerable reduction in the energy cost for production of H₂ and O₂

via overall water splitting. Here, we report that nanocomposites of carbon nanodots embedded in a C₃N₄ matrix perform as an excellent photocatalyst fulfilling the above requirements.

C₃N₄ is commercially available (e.g., from Carbo-deon) and can be easily fabricated (e.g., from urea) (19). It is an Earth-abundant and low-cost photocatalyst capable of generating H₂ and H₂O₂ from water even in the absence of catalytic metals, albeit with a low QE (19, 22–26). C₃N₄ belongs to the oldest reported polymer materials prepared by chemists (by Berzelius in ~1830) and first termed “Melon” (27). In 2006 it was determined that the visible light activity of TiO₂ after treatment with urea was due to “Melon” (28). In 2009, Antonietti and colleagues described in detail the optical properties, electronic structure, and photocatalytic activity of C₃N₄ (29). Following this work, many groups attempted to optimize the catalytic properties of C₃N₄, motivated by its relatively low band gap energy E_g of 2.7 eV, and high valence band and conduction band positions (29) [1.8 and –0.9 eV versus reversible hydrogen electrode (RHE)]. Many heterojunction composites with oxide semiconductors as well as photocatalyst systems were investigated. The latter included systems with a variety of oxides (30) and sulfides (31) along with pure metals (19) and even graphene (32) and carbon nanotubes (33). Different preparation methods were studied in an effort to increase the surface area of C₃N₄ and to improve its catalytic activity. The QE values obtained using C₃N₄ as a catalyst for water splitting to H₂ and O₂ have been low (maximum 3.75% at 420 nm and less than 0.5% for 500 nm), and generally the use of a sacrificial reagent has been necessary (19, 24, 26, 30–32, 34). The efficiency at 700 nm can be largely increased by applying dye molecules, but again a sacrificial reagent is a must (35). During water splitting C₃N₄ suffers from poisoning by the produced H₂O₂, which is difficult to remove from the C₃N₄ surface (19). Different methods including stirring, bubbling, and/or addition of chemical agents have been attempted for regeneration of the poisoned C₃N₄ catalyst (19).

Carbon nanodots (CDots; monodisperse graphite particles less than 10 nm in diameter) exhibit unique photo-induced electron transfer, photoluminescence, and electron reservoir properties (36). In particular, CDots possess high catalytic activity (by chemical catalysis; no light is needed) for H₂O₂ decomposition (37). Given the photocatalytic properties of CDots and C₃N₄, we hypothesized that a combination of CDots and C₃N₄ could constitute a high-performance composite photocatalyst for water splitting via the stepwise two-electron/two-electron process: (i) 2H₂O → H₂O₂ + H₂; (ii) 2H₂O₂ → 2H₂O + O₂.

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