CdS-sensitized TiO_2 photoelectrodes for quantum dots-based solar cells

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Hydrothermally grown TiO_2 nanorod (NR) photoelectrodes were prepared by sensitizing CdS quantum dots to improve visible light activity of the TiO_2. The CdS-sensitized photoelectrodes were heat-treated to obtain enhanced performance of the photoelectrode under visible light. Furthermore, performance of the TiO_2 NR-based photoanodes was compared with those made of TiO_2 nanotubes (NTs). Photocurrent measurement and overall cell efficiency of the NR-based solar cells showed higher efficiency compared to NT-based solar cell.

I. INTRODUCTION

Dye-sensitized solar cells (DSSC) are considered to be a potential candidate for solar energy conversion devices due to their environmental friendly, cost-effective, and simple fabrication characteristics.[1–10] One of the important issues for designing high efficient solar cell devices is to find efficient photoelectrode materials with suitable nanostructures and electronic band structure. TiO_2 is one of the most promising candidate material widely investigated for use in photocatalysis, photoelectrodes, and solar cells. Wide band gap (3.2 eV) of the TiO_2 limits a photocatalytic property in the visible light region. To extend the activity of a photoelectrode into the visible light region, various approaches were used including doping TiO_2 with other impurities and sensitization with semiconductors, which can absorb light in the visible light region. Semiconductor nanocrystals, known as quantum dots (QDs), as an alternative to photosensitive dyes offer various advantages over dyes. It was recently established that QDs generate multiple electron–hole pairs per photon, improving device efficiency. Semiconductor QDs such as CdS, CdSe, PbS, PbSe, and InP have been studied as sensitizers of photoelectrodes using several TiO_2 structures.[8,11] Among these, cadmium sulfide (CdS) is relatively suitable and more stable in the presence of sacrificial reagents. TiO_2 nanotubes (NTs) and nanorods (NRs) were found to be competent structures due to their direct electrical pathway for photogenerated electrons, which increases the electron transport rate and in turn may improve the performance of the photovoltaic application.[12–14]

In this study, we evaluated CdS QD-sensitized TiO_2 NRs (single crystalline) on fluorine-doped tin oxide (FTO)-coated glass substrate and polycrystalline TiO_2 NTs as a photoanode for a solar cell. Single crystalline NRs may significantly improve performance of the quantum dot solar cell due to the better charge transport and collection properties.[15,16] Structural defects in polycrystalline TiO_2 NTs provide recombination centers for electron–hole pairs, which also increase resistance in the nanostructure. Moreover, as-sensitized CdS/TiO_2 samples were heat-treated to improve the crystallization of CdS and CdS–TiO_2 interface. Measurements of photocurrent and overall cell efficiency confirmed that the NR-based solar cells showed higher photocatalytic performance, compared to NT-based solar cell without heat treatments.

II. EXPERIMENTAL DETAILS

Paces of FTO glass substrates (2 × 2 cm) were cleaned in solution containing deionized (DI) water:acetone:2-propanol (ratio1:1:1) in a supersonic cleaner. Hydrothermal solution contained 30 mL DI water, 1 mL titanium 2-butoxide (Sigma-Aldrich, St. Louis, MO), and 30 mL HCl. Cleaned samples were arranged in autoclave cell containing hydrothermal solution. Hydrothermal process conducted at 180 °C for 5 h. After cooling down until room temperature, samples were taken out and cleaned in DI water. Samples' colors were changed from transparent to white opaque color. After drying under nitrogen flow, samples were annealed at 450 °C for 30 min in tube furnace. TiO_2 NTs arrays were grown by electrochemical anodization of Ti foils with thickness of 0.1 mm and 99.6% purity (Alfa Aesar, Royston, UK). Substrates were thoroughly cleaned by sonication in trichloroethylene, acetone, and methanol before anodization. Anodization was carried out in electrolyte containing of 0.15 M NH_4F in solution with ratio of 19:1 in formamide and DI water and 35 V for 3 h at room temperature using a platinum foil as the counter electrode. Amorphous TiO_2 NTs formed by the anodization processes were annealed for crystallization at 550 °C in air for 4 h. Further, both NRs and NT samples were sensitized

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with CdS QDs by using successive ionic layer adsorption and reaction (SILAR) method. In typical experimenters, 0.1 mol $CdSO_4$ and 0.1 M Na_2S were used as Cd and S sources, respectively. Samples were dipped in to each source solution (Cd and S) for 3 min. After each dipping samples were rinsed with DI water. Dipping and rinsing (Cd→DI→S→DI) was comprised as a one cycle. Desired amount of CdS was obtained after 10 SILAR cycles. Each time after dipping into each source, samples were washed with DI water and dried under nitrogen gas flow. TiO_2 NR/NT after CdS QD sensitization was heat-treated at 300 °C for 30 min in an inert environment (in nitrogen-filled glove box) to avoid oxidation. Counter electrodes were prepared by spin coating of platinum solution containing $H_2PtCl_6{\cdot}6H_2O$ on FTO. QDs-based solar cells were assembled by sandwiching a ~25-μm-thick Surlyn frame (Solaronix, Aubonne VD, Switzerland) between the prepared electrodes and a platinized FTO electrode. Photoelectrochemical measurements were performed under AM 1.5 sun condition using polysulfide electrolyte [2 M S, 0.5 M Na_2S, and 0.5 M KCl in DI water:methanol solution (7:3 vol%)].

III. RESULTS AND DISCUSSION

Morphologies of the grown NT and NRs were studied by using a field emission scanning electron microscope (FE-SEM). Figures 1(a) and 1(b) show cross-sectional and surface FE-SEM images of TiO_2 NTs obtained by anodizing method and Figs. 1(c) and 1(d) show cross-sectional and surface image of TiO_2 NRs grown by using hydrothermal method. It is confirmed that morphology of the NRs can be controlled by changing experimental parameters such as time, temperature, and concentration of the solution. Average length of the NTs and NRs was 6 and ~1 μm, respectively. Figure 2 shows transmission electron microscope (TEM) images of TiO_2 NTs (a) and CdS-sensitized TiO_2 NTs (b), respectively. Bare TiO_2 NRs and after sensitization with CdS can be seen in Figs. 2(a) and 2(b) respectively. From TEM images shown in Fig. 2(b), we can see well-isolated CdS nanoparticles with average size of 10 ± 3 nm. Nanoparticles are regularly distributed inside and outside the NT as indicated with arrowheads. In NR case, CdS nanoparticles are mainly distributed on the outside surface of NRs. Figure 3 shows x-ray diffraction (XRD) pattern of the TiO_2 NRs and NTs along with bare FTO glass as a reference. From the XRD result of TiO_2 NTs, we can see that it is polycrystalline in nature and composes of mixed anatase and rutile phases. However, NRs show only rutile single crystalline TiO_2 phase, compared to NTs, and (002) diffraction peak was increased, indicating that NRs are oriented perpendicular to the FTO surface and grow in the [001] direction. Photoelectrochemical tests of the samples were performed in three-electrode system in Na_2S electrolyte and results are shown in Fig. 4. Photocurrent densities of the bare TiO_2 and CdS/TiO_2 NRs under white and visible light irradiations are shown in Figs. 4(a) and 4(b), respectively. After CdS

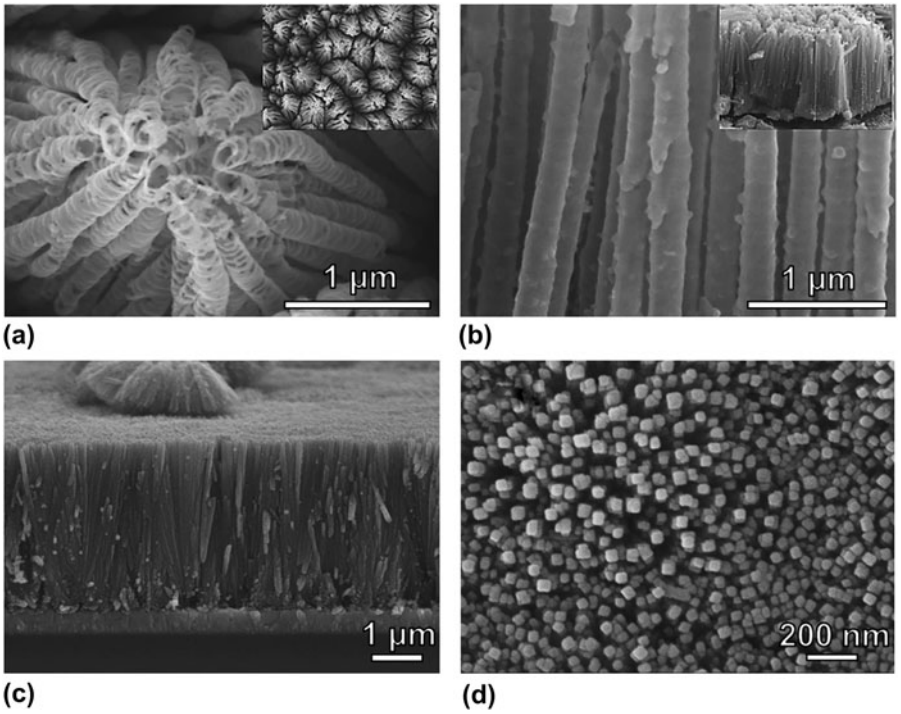


FIG. 1. FE-SEM images of the surface (a) and cross-sectional (b) views of TiO_2 NTs; (c) and (d) show surface and cross-sectional images of the hydrothermally grown NRs on FTO, respectively.

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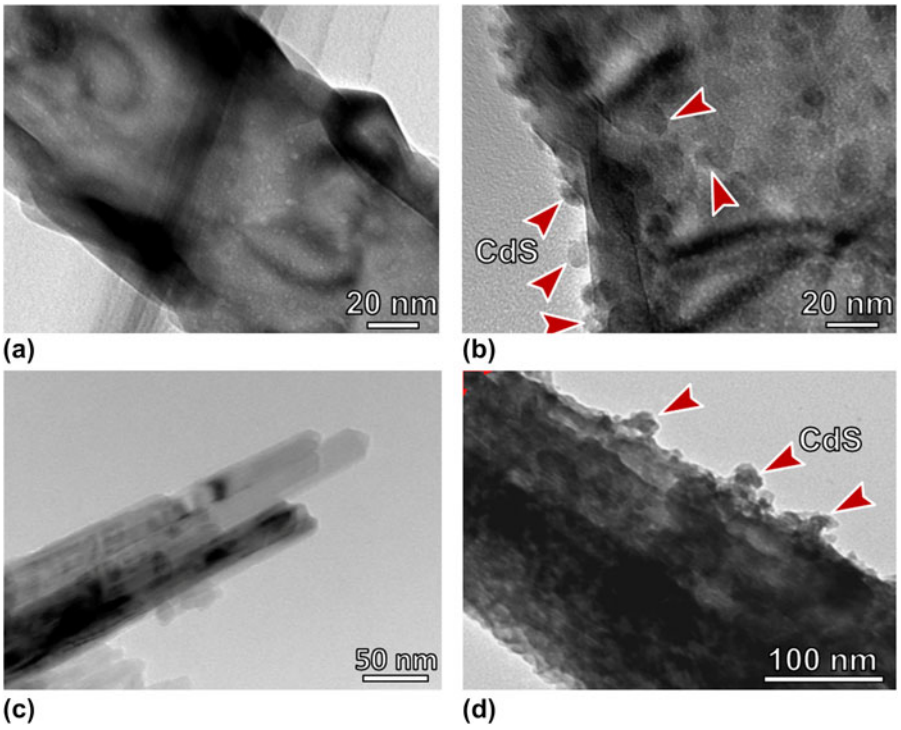


FIG. 2. Bright field TEM images of the TiO_2 NTs before (a) and after (b) CdS sensitization process. (c) shows bright field image of the TiO_2 NRs. TiO_2 NRs after CdS sensitization are shown in (d).

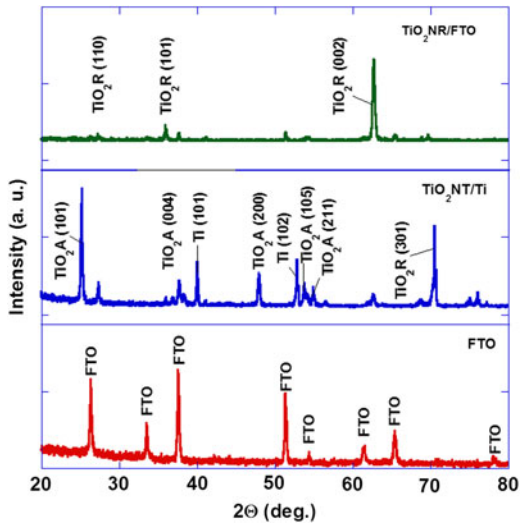


FIG. 3. XRD analysis of hydrothermally grown TiO_2 NRs and anodized TiO_2 NTs.

sensitization, photoresponse of CdS/TiO_2 samples under visible light was greatly increased. Further heat treatment of the CdS/TiO_2 at 300 °C for 30 min even more improved photoresponse of the samples under both white and visible light. Identically, TiO_2 NTs and CdS/TiO_2 NTs show similar behavior to NRs in terms of additional heat treatment of the CdS/TiO_2 as shown in Figs. 4(c) and 4(d). Improved CdS/TiO_2 photoresponses of the electrodes after heat treatment are attributed to several factors. As-deposited CdS has a very low degree of crystallization, which improves after heat treatment as reported in Ref. 17. Furthermore, during heat treatment, CdS nanocrystallites increase in size; this in turn results in decreasing the band gap of the CdS QDs according to the quantum confinement theory. Consequently, CdS with decreased band gap absorbs light in the larger portion of the visible light region. Figure 5 shows I-V curves of the CdS-sensitized solar cells using TiO_2 NR and NTs photoanodes. Overall photocurrent efficiency measurements were carried out under standard conditions (light intensity: 1000 W/m^2, illumination condition: AM 1.5, working electrode: FTO glass/CdS QDs-sensitized TiO_2 NRs, counter electrode: FTO glass/Pt film). Table I shows summary of all the studied cells' performances. As seen from the results, efficiency of the CdS/TiO_2 NR was 0.38% and increased up to 0.68% after heat treatment. Efficiency of the CdS/TiO_2 NTs-based solar cells is lower (0.065%) than NR-based solar cell; however, it shows similar trend, i.e., increasing (0.14%) after heat treatment. Superior performance of the NR could be explained due to the single crystalline nature of NRs, which has less structural defects. Crystal structure and crystallites of the semiconductor have crucial effect on solar cell performance. The defects operate as trapping and recombination centers between photogenerated electrons and holes, resulting in a decrease in the electron–hole mobility. In the TiO_2 NTs,

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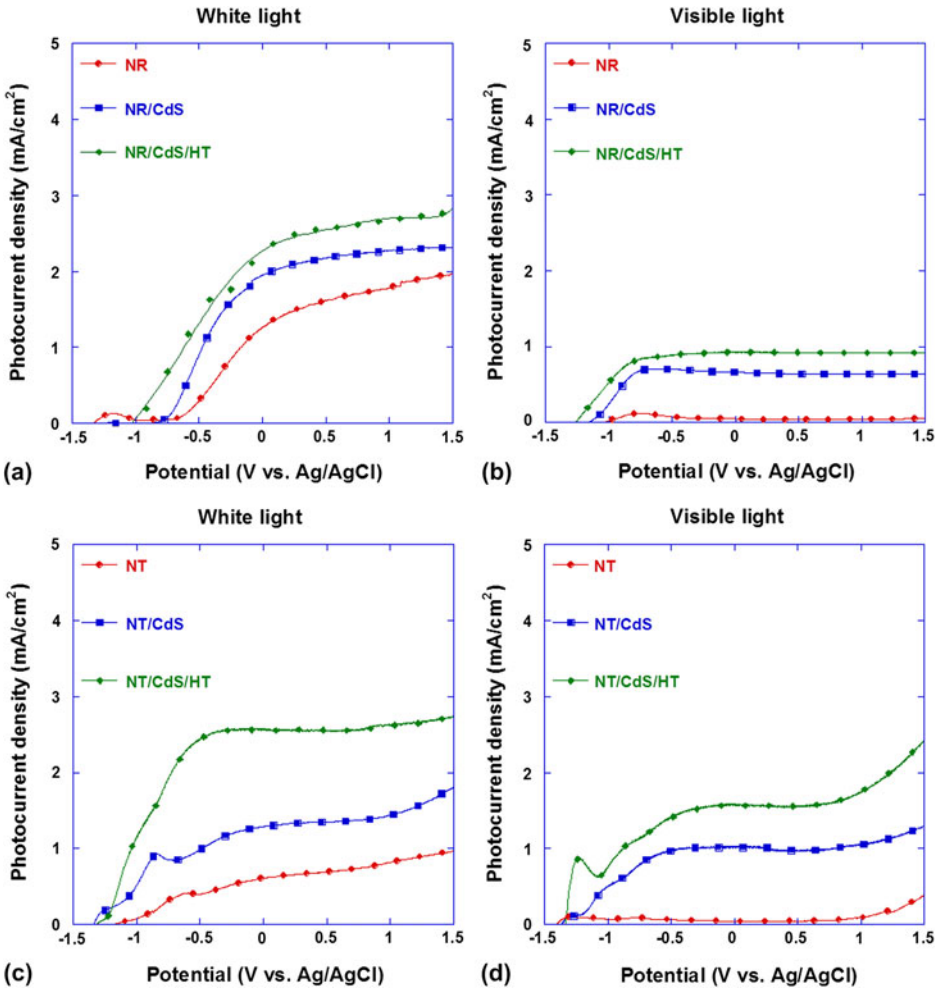


FIG. 4. Photocatalytic properties of the TiO_2 NRs and NTs. Photocurrent density of TiO_2 NRs under white (a) and visible light (b) illumination. (c) and (d) show photocurrent density of TiO_2 NTs under white and visible light irradiation, respectively.

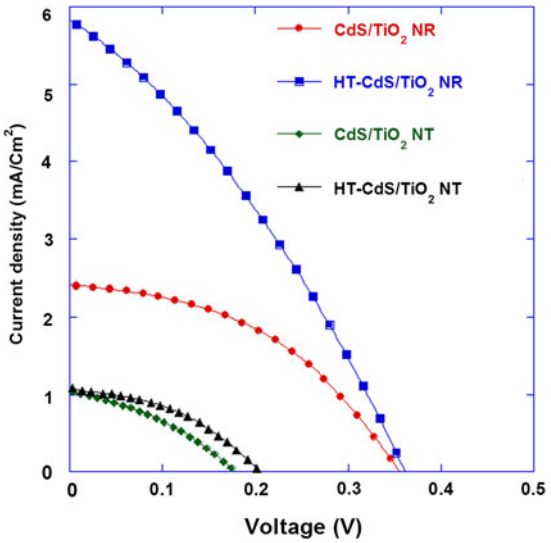


FIG. 5. Overall photoconversion efficiency results (I-V curve) of CdS QDs-sensitized solar cells.

TABLE I. TiO_2 NR- and NT-based CdS QD-sensitized solar cells performance.

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor (FF)	Efficiency (%)
CdS/TiO_2 NR	0.36	5.9	0.32	0.38
Heat treatment (HT)-CdS/TiO_2 NR	0.36	2.4	0.44	0.68
CdS/TiO_2 NT	0.18	1.1	0.35	0.065
HT-CdS/TiO_2 NT	0.31	1.12	0.40	0.14

mainly, grain boundaries act as a recombination sites for photogenerated electron–holes. Therefore, effective charge transport and collection in polycrystalline TiO_2 NTs are lower than NRs, resulting lower photocurrent density. It is clear that cells efficiency is quite low compared to other research groups; however, it confirms the advantages of the single crystalline TiO_2 nanostructures over polycrystalline nanostructure for DSSC application.

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IV. SUMMARY

Single crystalline TiO_2 NRs arrays on FTO glass were fabricated by a hydrothermal method. Improved visible light activity of the photoanodes was achieved by sensitization with CdS nanoparticles. Photocatalytic measurements revealed that single crystalline NRs show higher photocurrent compared to polycrystalline NTs, which was attributed to low structural defects within the NRs. It was also confirmed that single crystalline NR-based solar cell showed higher efficiency than polycrystalline NT-based solar cell.

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REFERENCES

1. B. O'Regan and M. Grätzel: A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature* **353**, 737 (1991).
2. B. Liu and E.S. Aydil: Electron transport and recombination in dye-sensitized solar cells made from single-crystal rutile TiO_2 nanowires. *Chem. Phys.* **11**, 9648 (2009).
3. L. Yin and C. Ye: Review of quantum dot deposition for extremely thin absorber solar cells. *Sci. Adv. Mater.* **3**, 41 (2011).
4. P.V. Kamat: Quantum dot solar cells. Semiconductor nanocrystals as light harvesters. *Phys. Chem. C* **112**, 18737 (2008).
5. S.C. Lin, Y.L. Lee, C.H. Chang, Y.J. Shen, and Y.M. Yang: Quantum-dot-sensitized solar cells: Assembly of CdS-quantum-dots coupling techniques of self-assembled monolayer and chemical bath deposition. *Appl. Phy. Lett.* **90**, 143517-1–143517-3 (2007).
6. Q. Zhang, Y. Zhang, S. Huang, X. Huang, Y. Luo, Q. Meng, and D. Li: Application of carbon counterelectrode on CdS quantum dot-sensitized solar cells (QDSSCs). *Electrochem. Commun.* **12**, 327 (2010).
7. G.K. Mor, K. Shankar, M. Paulose, O.K. Varghese, and A. Craig: Grimes: Use of highly-ordered TiO_2 nanotube arrays in dye-sensitized solar cells. *Nano Lett.* **6**, 215 (2006).
8. T. Zeng, H. Tao, X. Sui, X. Zhou, and X. Zhao: Growth of free-standing TiO_2 nanorod arrays and its application in CdS quantum dots-sensitized solar cells. *Chem. Phys. Lett.* **508**, 130 (2011).
9. W.T. Sun, Y. Yu, H.Y. Pan, X.F. Gao, Q. Chen, and L.M. Peng: CdS quantum dots sensitized TiO_2 nanotube array photoelectrodes. *J. Am. Chem. Soc.* **130**, 1124 (2008).
10. Y.L. Lee and C.H. Chang: Efficient polysulfide electrolyte for CdS quantum dot-sensitized solar cells. *J. Power Sources* **185**, 584 (2008).
11. H. Wang, Y. Bai, H. Zhang, J. Li, and L. Guo: CdS quantum dots-sensitized TiO_2 nanorod array on transparent conductive glass photoelectrodes. *J. Phys. Chem. C* **114**, 16451 (2010).
12. Y.L. Lee, C.F. Chi, and S.Y. Liau: CdS/CdSe co-sensitized TiO_2 photoelectrode for efficient hydrogen generation in a photoelectrochemical cell. *Chem. Mater.* **22**, 922 (2010).
13. R.B. Kale and C.D. Lokhande: Studies on the effects of Cd ion sources and chelating reagents on atomic layer CdS deposition by successive ionic layer adsorption and reaction (SILAR) method. *Phys. Chem. Chem. Phys.* **3**, 3371 (2001).
14. C.H. Chang and Y.L. Lee: Chemical bath deposition of CdS quantum dots onto mesoscopic TiO_2 films for application in quantum-dot-sensitized solar cells. *Appl. Phys. Lett.* **91**, 053503 (2007).
15. B. Liu and E.S. Aydil: Growth of oriented single-crystalline rutile TiO_2 nanorods on transparent conducting substrates for dye-sensitized solar cells. *J. Am. Chem. Soc.* **131**, 3985 (2009).
16. X. Feng, K. Shankar, O.K. Varghese, M. Paulose, T.J. Latempa, and C.A. Grimes: Vertically aligned single crystal TiO_2 nanowire arrays grown directly on transparent conducting oxide coated glass: Synthesis details and applications. *Nano Lett.* **8**, 3781 (2008).
17. C.F. Chi, S.Y. Liau, and Y.L. Lee: The heat annealing effect on the performance of CdS/CdSe-sensitized TiO_2 photoelectrodes in photochemical hydrogen generation. *Nanotechnology* **21**, 1 (2010).

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