Solar driven hydrogen evolution from glucose over $Ni(OH)_2$ functionalized electroreduction-TiO_2 nanowire arrays

Shilei Xie,[a] Teng Zhai, [a] Wei Li, [a] Minghao Yu, [a] Chaolun Liang, [a,b] Jiayong Gan, [a] Xihong Lu,[*,a] and Yexiang Tong[*,a]

KLGHEI of Environment and Energy Chemistry, MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China E-mail: ce04lxh@mail2.sysu.edu.cn; chedhx@mail.sysu.edu.cn

b Instrumental Analysis and Research Centre, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China.

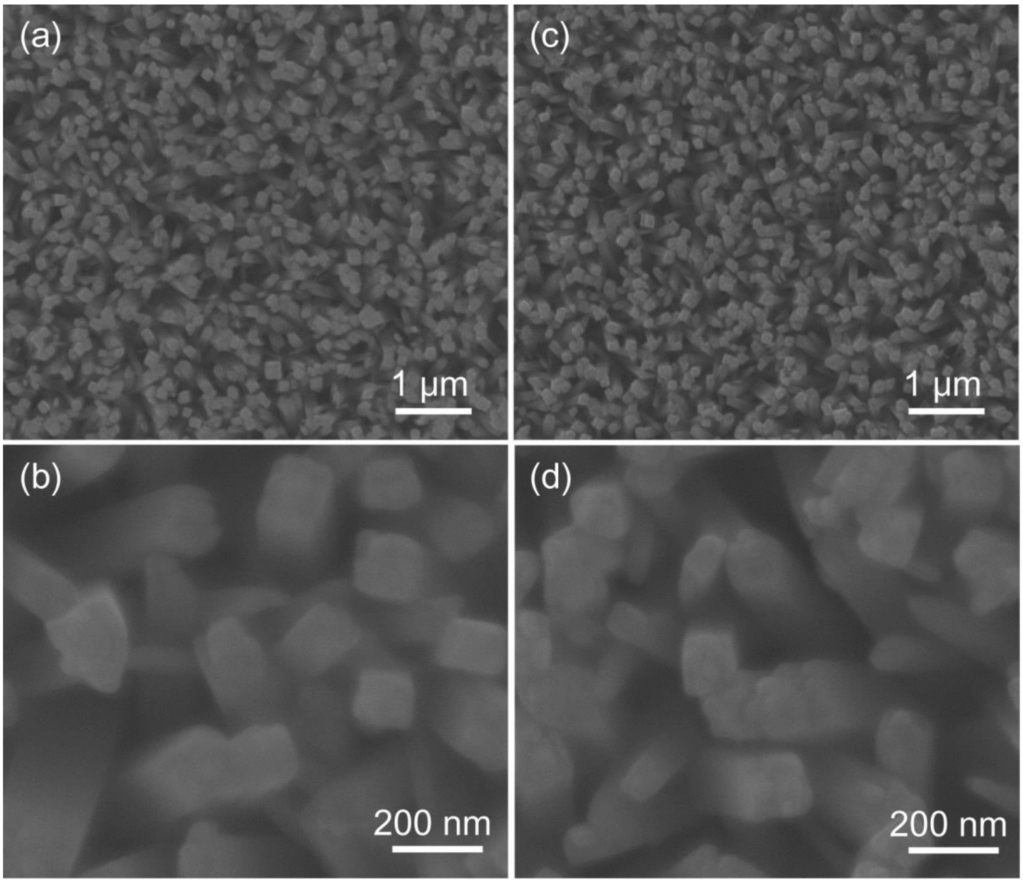

Fig. S1 SEM images of the (a, b) TiO_2 and (c, d) electro-reduced TiO_2 (R-TiO_2) NWAs

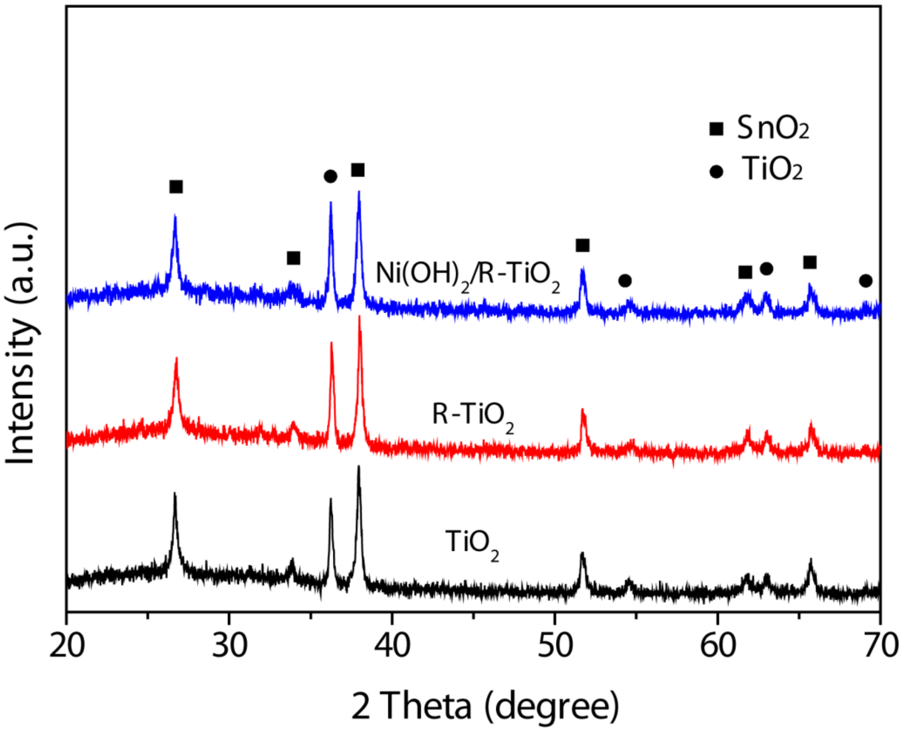

Fig. S2 XRD spectra collected for TiO_2, R-TiO_2 and $Ni(OH)_2$/R-TiO_2 NWAs on FTO substrate.

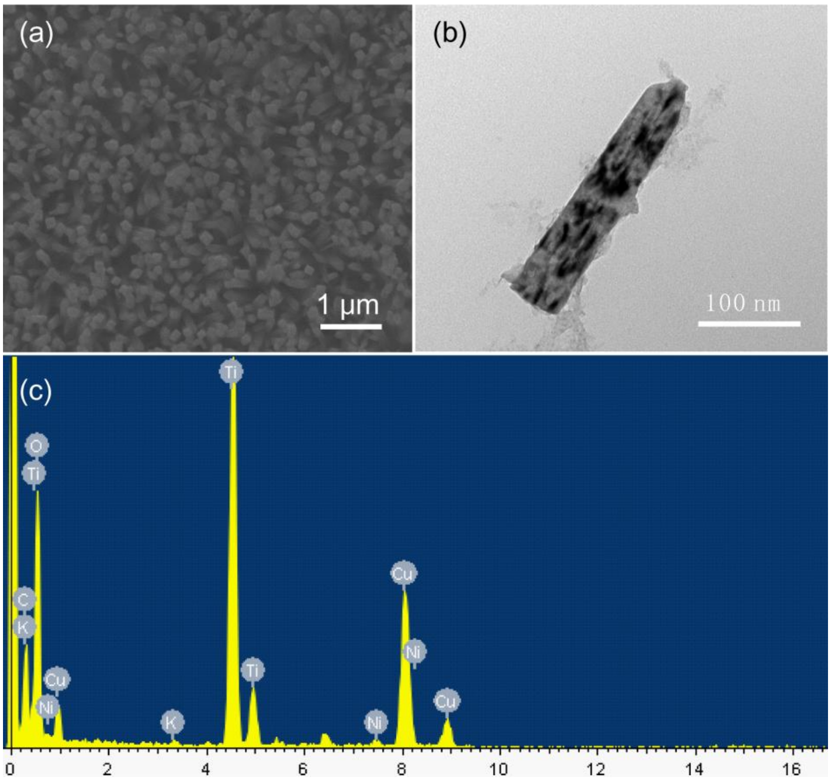

Fig. S3 (a) SEM image, (b) TEM image and (c) EDS spectrum of the $Ni(OH)_2$/R-TiO_2 NWs.

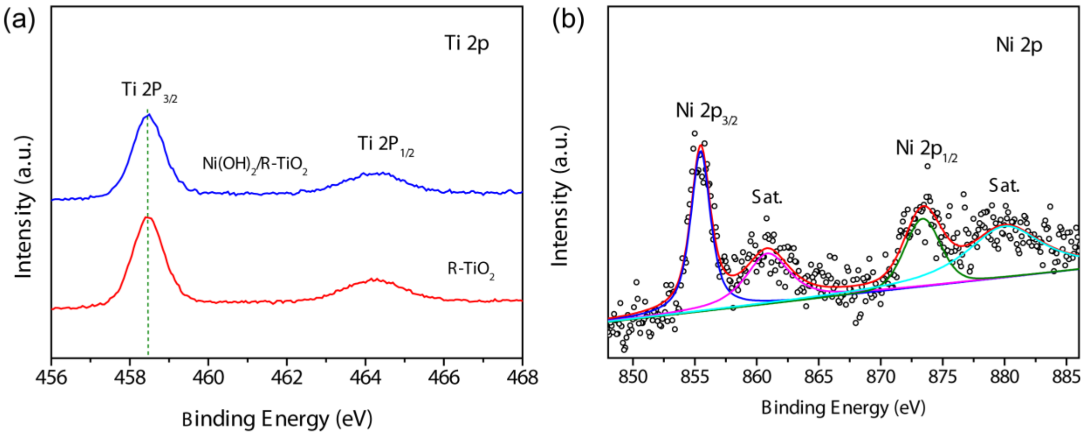

Fig. S4 (a) Normalized Ti 2p core level XPS spectra of R-TiO_2 and $Ni(OH)_2$/R−TiO_2 NWAs, showing that no any change in binding energy of the Ti 2p peaks after coated with $Ni(OH)_2$. (b) Ni 2p core level XPS spectrum of $Ni(OH)_2$/R−TiO_2 NWAs. The Ni $2p_{3/2}$ peak centered at about 855.6 eV, which is consisted with the characteristic binding energy of Ni $2p_{3/2}$ for $Ni(OH)_2$, [1] confirming the presence of the $Ni(OH)_2$ in $Ni(OH)_2$/R−TiO_2 NWAs.

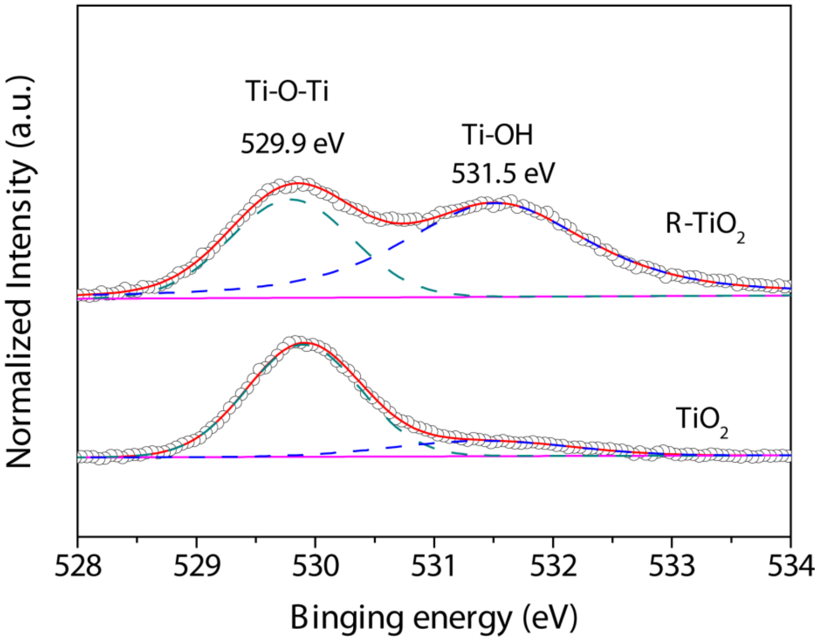

Fig. S5 O 1s core level XPS spectra of TiO_2 and R−TiO_2 NWAs

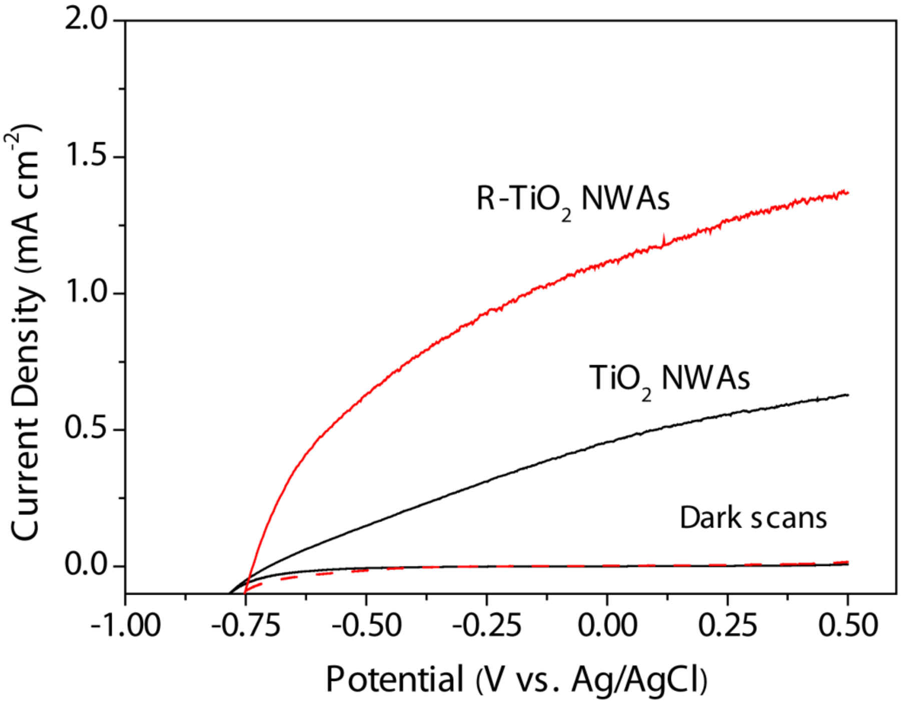

Fig. S6 LSW curves collected for TiO_2 and R-TiO_2 electrodes in the dark (dashed lines) and under light illumination (100 mW cm^{-2}) in 1 M KOH electrolyte.

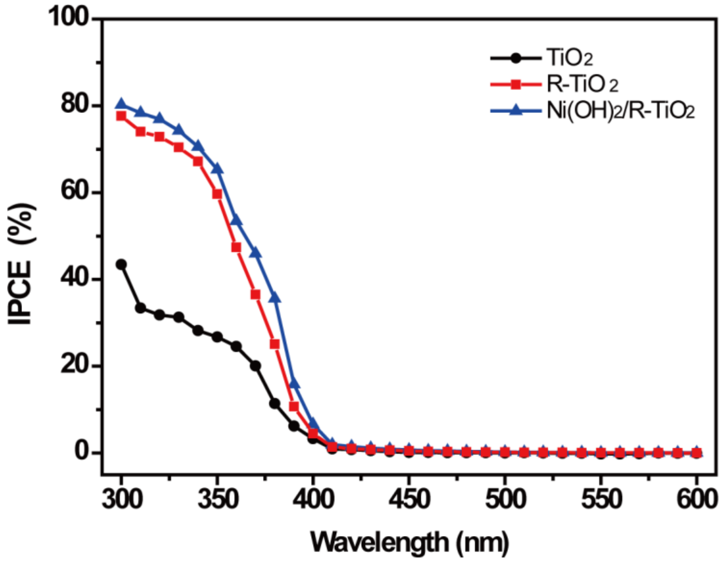

Fig. S7 IPCE spectra of TiO_2, R-TiO_2 and $Ni(OH)_2$/R-TiO_2 NWAs collected at the incident wavelength range from 300 to 600 nm at a potential of -0.6 V vs. Ag/AgCl.

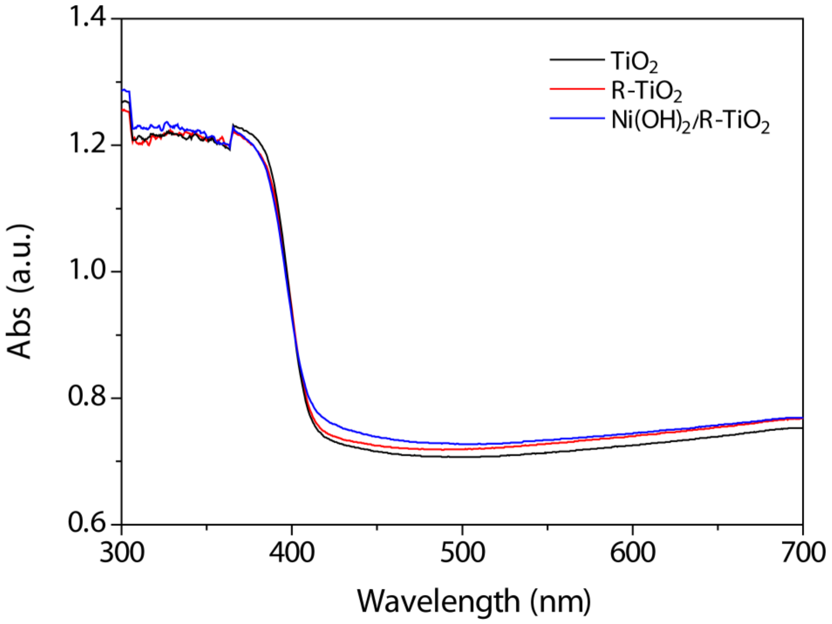

Fig. S8 UV-visible spectra collected for TiO_2, R-TiO_2 and $Ni(OH)_2$/R−TiO_2 NWAs on FTO substrate.

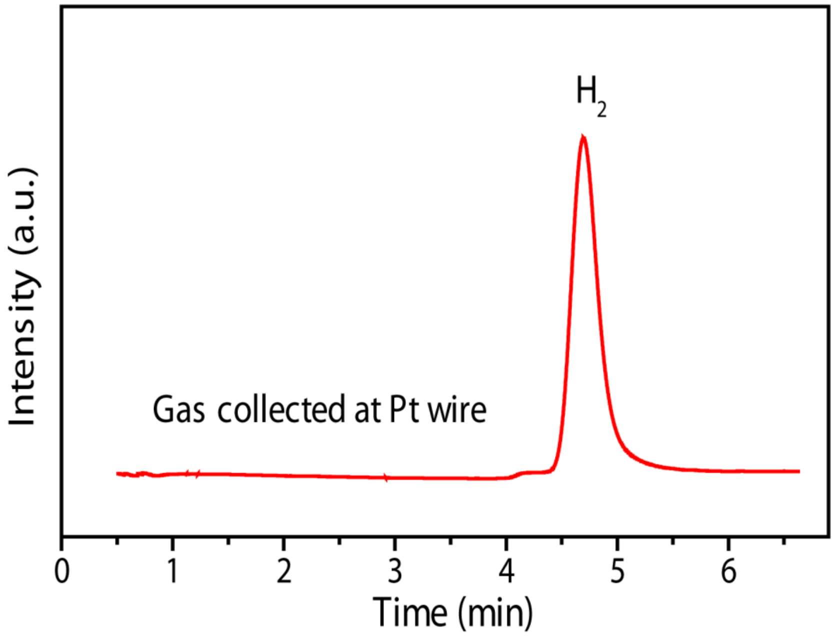

Fig. S9 The chromatogram retention times of the gas collected at Pt wire at -0.3 V (Ag/AgCl) under light irradiation for 1 h.

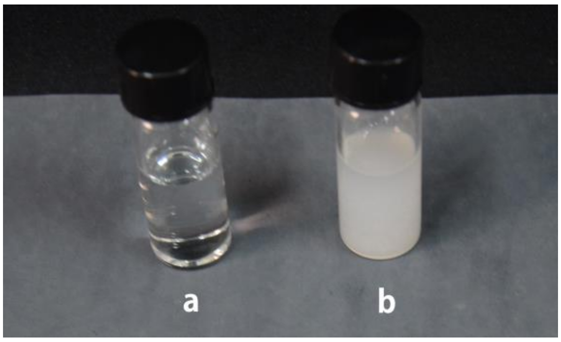

Fig. S10 The photo image of (a) blank saturated $Ca(OH)_2$ solution and (b) saturated $Ca(OH)_2$ after dropped 0.5 ml anode solution

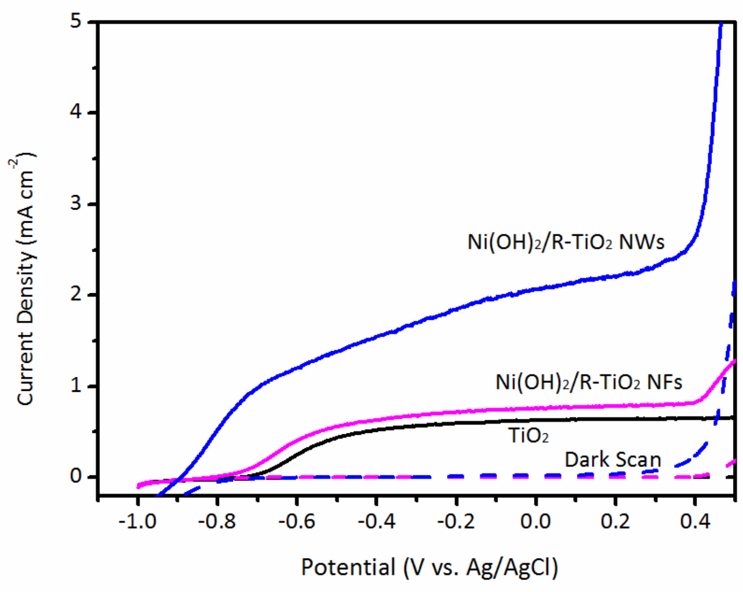

Fig. S11 LSW curves collected for TiO_2 NFs, $Ni(OH)_2$/R-TiO_2 NFs and $Ni(OH)_2$/R-TiO_2 NWs electrodes in the dark (dashed lines) and under light illumination (100 mW cm^{-2}) in a 1 M KOH aqueous solution with 0.1 M glucose.

Total Organic Carbon (TOC) and Inorganic Carbon (IC) were measured with total organic carbon analyzer (Shimadzu , TOC—VCPH). One milliliter of the solution close to the photoanodes after the 5h reaction was diluted to 50 ml with DI water before the analysis. The TOC was calculated from Eq (1):

$$\text{TOC} = \text{TC} - \text{IC} \qquad (1)$$

Where the TC is total carbon and IC is inorganic carbon. The generated CO_2 would dissolve into the base solution and form carbonate (CO_3^{2-} or HCO_3^{-}) even if after the dilution which the pH was 10.0 measured by pH meter (Shanghai Precision & Scientific Instrument Co. Ltd., PHS-3C), and then IC would contain the generated CO_2 and absorption of CO_2. As the IC of blank sample only can come from the absorption of CO_2 in air, the generated CO_2 of each samples should be calculated from Eq(2):

$$w_{CO_2} = \mathrm{IC} - \mathrm{IC}_{\mathit{blank}} \qquad (2)$$

After the reaction, the carbon of the initial carbon became TOC still in the solution, CO_2 transferring to carbonate and CO escaping into air. Then, we also can get the amount of the generated CO from Eq(3):

$$w_{CO} = \mathrm{TOC}_{\mathit{blank}} - \mathrm{TOC} - w_{CO_2} \qquad (3)$$

Furthermore, the efficiency of the glucose oxidation can be calculated by Eq(4):

$$\eta = [w(CO_2)+w(CO)]\times 100\% / w(C_6H_{12}O_6) \qquad (4)$$

Table S1 TOC, TC, IC, calculated generated CO_2, CO and efficiency of the glucose oxidation

	TOC	TC	IC	w_{CO_2}	w_{CO}	η
TiO_2	3485.5	5060.0	1574.5	1479.7	2143.3	51%
R-TiO_2	3612.1	5133.4	1521.3	1426.5	2069.9	49%
$Ni(OH)_2$/R-TiO_2	1478.2	3946.8	2468.6	2373.8	3256.5	79%
Blank *	7108.5	7203.3	94.8	0.0	--	--
DI water	0.6528	0.8702	0.2174	0.6528	--	--

* Blank stood for the solution without any catalyst under the irradiation.

1. K.-W. Park, J.-H. Choi, B.-K. Kwon, S.-A. Lee, Y.-E. Sung, H.-Y. Ha, S.-A. Hong, H. Kim and A. Wieckowski, *J Phy. Chem. B*, 2002, **106**, 1869.