Supporting Information

Reduced TiO$_2$ Nanotube Arrays for Photoelectrochemical Water Splitting

Qing Kang, a Junyu Cao, b Yuanjian Zhang, a Lequan Liu, a Hua Xu, a, b, c Jinhua Ye a, b, c, d

a International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
b Catalytic Materials Group, Research Unit for Environmental Remediation Materials, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
c Graduate School of Chemical Science and Engineering, Hokkaido University, Sapporo, Japan.
d TU-NIMS Joint Research Center, School of Materials Science and Engineering, Tianjin University, 92 Weijin Road, Nankai District, Tianjin 300072, P. R. China.

* Corresponding author E-mail: Jinhua.YE@nims.go.jp
Figure S1. Open circuit potential of the pristine and reduced TiO$_2$ NTAs under simulated solar light irradiation.

Figure S2. XRD patterns of the pristine and reduced TiO$_2$ NTAs.

Figure S3. High resolution TEM images of (a) pristine and (b) reduced TiO$_2$ NTAs.

XRD analysis reveals that all of the TiO$_2$ samples are indexed to the pure anatase structures (JCPDS No. 73-1764). And the NaBH$_4$ treatment does not change the TiO$_2$ bulk nanocrystal structure, which is in agreement with HRTEM observation.
Figure S4. XPS survey spectra of the reduced and pristine TiO$_2$ NTAs.

Figure S5. EPR spectra for reduced TiO$_2$ NTAs measured at 4K, 10K and 50K. Figure S5 shows EPR features for anisotropic g tensors are only apparent in 4K and 10K spectra with a noted narrowing of the lines with decreasing temperature.

Figure S6. Cyclic voltammetry (CV) test using different reference electrode. Figure S6 was tested in 1 M KNO$_3$ and 2 mM K$_3$Fe(CN)$_6$ solution, the working electrode was a Pt sheet and the counter electrode was a Pt wire. In the PEC progress, an Ag/AgCl (saturated KCl)
electrode was used as the reference electrode (as described in experimental details). To ensure the potential of the reference electrode stable during the experiments, CV was tested before and after the PEC experiment. Control experiment was test with a new Ag/AgCl reference electrode. As shown in Figure S6, these three CV curves match well, which means the used Ag/AgCl reference electrode was stable during PEC progress.