Supporting Information Available:

Experimental procedures

Catalyst Preparation. To prepare perovskite by solid state reactions, a stoichiometric mixture of PbO, Bi_2O_3, and Nb_2O_5 was ground in a mortar and dried in an oven. Pelletized powders were calcined at 1273 K for 24 h in static air and sintered at 1473 K for 24 h. $TiO_{2-x}N_x$ was prepared by the reported procedure[5]. Catalysts used for water decomposition were loaded with 0.1 wt% Pt by impregnation with $PtCl_2$.

Photocatalytic Activity Measurements. The photocatalytic water decomposition was carried out at room temperature in a closed system using a 450W tungsten-arc lamp (Oriel) with a UV cut-off filter (λ≥420nm) placed in an outer irradiation-type pyrex reaction cell with a volume of 200 ml. For 1g of catalyst, H_2 production was performed in a stirred aqueous methanol solution (methanol 30ml + distilled water 170ml), while O_2 production was performed in an aqueous $AgNO_3$ solution (0.05 mol/l, 200ml). The materials were also tested under UV-light irradiation by removing the cut-off filter under otherwise the same conditions. The O_2 or H_2 was generated at much higher rates, establishing that these materials were also active for water decomposition under UV light. The quantum yield was calculated using the following equation: QY = 2 × number of H_2 or 4 × number of O_2 generated per number of photon absorbed by photocatalyst. The number of absorbed photons was determined by light flux meter (1815-C, Newport) with the light sensor attached to the photocatalytic reactor. First, the light absorbed by the whole photocatalytic reactor system was obtained by the difference in light flux with and without the photocatalytic reactior between the light source and the light sensor. The loss of light intensity due to scattering and absorption by materials in the light path other than the photocatalyst was determined for the same reactor containing suspended La_2O_3 powders (instead of the photocatalyst), which did not absorb visible light. The net absorption by the photocatalyst was obtained by the difference of these two values. About 200 ppm of gaseous isoporpyl alcohol (IPA) was injected into a Pyrex reaction cell with a volume of 500 ml. The concentrations of reaction products (H_2, O_2, CO_2) were determined by a gas chromatograph equipped with a thermal conductivity detector and a molecular sieve 5Å column. For Photoelectrochemical measuremens, 25 mg of a photocatalyst was suspended in distilled water (75ml) containing acetate (0.1 M) and Fe^{3+} (0.1 mM) as an electron donor and an acceptor, respectively, and the suspension pH was adjusted to 1.4 with $HClO_4$. A platinum plate (1x1 cm^2, 0.125 mm thick, both sides exposed to the solution), a saturated calomel electrode (SCE), and a platinum gauze was immersed in the reactor as working (collector), reference, and counter electrodes, respectively. With continuous N_2 purging of the suspension, photocurrensts were measured by applying a potential (+0.6 V vs SCE) to the Pt working electrode using a potentiostat (EG&G).

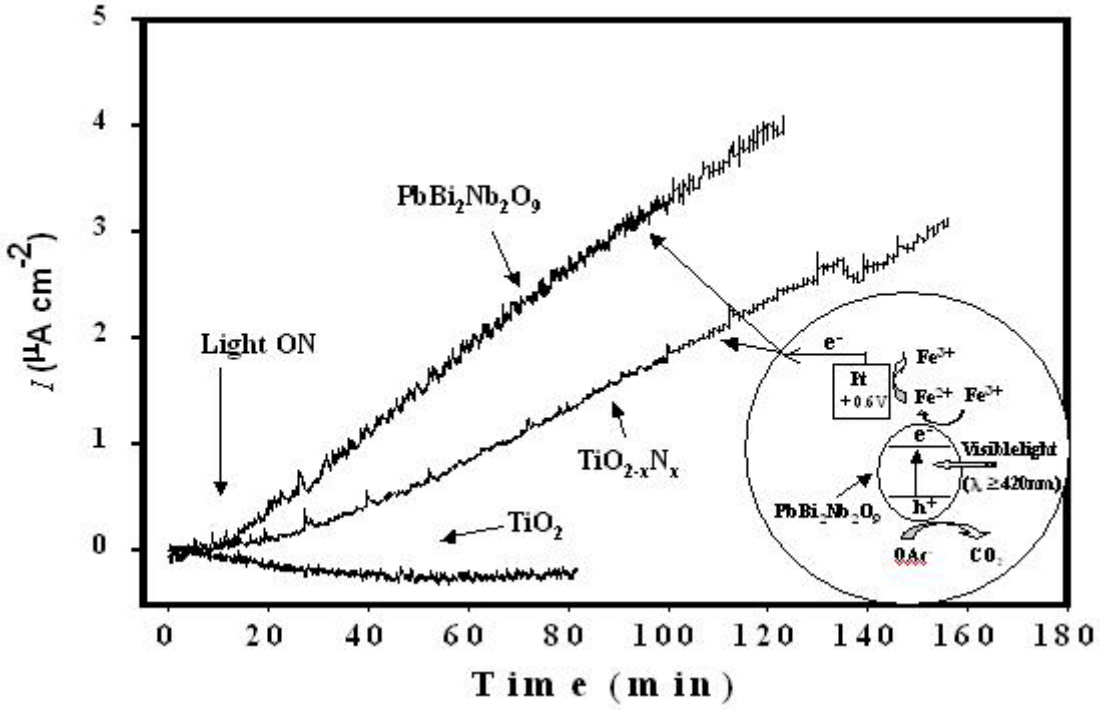

Figure S1. Photocurrent generation under visible light (>420nm) in aqueous photocatalysts suspensions with acetate and Fe^{3+}, as an electron donor and an acceptor, respectively.

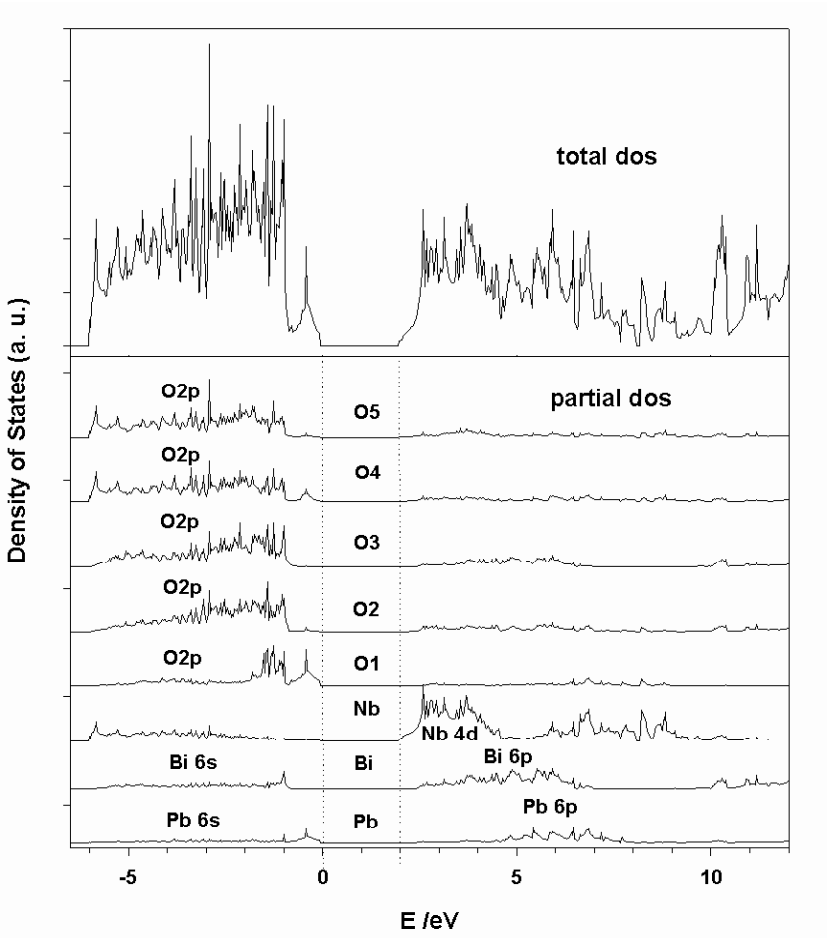

Figure S2. Calculated total and partial density of states (DOS) of $PbBi_2Nb_2O_9$. The electronic band structure was calculated with Wien97 package based on the Full Potential Linearized Augmented Plane Wave (FLAPW) method[14], which used the generalized gradient approximation (GGA) within density functional theory (DFT). The conduction and valence bands of this compound consist of empty Nb4d and occupied O2p orbital, with the latter hybridized with Bi6s and Pb6s, giving the smaller band gap compared to compounds that do not contain Pb and Bi in their structure

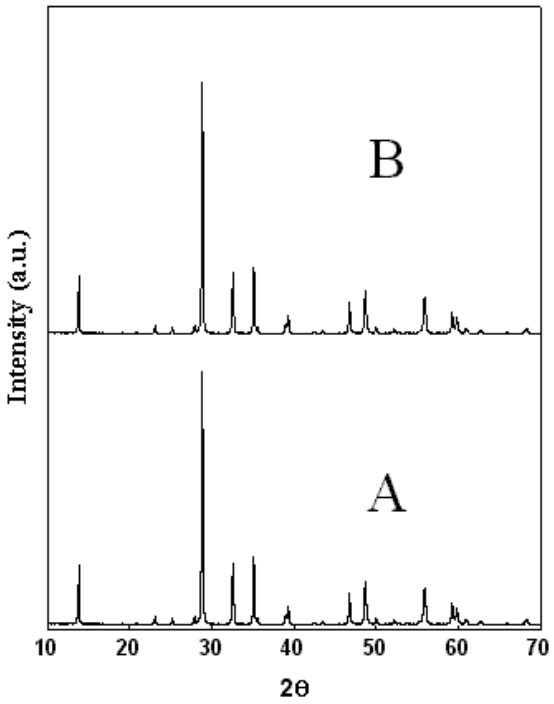

Figure S3. X-ray Diffraction Patterns of $PbBi_2Nb_2O_9$ before (A) and after (B) O2 production from aqueous silver nitrate solution under visible light (λ≥420nm) for 100 h show no difference and thus demonstrate that the photocatalyst is stable under the light illumination. The ICP analysis of the reaction solution after the reaction also did not indicated the presence of dissolved catalyst components above the detection limit of the analysis (1 ppm)