## Electrocatalytic and Photocatalytic Hydrogen Production from Acidic and Neutral-pH Aqueous Solutions Using Iron Phosphide Nanoparticles

Juan F. Callejas, <sup>†,§</sup> Joshua M. McEnaney, <sup>†,§</sup> Carlos G. Read, <sup>†,§</sup> J. Chance Crompton, <sup>‡</sup> Adam J. Biacchi, <sup>†</sup> Eric J. Popczun, <sup>†</sup> Thomas R. Gordon, <sup>†</sup> Nathan S. Lewis, <sup>‡,\*</sup> and Raymond E. Schaak <sup>†,\*</sup>

## **Supplementary Figures**

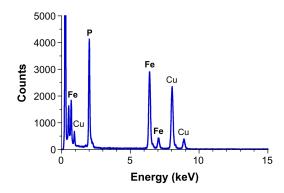
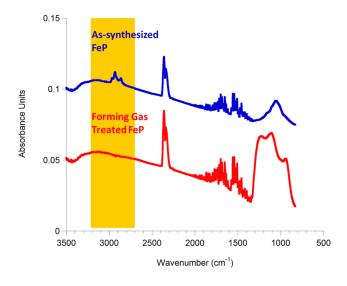


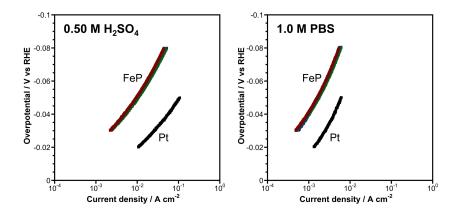
Figure S1. EDS spectrum of the as-synthesized FeP nanoparticles.



**Figure S2.** DRIFT spectra of FeP nanoparticles as-synthesized (top) and after heating under  $H_2(5\%)/Ar(95\%)$  to 450 °C (bottom). The region corresponding to the C-H stretching frequencies (present because of the surface ligands in the as-synthesized sample and absent after annealing) is highlighted.

<sup>&</sup>lt;sup>†</sup> Department of Chemistry and Materials Research Institute, The Pennsylvania State University, University Park, PA 16802 (USA). <sup>‡</sup> Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125 (USA).

<sup>§</sup> These authors contributed equally



**Figure S3.** Tafel plots of overpotential vs. log(current density) of several FeP/Ti electrodes and of a Pt electrode. The slopes were obtained by applying a linear fit between -30 mV to -80 mV for the FeP samples and -20 mV to -50 mV for the Pt electrode.

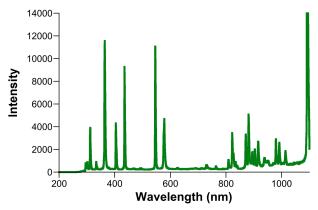
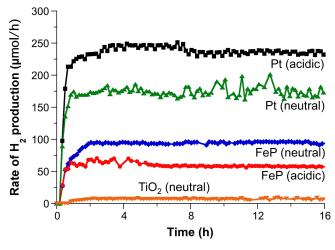
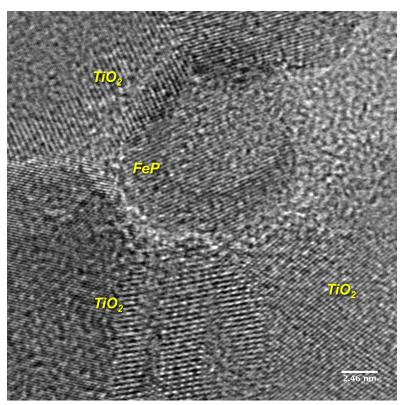


Figure S4. Spectrum of the 200 W Hg(Xe) arc lamp used for the photocatalysis experiments.



**Figure S5.** Plot showing the rate of photocatalytic  $H_2$  production vs. time for  $Pt/TiO_2$  and  $FeP/TiO_2$  samples, each in acidic and neutral-pH solutions, as well as a  $TiO_2$  control. The FeP data are also included in Figure 4b of the main text. The apparent quantum yields for  $Pt/TiO_2$  in acidic and neutral-pH solutions were 0.222 and 0.163, respectively.



**Figure S6.** HRTEM image of the FeP/TiO $_2$  sample after 16 h of photocatalytic testing in acidic solution, showing that the size, morphology, and crystallinity of the FeP nanoparticle persisted, as did its interface with the TiO $_2$  support.

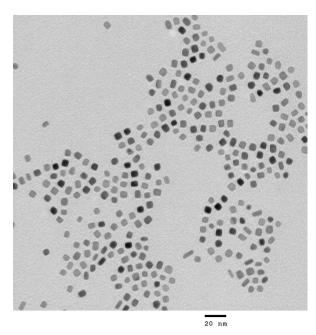


Figure S7. TEM image of Pt nanoparticles used as a control in the photocatalysis experiments.