Supporting Information

**Distinguishing Surface Effects of Gold Nanoparticles from Plasmonic Effect on Photoelectrochemical Water Splitting by Hematite**

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Figure S1. Immobilization of Au@SiO2 nanoparticles on the hematite nanorod array. The Au nanoparticles were first coated with a SiO2 layer, and then modified with the COOH-terminated silane, which allowed anchoring of the Au@SiO2 on the hematite nanorod array. Finally the Au@SiO2/hematite samples were heat treated at 350 oC.



Figure S2. XPS spectra for Fe (left) and Au (right) in the Au-hematite sample. The data show that Fe exists as Fe3+ in the oxide, while Au exists as a metal, indicating that Au has been completely reduced through the co-precipitation method.



Figure S3. Light absorption enhancement from plasmonic nanoparticles on the hematite nanorod array versus free-standing in an aqueous solution. (a) Bare Au nanoparticles and enhancement for Au/hematite, (b) Au@SiO2 and light absorption enhancement for Au@SiO2/hematite.



**Figure S4**. Schematic diagram of the effects of gold nanoparticles on hematite surface. (*a*) Plasmonic effect. (*b*) Fermi level equilibration effect, and (*c*) surface passivation effect.