Chemistry SELECT

Supporting Information

A Non-Pt Electronically Coupled Semiconductor Heterojunction for Enhanced Oxygen Reduction Electrocatalytic Property

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Experimental Section

Chemicals and Materials:

Silver acetate (CH₃COOAg, 99.5%), Sodium phosphate (Na₂HPO₄, 99.99%), Potassium hydroxide (KOH, 99.99%) and Hydroxylamine hydrochloride (NH₂OH·HCl, 99%) were obtained from Aladdin. Silver nitrate (AgNO₃, 99.8%) and Ammonia solution (NH₃·H₂O) were got from Shanghai Ling Feng Chemical Reagent Co., Ltd. Phosphoric acid (H₃PO₄, 85.0%) and Cuprous chloride (CuCl₂·2H₂O, 99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol (CH₃CH₂OH, 99.7%) was received from Changshou City Yangyuan Chemical Co., Ltd. Carbon (C, Vulcan®XC-72R) taken from Cabot was used as support materials. Oxygen (O₂, 99.999%) and Argon (Ar, 99.999%) were obtained from Shanghai Weichuang Standard Gas Analytical Technology Co., Ltd. All chemicals were used as received without further purification.

Synthesis of Ag₃PO₄ Crystals:

Tetrahedron-, rhombic dodecahedron- and cube-Ag₃PO₄ crystals were synthesized according to our previously reported recipes.[1]

Synthesis of Cu₂O Cube:

Cu₂O cube was synthesized by a simple method.[2] Firstly, 89.2 mL of deionized water was added to the beaker in a water bath preheated to 33 °C. Then 5 mL of 0.1 M CuCl₂ solution and 0.87 g sodium dodecyl sulfate (SDS) powder were added to the beaker under stirring. 1.8 mL of 1.0 M NaOH solution was dropped in the solution after CuCl₂ and SDS powder were sufficiently dispersing. The mixed solution turned light blue

immediately, indicating the formation of $Cu(OH)_2$ sediment. Finally, 24 mL of 0.1 M $NH_2OH \cdot HCl$ was injected into the beaker quickly. The obtained solution was kept in the water bath for 1 hour for nanocrystal growth. After completing the chemical reaction, the solution was centrifuged at 5000 rpm for 3 minutes, then the precipitate was washed with water and ethanol with 1:1 volume ratio for 3 times to remove unreacted chemicals. The final precipitate was dispersed in 6 mL ethanol for storage and analysis.

Preparation of Catalysts:

The faceted Ag_3PO_4 and Cu_2O crystals were mixed at the mass ratio of 1:1, 1:0.5, 1:0.25, 1:0.125 and 1:0.1, respectively. To improve the conductivity and dispersion of the catalyst, Vulcan XC-72 carbon was chosen as the carbon support. The carbon was dissolved in methanol, after sonicating 1 hour, pure Ag_3PO_4 or hybrid Ag_3PO_4/Cu_2O composite material was added. And the mass ratio of catalyst and carbon is 1:4. The mixture was stirred over 24 hours. Afterward, the solid products were obtained by centrifugation. Finally, the samples were freeze-dried for ORR test.

Morphology Characterization Method:

The morphology of the crystals was observed by field-emission scanning electron microscope (SEM; FEI Sirion 200, 5 kV) and transmission electron microscope (TEM; JEOL-2100F). The crystalline phase was researched by X-ray diffraction (XRD; Rigaku, Ultima IV) analysis using Cu K_α radiation. The XRD patterns were recorded from 10° to 80° with a scanning rate of 10 °/min. The XPS measurements were

performed on an X-ray photoelectron spectroscopy (Axis Ultra DLD, Kratos Analytical, UK) using monochromated Al K_α (1486.6 eV) source at 15 kV.

Evaluation of ORR Performance:

The electrochemical ORR performance was studied using an electrochemical workstation (CHI760E) with the three-electrode system in 0.1 M KOH solution at room temperature. The glassy-carbon rotating disk electrode (RDE) was used as the working electrode. The platinum wire was applied to the counter electrode. And the reference electrode was a reversible hydrogen electrode (RHE). The scan rate for ORR measurement was 10 mV/s.

The Density Functional Theory (DFT) Calculation Method:

The theoretical calculations were conducted at the standard of DFT using the Vienna ab-initio simulation package (VASP)[3]. The core and valence electrons were represented by the projector augmented wave (PAW)[4] method and plane-wave basis functions with a kinetic energy cut-off of 520 eV. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used in the calculations.[5] The Monkhorst-Pack grid of $4 \times 2 \times 1$ was chosen as the Brillouin zone for Ag_3PO_4 (110) surface slab supercell, separated by 15.0 Å thick vacuum layer. The energy convergence criterion is 0.0001 eV/atom for electronic minimization steps. To elucidate the dependence of the d-band center of Ag in Ag_3PO_4 on the extra positive charge, extra valence electrons of -1 e^-, 0 e^-, 1 e^- are applied to the Ag_3PO_4 (110) surface slab supercell. The atomic extra charge distribution

on each atom is counted by bader charge analysis[6]. The d-band center (ε_d) of atoms on surface charged different extra e^- density was calculated using the following formula:

$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} n_d(\varepsilon)\varepsilon d\varepsilon}{\int_{-\infty}^{+\infty} n_d(\varepsilon)d\varepsilon}$$

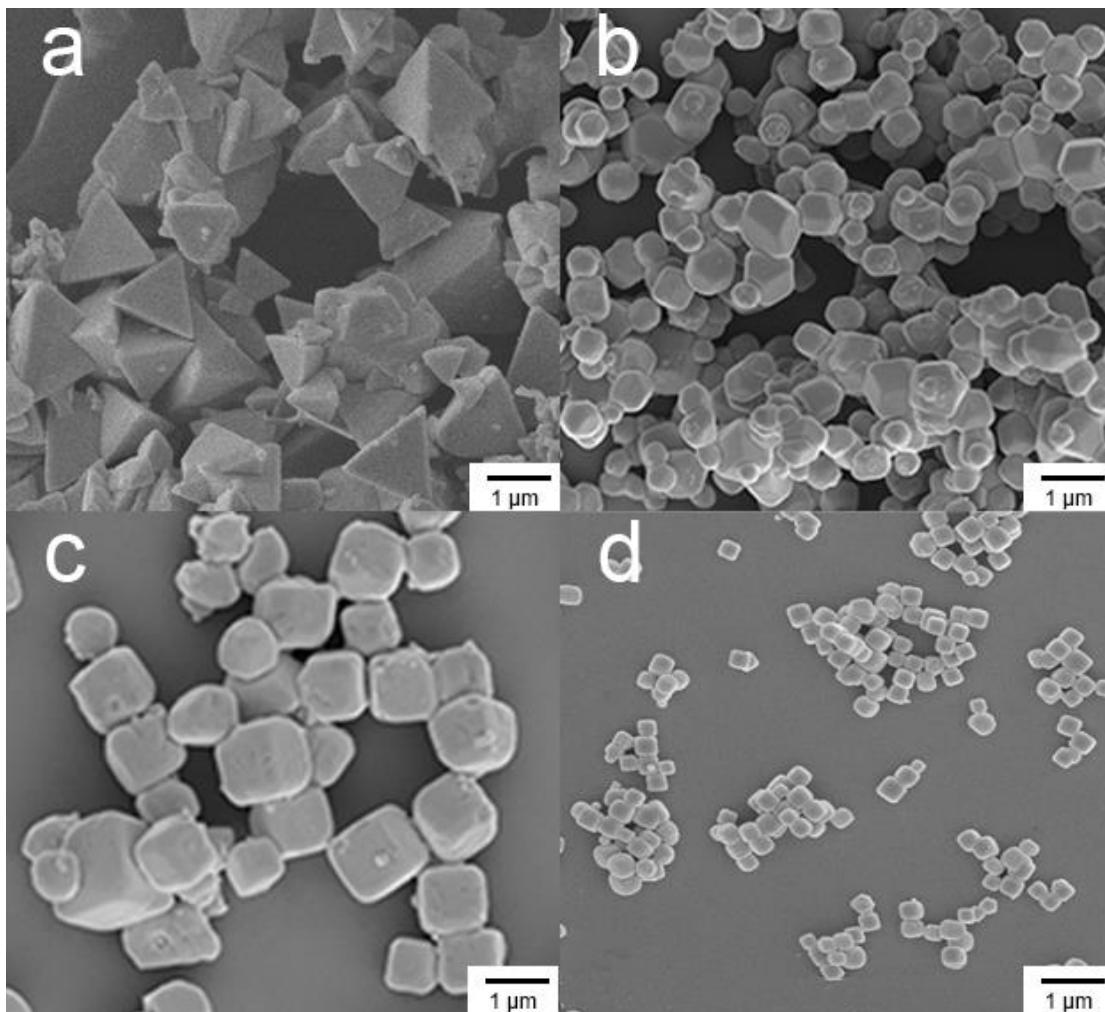where ε_d is the d-band center, $n_d(\varepsilon)$ is the density of states about d-band and ε represents the energy.

Figure S1 SEM micrographs of crystals (a) Ag_3PO_4 tetrahedron, (b) Ag_3PO_4 rhombic dodecahedron, (c) Ag_3PO_4 cube, (d) Cu_2O cube.
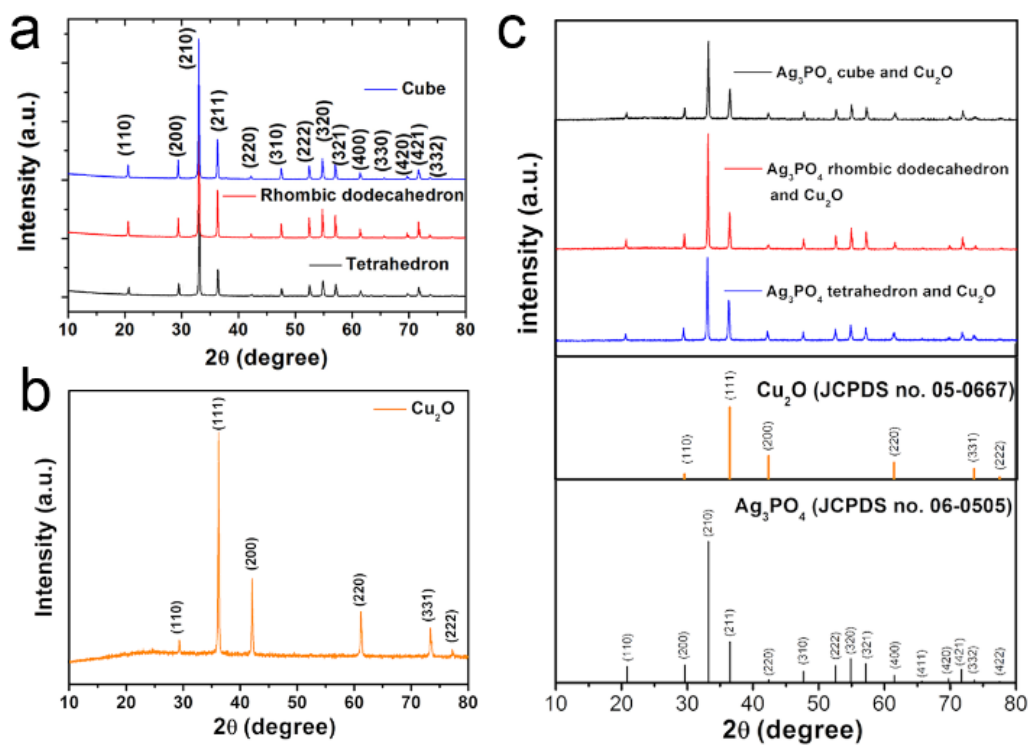
Figure S2 XRD pattern of (a) faceted-Ag_3PO_4, (b) cube-Cu_2O, (c) hybrid faceted-Ag_3PO_4 and cube-Cu_2O crystals. The standard diffractions (JCPDS no. 05-0607 and JCPDS no. 06-0505) were drawn using orange and black lines, separately.
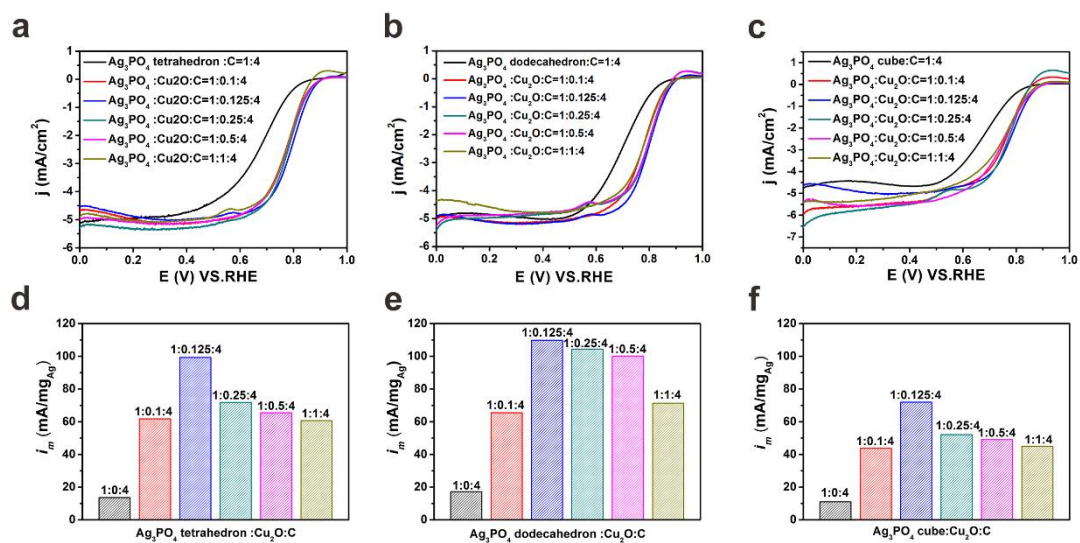
Figure S3 Comparison of electrocatalytic properties of various Ag_3PO_4 and Cu_2O supported on carbon: ORR polarization curves of (a) tetrahedron-, (b) rhombic dodecahedron-, (c) cube-Ag_3PO_4 and cube-Cu_2O composites supported on carbon in different proportions; mass-specific activity of (d) tetrahedron-, (e) rhombic dodecahedron-, (f) cube-Ag_3PO_4 and cube-Cu_2O hybrid catalysts supported on carbon in different proportions.
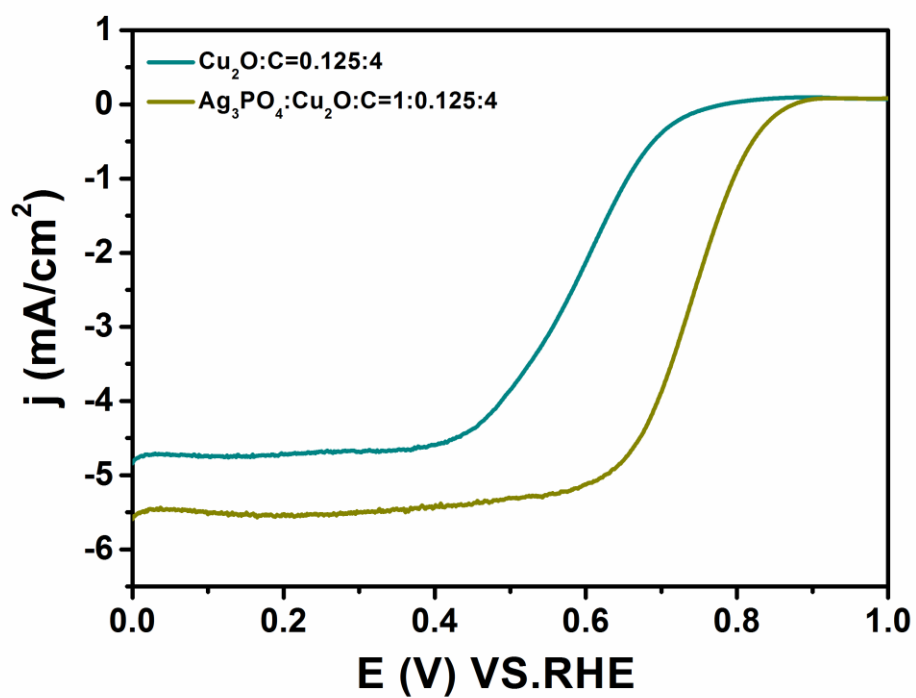
Figure S4 ORR polarization curves of cube-Cu_2O/C sample versus rhombic dodecahedron-Ag_3PO_4/cube-Cu_2O/C catalyst.
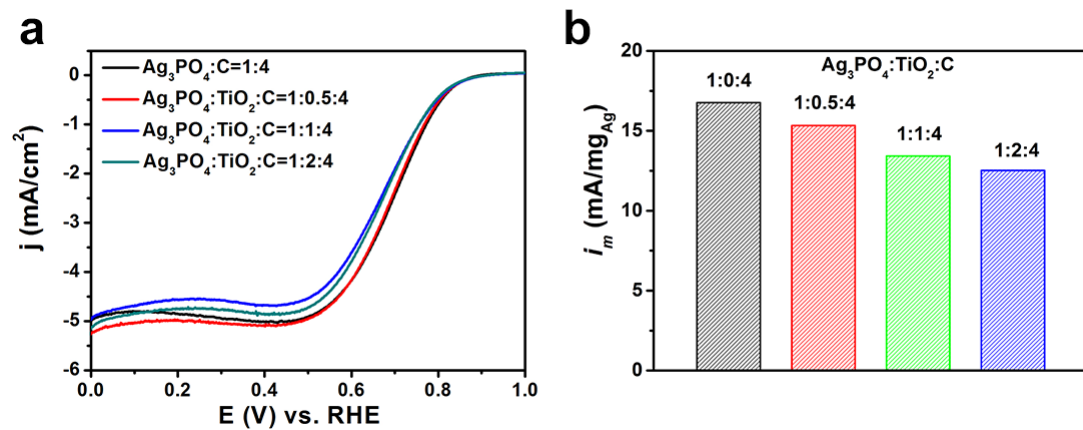
Figure S5 (a) ORR polarization curves and (b) mass-specific activity of Ag$_3$PO$_4$/TiO$_2$/C in different mass ratio. (The rhombic dodecahedral Ag$_3$PO$_4$ and commercial TiO$_2$ nanocrystals were selected to obtain the hybrid materials.)
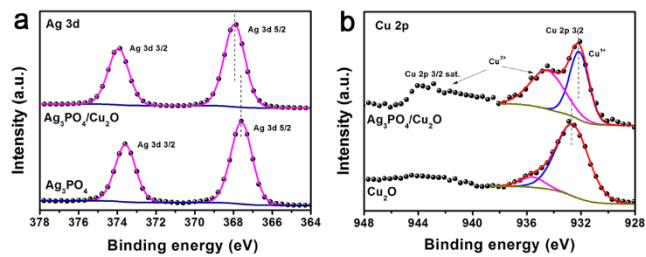
Figure S6 (a) XPS spectra in the Ag 3d regions for rhombic dodecahedron-Ag₃PO₄ and rhombic dodecahedron-Ag₃PO₄/cube-Cu₂O; (b) XPS spectra in the Cu 2p regions for cube-Cu₂O and rhombic dodecahedron-Ag₃PO₄/cube-Cu₂O.
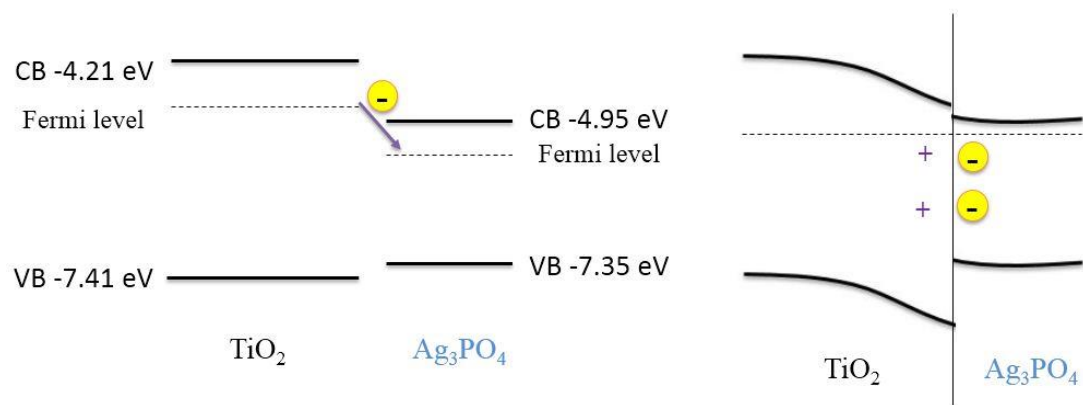
Figure S7 A schematic diagram of the energy band structure and expected electron transfer behavior at the interface of TiO_2 and Ag_3PO_4.

Table S1. Mass-specific ORR activity of catalysts for tetrahedron-Ag_3PO_4 system*

Sample	Mass activity[mA/mg_{Ag3PO4}]	Mass activity[mA/mg_{Ag}]
Ag_3PO_4:C=1:4	38.51	49.82
Ag_3PO_4:Cu_2O:C=1:0.1:4	47.69	61.69
Ag_3PO_4:Cu_2O: C=1:0.125:4	**76.76**	**99.30**
Ag_3PO_4:Cu_2O:C=1:0.25:4	55.51	71.81
Ag_3PO_4:Cu_2O:C=1:0.5:4	50.64	65.51
Ag_3PO_4:Cu_2O:C=1:1:4	46.88	60.65

*The calculation method of mass-specific ORR activity is the same as the method used in our previous work.[1]

Table S2. Mass-specific ORR activity of catalysts for the rhombic dodecahedron-Ag_3PO_4 system*

Sample	Mass activity[mA/mg$_{Ag3PO4}$]	Mass activity[mA/mg$_{Ag}$]
Ag_3PO_4:C=1:4	13.29	17.20
Ag_3PO_4:Cu_2O:C=1:0.1:4	50.64	65.51
Ag_3PO_4:Cu_2O: C=1:0.125:4	**84.88**	**109.80**
Ag_3PO_4:Cu_2O:C=1:0.25:4	80.64	104.32
Ag_3PO_4:Cu_2O:C=1:0.5:4	77.42	100.15
Ag_3PO_4:Cu_2O:C=1:1:4	55.12	71.31

*The calculation method of mass-specific ORR activity is the same as the method used in our previous work.[1]

Table S3. Mass-specific ORR activity of catalysts for cube-Ag$_3$PO$_4$ system*

Sample	Mass activity[mA/mg$_{Ag3PO4}$]	Mass activity[mA/mg$_{Ag}$]
Ag$_3$PO$_4$:C=1:4	8.52	11.02
Ag$_3$PO$_4$:Cu$_2$O:C=1:0.1:4	33.74	43.64
Ag$_3$PO$_4$:Cu$_2$O: C=1:0.125:4	**55.61**	**71.95**
Ag$_3$PO$_4$:Cu$_2$O:C=1:0.25:4	40.27	52.10
Ag$_3$PO$_4$:Cu$_2$O:C=1:0.5:4	37.94	49.08
Ag$_3$PO$_4$:Cu$_2$O:C=1:1:4	34.76	44.96

*The calculation method of mass-specific ORR activity is the same as the method used in our previous work.[1]

Reference

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