Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Highly Efficient Hydrolysis of Ammonia Borane by Anion ($^-$OH, F$^-$, Cl$^-$)-Tuned Interactions between Reactant Molecules and CoP Nanoparticles

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Experimental Methods

Materials: AB (97%, Aldrich), $CoNO_3 \cdot 6H_2O$ (99%, Guangdong Guanghua Sci-Tech Co., Ltd.), NaH_2PO_2 (99%, Aladdin), sodium citrate (99.0%, Beijing Chemical Corp.), NaF (98%), NaCl (99.5%), and NaOH (96%, Beijing Chemical Work), were analytical grade and used as purchased without further purification.

Synthesis of CoP NPs: CoP NPs were synthesized from a Co precursor using the NaH_2PO_2-reduction method. In a typical synthesis, a mixture of $CoNO_3 \cdot 6H_2O$ (2.3 g), $CO(NH_2)_2$ (2.4 g), NH_4F (0.7 g), and sodium citrate (0.6 g) in deionized water (160 mL) was stirred vigorously for 1 h, giving a colloidal dispersion. The gel was transferred to a dried Teflon-lined autoclave of capacity 100 mL. The autoclave was sealed and heated to 393 K at a ramping rate of 2 degrees min^{-1} and held at that temperature for 6 h. After naturally cooling to room temperature, the solid was separated by centrifugation, washed with water, and dried. A light-violet Co precursor was obtained. The Co precursor (0.3 g) was mechanically ground to a powder using an agate mortar and pestle. The Co precursor powder was uniformly dispersed on Ni foam (2 cm × 4 cm), which was placed over a porcelain boat loaded with NaH_2PO_2. The amount of the reducing agent (ca. 1.5 g) was over five times that of the Co precursor. The porcelain boat loaded with the reagents was placed in a tube furnace and heated directly to 573 K at a ramping rate of 2 degrees min^{-1}; the temperature was maintained for 120 min, in an Ar flow. After cooling naturally in a continuous Ar flow, the black powder was collected and washed with dilute hydrochloric acid solution, deionized water, and n-hexane, respectively. The product was dried in a vacuum oven at 353 K overnight; CoP NPs of average size 15 nm were obtained and stored under Ar.

Instrumentation: Powder XRD patterns were recorded using a Bruker AXS D8 X-ray diffractometer with Cu K_α (λ = 1.54056 Å) radiation. EDX spectroscopy measurement, the morphology and lattice fringes of sample were conducted using TEM (JEM 2100F) at an accelerating voltage of 200 kV. Elemental analysis data for CoP were obtained using ICP-AES (Vista-MPX, USA). XP spectra were obtained using a ThermoScientific ESCALAB 250XI instrument; an Al K_α X-ray source and a power of 250 W were used. Calibration was performed using the C 1s binding energy.

H_2 evolution: Hydrolytic dehydrogenation experiments in the presence or absence of NaOH were performed in a 10-mL two-necked round-bottomed flask; one neck was connected to a gas burette and the other was sealed with a rubber cap. The reaction temperature was maintained at the desired value using a constant-temperature bath. A certain amount of catalyst was placed in the two-necked round-bottomed flask, and AB aqueous solution (5 mL) was quickly injected using a syringe. The H_2 generated by the system was identified using a gas chromatograph (GC-14C, Shimadzu) equipped with a 5 Å molecular sieve column (3 m × 2 mm) and thermal conductivity detector; the carrier gas was N_2. The amount of gas was measured quantitatively, using a gas burette, to an accuracy of ±0.5 mL.

The reusability of the CoP catalyst was performed in room temperature. At starting stage, many parallel experiments were carried out at the same time, after that, catalysts in the experiments were collected and combined together, washed with deionized water, and n-hexane, respectively. The restored catalyst was dried in a vacuum oven at 353 K for next use, the cycle repeats seven times according to the experimental process.

Computational methods: First-principles calculations were performed using the ultrasoft pseudopotentials[1] and generalized gradient approximation in the Perdew−Burke−Eruzerhof scheme,[2] with exchange-correlative potentials, based on density functional theory.[3] The CASTEP package[4] was used to determine the electronic structures, including the total and partial densities of states. Kinetic energy cutoffs of 800 eV and Monkhorst−Pack k-point meshes[5] with spans less than 0.07/Å^3 in the Brillouin zone were used. The bond lengths and angles were fully optimized using the BFGS method.[6] The convergence thresholds between optimization cycles for energy change, maximum force, maximum stress, and maximum displacement were set at 5.0×10^{-6} eV per atom, 0.01 eV per Å, 0.02 GPa, and 5.0×10^{-4} Å, respectively. The optimization was terminated when all these criteria were satisfied. The CoP (010) surface was selected as the active catalytic surface.

References

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Table S1. The atomic Mulliken population of Co atom

	s	p	d	f	total
Co atom in single CoP surface	0.46	0.45	8.36	0.00	9.27
Co atom in hydroxyl-adsorbed CoP surface	0.42	0.55	8.32	0.00	9.30

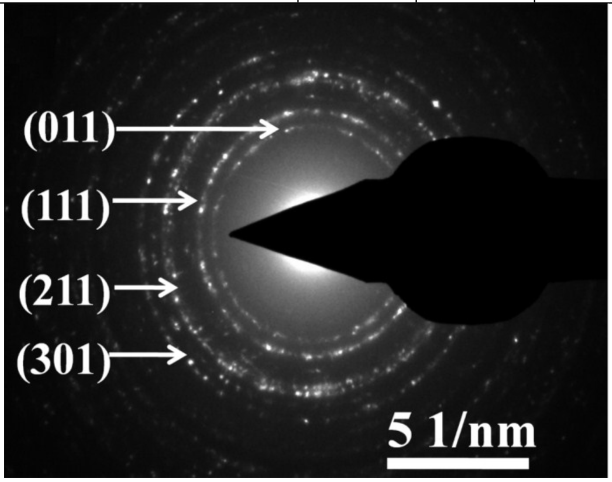

Fig. S1 Selected area electron diffraction pattern of CoP NPs.

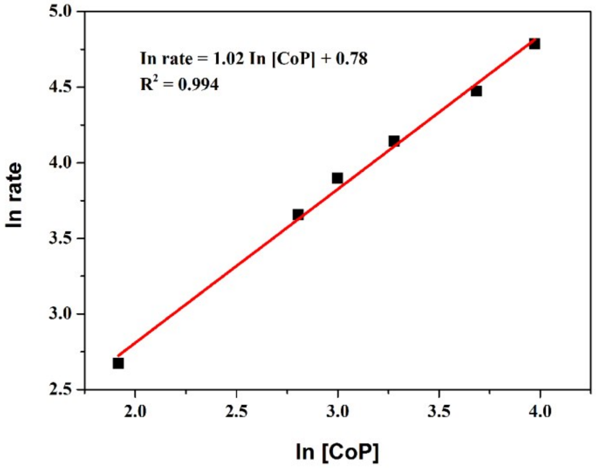

Fig. S2 Logarithmic plots of H_2 generation rate versus CoP concentration in pure H_2O at 298 K.

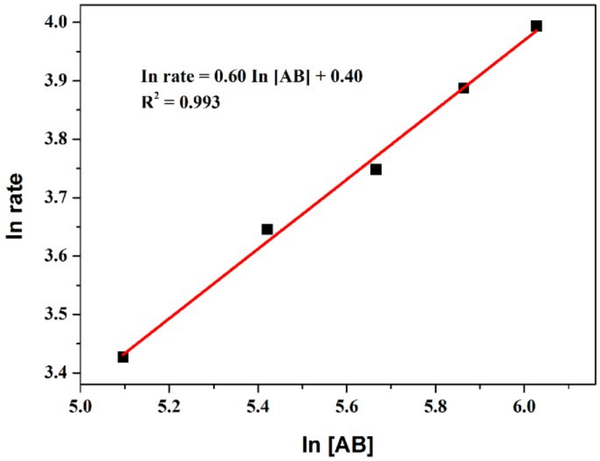

Fig. S3 Logarithmic plots of H_2 generation rate versus AB concentration in pure H_2O at 298 K.

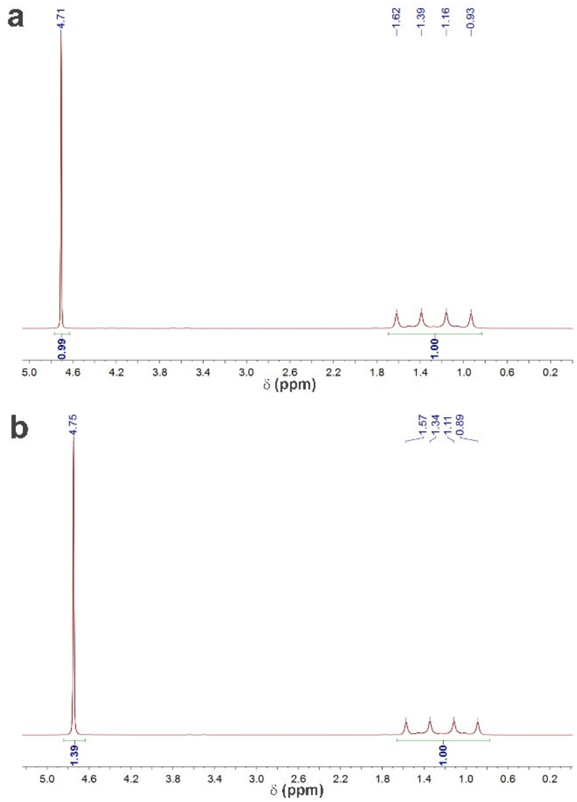

Fig. S4 ^{1}H NMR spectra of AB solution in D_2O at 298 K, (a) after storing sample for 1 week and (b) after addition of NaOH and storing for 1 week.

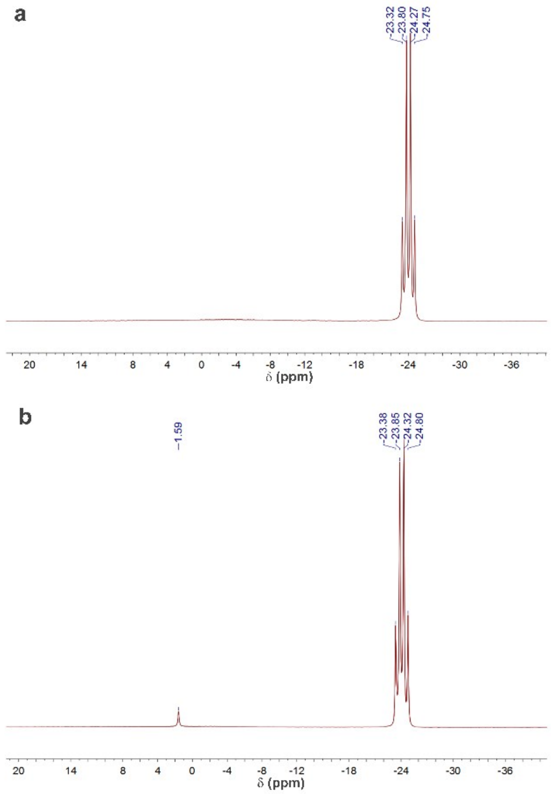

Fig. S5 ^{11}B NMR spectra of AB solution in D_2O at 298 K (a) after storing sample for 1 week and (b) after addition of NaOH and storing for 1 week.

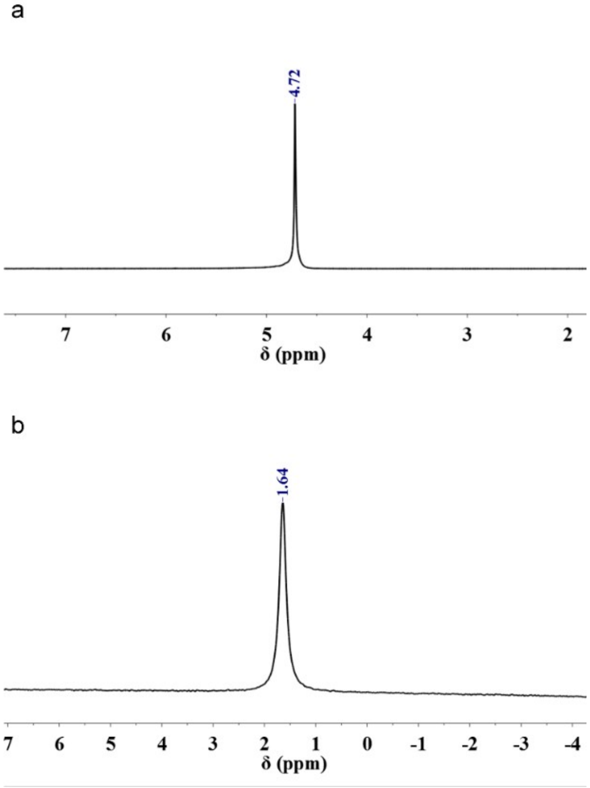

Fig. S6 ^{1}H NMR (a) and ^{11}B NMR (b) spectra recorded after reaction of AB solution in D_2O containing CoP and 0.3 M NaOH at 298 K.

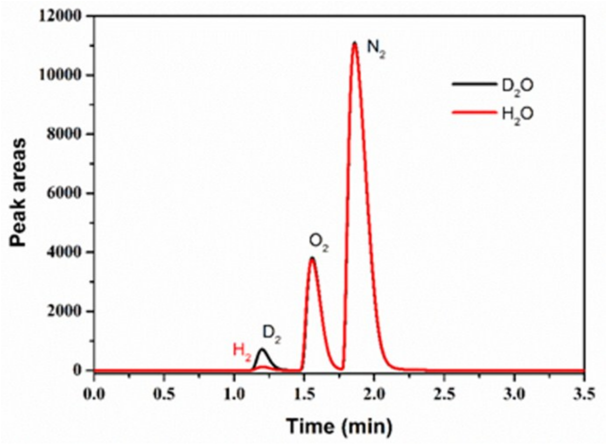

Fig. S7 Recorded peak areas of isovolumetric gases corresponding to labeled and unlabeled H_2 produced in reaction systems containing CoP (2 mg), AB (10 mg), NaOH (10 mg), and D_2O or H_2O (2 mL) at 298 K. Results are based on gas chromatographic response to D_2 over H_2, with He as carrier gas.

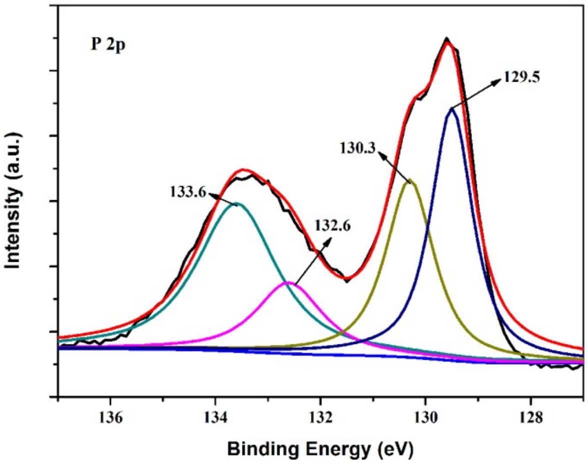

Fig. S8 High-resolution XPS survey spectra of P 2p core level for CoP NPs before adding NaOH.

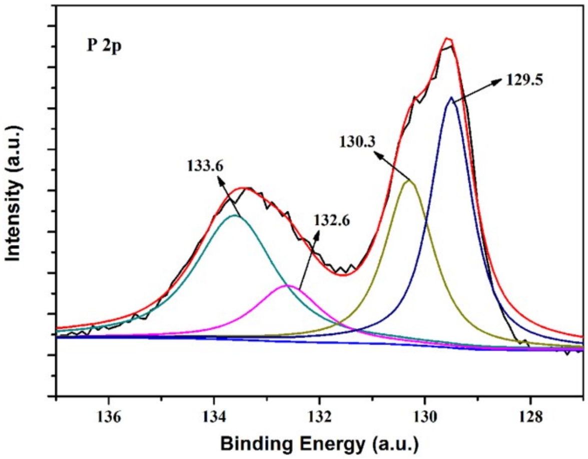

Fig. S9 High-resolution XPS survey spectra of P 2p core level for CoP NPs after adding NaOH.

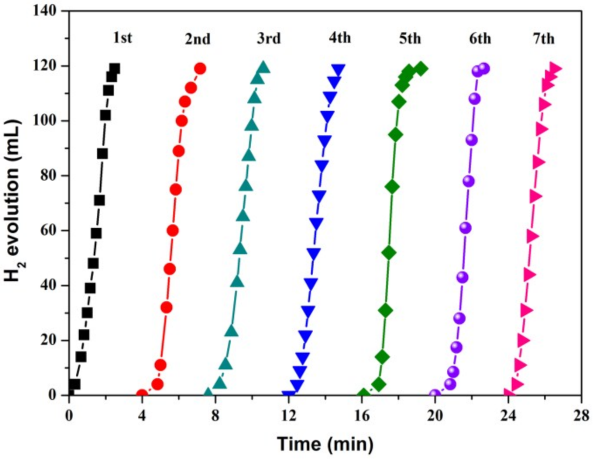

Fig. S10 Reusable CoP (0.089 mmol) catalyst with AB (1.62 mmol) aqueous solution (5 mL) in absence of NaOH at 298 K.

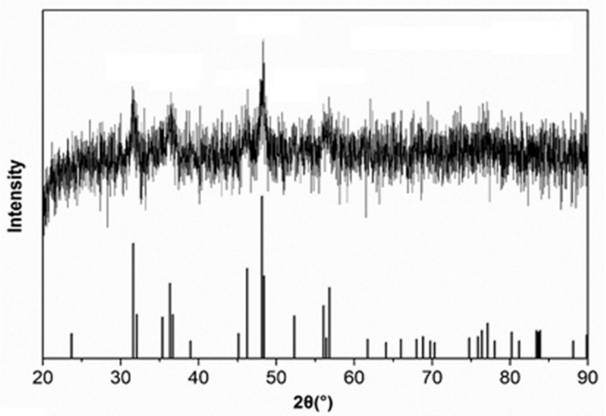

Fig. S11 XRD pattern of CoP catalyst after recycling seven times for system containing aqueous solution of AB at 298 K.

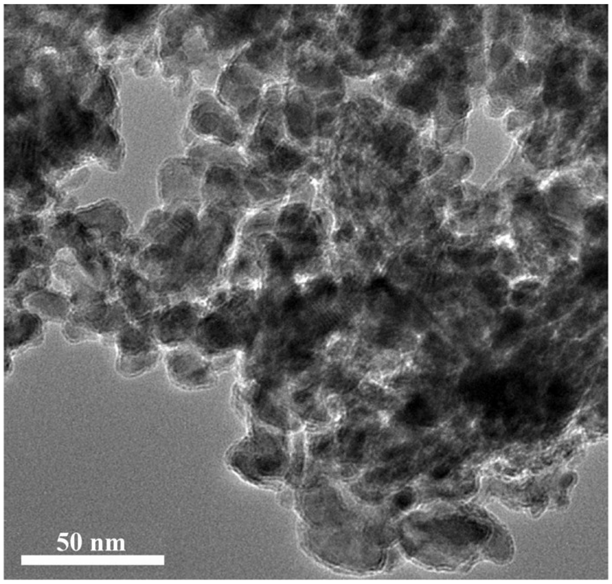

Fig. S12 TEM image of CoP catalyst after recycling seven times for system containing aqueous solution of AB at 298 K.