

## Electronic Supplementary Information (ESI)

### Experimental Section:

**Materials and instrumentation.** Iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), sodium acetate (NaAc), ethylene glycol (EG), chloroauric acid ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ), trisodium citrate (cit), 3-(trimethoxysilyl)-1-propanamine (APTMS), formaldehyde (HCHO), cupric chloride ( $\text{CuCl}_2$ ), nickel chloride ( $\text{NiCl}_2$ ), sodium hydroxide (NaOH), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), ethanol and hexane were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Tetrakis hydroxymethyl phosphonium chloride (THPC), 3-bromopyridine, phenylboric acid, palladium(II) chloride ( $\text{PdCl}_2$ ), palladium(II) acetate ( $\text{Pd}(\text{OAc})_2$ ), palladium 5% on carbon (Pd/C) (wetted with ca. 55% water), 3-bromo-5-chloropyridine and 3-bromo-5-methylpyridine were obtained from Sigma–Aldrich Co. All chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared using Milli-Q water.

Scanning electron microscopy (SEM) images were captured under a Hitachi S-4700 with an accelerating voltage of 5 kV. Raman spectra were recorded using a confocal micro-Raman system (XploRA PLUS, Jobin Yvon, France). The microscope attachment, which was based on an Olympus BX40 system, used a  $50\times$  long-working-length objective ( $\sim 8$  mm). All experiments were carried out at an excitation line of 638 nm from an internal He-Ne laser with a power of 3.5 mW.

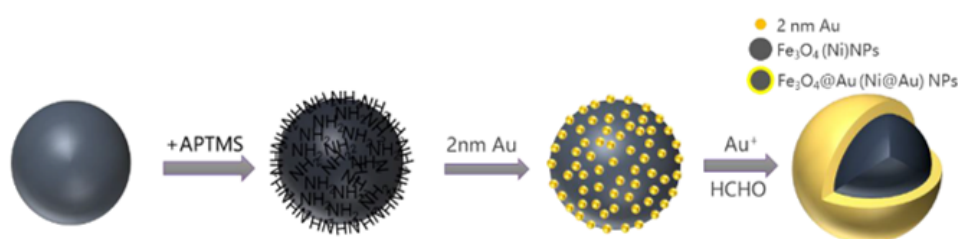
### Synthesis of $\text{Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4@$ Au nanoparticles

In a typical synthesis<sup>[1]</sup>, 0.65 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 20 mL of EG, and then 0.2 g of cit and 1.2 g of NaAc were added. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated at 200 °C for 10 h. The black products were washed several times with ethanol and then redispersed in water.

$\text{Fe}_3\text{O}_4@$ Au nanoparticles were prepared through the seed-growth method using chloroauric acid solution.<sup>[2]</sup> First,  $\text{Fe}_3\text{O}_4$  nanoparticles were functionalized with APTMS and then linked with 2 nm Au nanoparticles.<sup>[3]</sup> Preparation of 2 nm Au nanoparticles<sup>[1]</sup>: 1.5 mL 0.2 mol/L NaOH was mixed with 45.5 mL water, and 1 mL 1.2 wt.% THPC aqueous solution was added. After vigorous stirring for 5 min, 2 mL 1 wt.%  $\text{HAuCl}_4$  solution was added dropwise, and the solution showed a colorless-

yellow-brownish black transition. After continuous stirring for 2 h, the solution was placed at 4 °C for future use. The suspension of as-prepared Fe<sub>3</sub>O<sub>4</sub>-Au nanoparticles was poured into a three-necked flask and then the Au seed solution was added under vigorous stirring at room temperature using Teflon tubes and a peristaltic pump with HCHO. Finally, Fe<sub>3</sub>O<sub>4</sub>@Au nanoparticles were magnetically separated, washed and redispersed in water for further use.

Fig. S1(a-c) are the SEM images of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-2 nm Au and Fe<sub>3</sub>O<sub>4</sub>@Au nanoparticles. Fig. S1d is the SERS spectra of Fe<sub>3</sub>O<sub>4</sub>@Au nanoparticles characterized with the probe of TP. It indicated that the particle diameter is 410 nm, the Au shell thickness is 20 nm, and it has magnetism and SERS activity.



Scheme S1. Schematic diagram of synthesis of Fe<sub>3</sub>O<sub>4</sub>@Au.

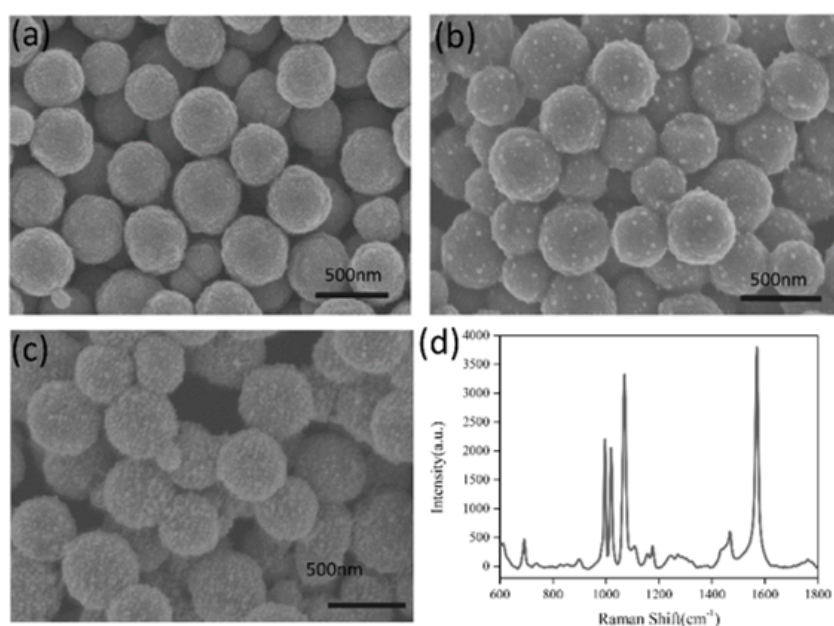


Fig. S1 SEM images of (a) Fe<sub>3</sub>O<sub>4</sub> nanoparticles, (b) Fe<sub>3</sub>O<sub>4</sub>-2 nm Au nanoparticles, and (c) Fe<sub>3</sub>O<sub>4</sub>@Au nanoparticles. (d) Corresponding SERS spectra of the as-prepared Fe<sub>3</sub>O<sub>4</sub>@Au nanoparticles characterized with the probe of TP.

### Self-assembly of a film of Fe<sub>3</sub>O<sub>4</sub>@Au nanoparticles

Liquid metal-like films of Fe<sub>3</sub>O<sub>4</sub>@Au nanoparticles could be obtained at the hexane/water interface by self-assembly.<sup>[4]</sup> Typically, 1 ml of as-prepared Fe<sub>3</sub>O<sub>4</sub>@Au

nanoparticles was first transferred to a plastic tube, and then hexane was injected to form a layer of  $\sim 0.3$  cm thickness. With the aid of ethanol,  $\text{Fe}_3\text{O}_4@Au$  nanoparticles slowly floated toward the hexane/water interface. Finally, a visible  $\text{Fe}_3\text{O}_4@Au$  monolayer film formed at the interface. It should be noted that an external magnetic field parallel to the film was applied when time-dependent SERS measurements were performed and the film was removed.

### SERS spectra of standard substances of reactants, products and byproducts in the reaction.

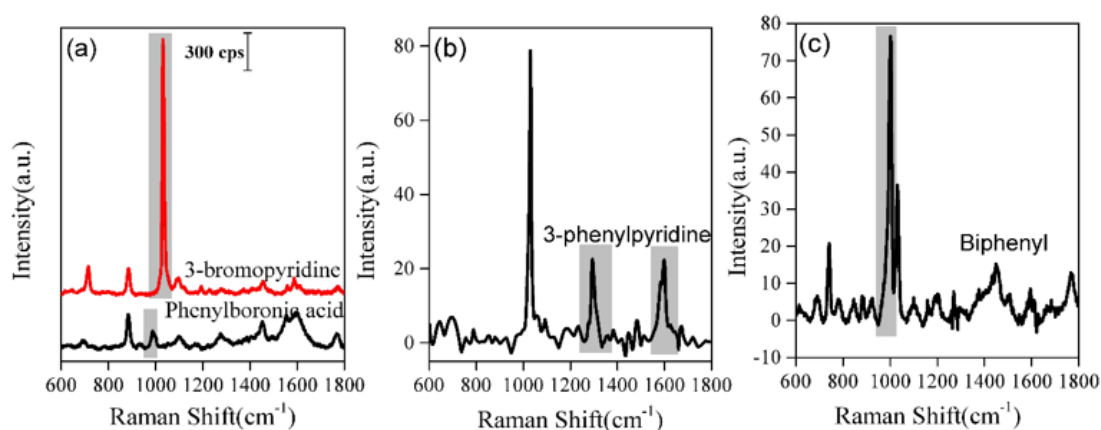


Fig. S2 SERS standard spectra of (a) 3-bromopyridine and phenylboronic acid, (b) 3-phenylpyridine, and (c) biphenyl.

### Influence of different conditions (reaction time, solvent and substrate) on the reaction, the SERS spectrum of the reaction solution and the ratio of product to byproduct.

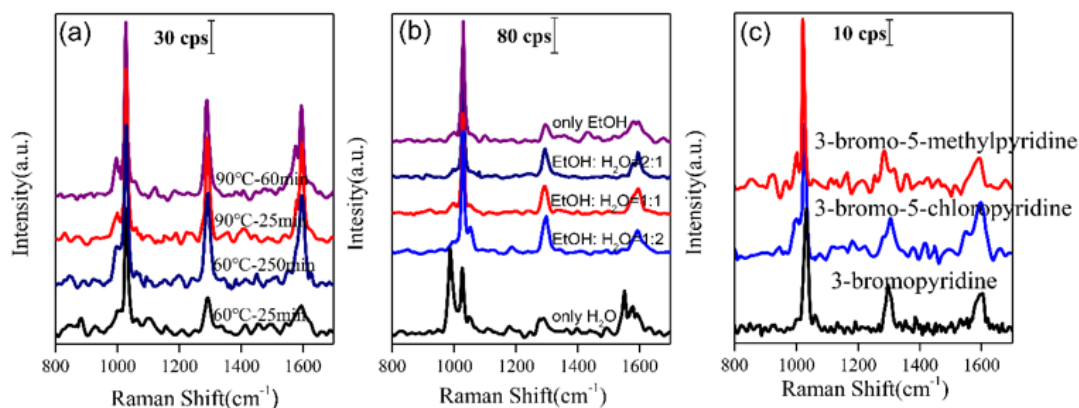


Fig. S3 SERS spectra of the Suzuki reaction with different reaction time(a), solvent(b) and substrate(c).

Tab. S1 Ratio of SERS strength of product to byproduct with different reaction time, solvent and substrate.

The intensity ratio of bands at 1000 cm <sup>-1</sup> and 1595 cm <sup>-1</sup>					
Reaction time	60°C-25min	60°C-250min	90°C-25min	90°C-60min	
Ratio	0.834	0.4232	0.2799	0.4246	
Solvent	EtOH	EtOH: H <sub>2</sub> O=2:1	EtOH: H <sub>2</sub> O=1:1	EtOH: H <sub>2</sub> O=1:2	H <sub>2</sub> O
Ratio	0.4488	0.3366	0.4054	0.5049	/
Reactant	3-bromopyridine	3-bromo-5-chloropyridine	3-bromo-5-methylpyridine		
Ratio	0.3081	1.1653	0.6845		

## HPLC verification of online SERS results

The SERS determination was verified by the HPLC measurements.

Acetonitrile/water (55:45) was used as the mobile phase at the flow rate of 1 mL/min. The HPLC chromatograms under each condition are shown in Fig. S4. The peaks at 3.7, 4.6, 5.9 and 15.1 min correspond to phenylboronic acid, 3-bromopyridine, 3-phenylpyridine and biphenyl, respectively<sup>[3]</sup>. The proportion of byproducts to products is defined by the ratio of the peak intensities at 5.9 and 15.1 min (Tab. S2).

For the system without catalyst or with NiCl<sub>2</sub>, the peaks of products and byproducts were not detected at 5.9 and 15.1 min. By adding the CuCl<sub>2</sub>, or Pd/C as catalysts, obvious peaks of reactants phenylboronic acid and 3-bromopyridine were observed at 3.7 and 4.6 min, and the peaks at 5.9 and 15.1 min were very weak and is neglectable. This indicated that the occurrence of reaction was difficult under the above conditions. However, when PdCl<sub>2</sub> and Pd(OAc)<sub>2</sub> were used as catalysts, both products and byproducts have obvious chromatographic peaks. For the Pd(OAc)<sub>2</sub> as catalyst, the proportion of the byproducts was higher than that of PdCl<sub>2</sub>. The results indicated that the introduction of Pd<sup>2+</sup> ion compounds allowed to trigger the occurrence of the reaction and the catalytic activity of PdCl<sub>2</sub> was better, which was in accordance with the results of SERS.

When different salts or alkali were introduced to adjust pH of the reaction, only weak peaks of the product and byproduct were detected without adding any alkali or salt, but the peaks of both were not detected when NaCl was added, however, there existed weak bands of products and byproducts in the SERS spectra, indicating that the content was quite low and unable to identify by HPLC due to sensitivity limitations. Obvious peaks of products and byproducts were observed when the solution was alkaline. When pH was adjusted by NaHCO<sub>3</sub>, the proportion of byproducts was significantly lower than that of Na<sub>2</sub>CO<sub>3</sub> and NaOH. It indicated that a large number of product could be produced under alkaline condition, but the excessive alkali was not conducive to the reaction.

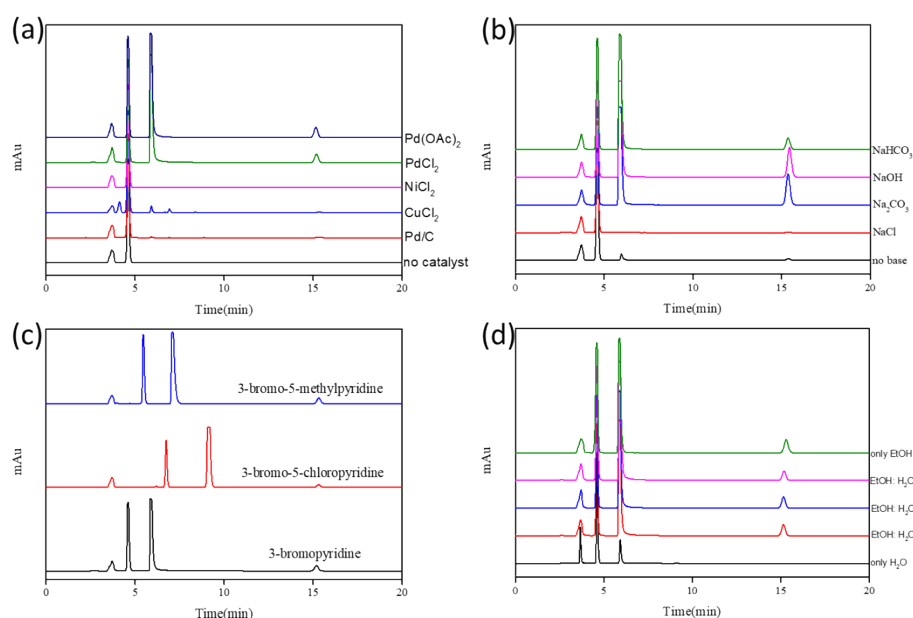


Fig. S4 Chromatogram of the Suzuki reaction with different catalyst (a), bases and salts (b), substrate (c) and solvent (d).

Tab. S2 Ratio of HPLC and SERS of byproduct to product calculated by HPLC and SERS with different catalysts, bases and solvent.

Catalysis	No cata.	CuCl <sub>2</sub>	NiCl <sub>2</sub>	PdCl <sub>2</sub>	Pd(OAc) <sub>2</sub>	Pd/C
Ratio(HPLC)	/	/	/	0.0802	0.1180	/
Ratio(SERS)	/	/	/	0.2909	0.5705	/
Base	No base	NaCl	NaHCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	NaOH	
Ratio(HPLC)	0.2739	/	0.1023	0.3181	0.3076	
Ratio(SERS)	1.298	1.405	0.3996	0.5848	0.5623	

Solvent EtOH/H <sub>2</sub> O	1:0	2:1	1:1	1:2	0:1	
Ratio(HPLC)	0.1167	0.0802	0.0960	0.1018	/	
Ratio(SERS)	0.4488	0.3366	0.4054	0.5049	/	

There were reactants and extremely weak product peaks in the reaction by using pure water as solvent and the peak of 15.1 min was not detected in HPLC. The peaks of reactants, products and byproducts were all observed when pure ethanol and ethanol/water mixture were used as solvent. The table shows that the proportion of byproducts is the lowest when the ethanol/water volume ratio is 2:1, which was in accordance with the results of SERS.

The peaks of 3-bromopyridine and 3-phenylpyridine at 4.6 and 5.9 min were shifted under different substrates, while the peaks of biphenyl at 15.1 min were not shifted. This indicated that the introduction of substituents resulted in the difference of 3-phenylpyridine and the shift of the spectral peak of 3-bromopyridine and 3-phenylpyridine. Biphenyl was generated by self-coupling of phenylboronic acid, which was not related to the introduction of substituents in 3-bromopyridine. However, only the SERS bands of the product was shifted, and the introduction of the substituent did not affect the characteristic band of 3-bromopyridine at 1031 cm<sup>-1</sup>.

Therefore, the above experimental facts indicated that the SERS provided the quantitative information by the association SERS intensities with the concentration of bulk solution.

### Kinetic studies at different pH values

The Suzuki reaction is a quasi-first-order kinetic reaction, and taking the effect of pH on reaction kinetics as an example to investigate the influence of reaction conditions on reaction kinetics. The reaction process at different pH were monitored (0.33 mmol of alkali or salt was added and other conditions remained unchanged) and the following formula was used for calculation to draw the relationship between  $\ln x$  and time  $t^{[6]}$ . As shown in Fig. S5, the reaction rate constants  $K$  were 0.03572 (no base), 0.03736 (NaCl), 0.08304 (NaHCO<sub>3</sub>), 0.05159 (Na<sub>2</sub>CO<sub>3</sub>), and 0.06226 (NaOH), respectively. With the increase of pH,  $K$  firstly increased and then decreased, which indicated that the reaction rate and conversion first increased and then decreased with the increase of pH. The reaction rate was the fastest and the conversion was the

highest when the pH was adjusted to 9.5 with NaHCO<sub>3</sub>. The base attacked phenylboronic acid to form the corresponding organoborate, which increased its reactivity toward the Pd(II) complex. However, high alkalinity made phenylboronic acid homogeneously coupled in water. The results indicated that the kinetics could be analyzed by using SERS to monitor the reaction process.

$$x = \frac{I_{lim} - I_t}{I_{lim}}, \quad \ln x = -kt$$

$I_{lim}$  is the SERS intensity at 1595 cm<sup>-1</sup> after the reaction.  $I_t$  is the SERS intensity at 1595 cm<sup>-1</sup> when the reaction time is  $t$  in the reaction process.  $t$  is the reaction time.

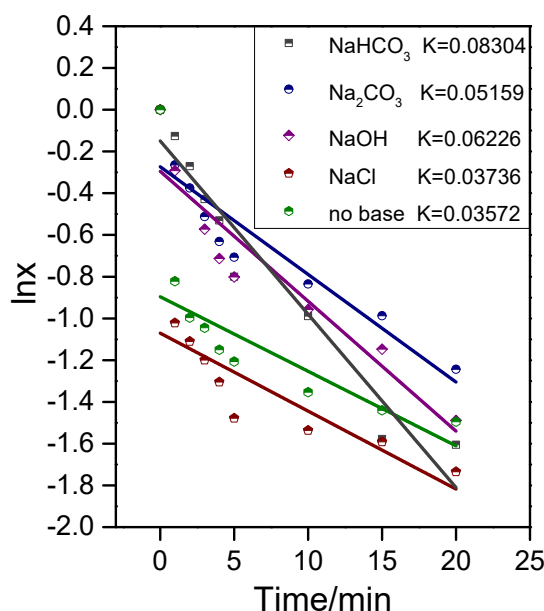


Fig. S5 Diagram of  $\ln x$  during reaction with different alkali or salt.

It can be inferred from the screened spectra of reaction conditions that with the increase of temperature, the product content gradually increased, indicating that the conversion and reaction rate should increase with the increase of temperature. With the increase of pH, the product increased first and then decreased, indicating that the conversion and reaction rate should increase firstly and then decrease with the increase of pH, and the optimum condition was pH=9.5. The conversion and reaction rate of PdCl<sub>2</sub> catalyst were higher than those of Pd(OAc)<sub>2</sub>. Among the different solvents, the conversion and reaction rate were the highest when ethanol/water volume ratio was 2: 1. This result is completely consistent with that reported in the literature<sup>[7]</sup>.

---

## References

- [1]H. Deng, X. Li, Q. Peng, X. Wang, J. Chen, Y. Li, *Angew. Chem. Int. Ed.*, **2005**, 44, 2782–2785.
- [2]K. R. Brown, M. J. Natan, *Langmuir*, **1998**, 14, 726–728.
- [3]S. L. Westcott, S. J. Oldenburg, T. R. Lee, N. J. Halas, *Langmuir*, **1998**, 14, 5396–5401.
- [4]D. Yogeve, S. Efrima, *J. Phys. Chem.*, **1988**, 92, 5754–5760.
- [5]C. L. Jiao, W. Wang, J. Liu, Y. X. Yuan, M. M. Xu, J. L. Yao, *Acta Chim. Sin.*, **2018**, 76, 526–530.
- [6]C. Amatore, A. Jutand, G. Le. Duc, *Chem. Eur. J.*, **2011**, 17, 2492–2503.
- [7]C. Boztepe, A. Künkül, N. Gürbüz, İ. Özdemir, *Int. J. Chem. Kinet.*, **2019**, 51, 931–942.