

Supporting Information

**Facile Synthesis of Highly Stable Gold Nanoparticles and Their
Unexpected Excellent Catalytic Activity for Suzuki-Miyaura
Cross-Coupling Reaction in Water**

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1. Chemicals

2-Aminothiophenol monomer (ABCR GmbH & Co. KG) was distilled under reduced pressure. All other reagents were purchased from Aldrich and used without further purification. The water used in this study was deionized by milli-Q Plus system (Millipore, France), having $18.2\text{ M}\Omega$ electrical resistivity.

2. Preparation of determination of polymer supported Au catalysts

In a typical synthesis, 2-aminothiophenol (100.0 mg, 0.4 mmol) was dispersed in HCl aqueous solution (1.0 M, 20 ml) with magnetic stirring at room temperature for 1 h to obtain a uniform solution. After that, the mixture was maintained at $20\text{ }^{\circ}\text{C}$ for 0.5 h before oxidative polymerization. Then a quantitative amount of HAuCl_4 aqueous solution (0.1 M) was added to the above mixture in one portion. The resulting solution was stirred for another 0.5 min to ensure complete mixing and then the reaction was allowed to proceed with agitation for 24 h at $20\text{ }^{\circ}\text{C}$. Finally, the products were washed with deionized water till the filtrate became colorless and then dried in a vacuum at $60\text{ }^{\circ}\text{C}$ for 24 h.

The resulting molar of Au nanoparticles was determined by atomic absorption spectroscopy (AAS) analysis. After formation of PATP stabilized gold nanoparticles as precipitation at bottom of reaction vessel, the upper transparent solution was analyzed by AAS to confirm the remaining of unreacted raw material of AuCl_4^{-1} . As detected, the remaining AuCl_4^{-1} is neglectable as compared with the initial charge (0.0018 %). This confirms that the redox reaction between 2-aminothiophenol and HAuCl_4 is almost completed. And the molar of Au nanoparticles in product can be seen as equal as the initial charge.

3. Characterization of polymer supported Au catalysts

The morphologies of products were examined by a transmission electron microscopy (TEM, Tecnai-12 Philip Apparatus Co., United States).

Fourier-transform infrared (FTIR) spectrum of polymer supported Au catalysts was recorded in the range of $400 \sim 4000 \text{ cm}^{-1}$ using FTIR spectroscopy (Nicolet-740, United States). The sample was prepared in a pellet form with spectroscopic-grade KBr.

X-ray diffraction (XRD) patterns of samples were recorded on a German Brucker AXS D8 ADVANCE X-ray diffractometer.

X-ray photoelectron spectroscopy (XPS) data were recorded on a Thermo ESCALAB 250 using a non-monochromatized Al K α X-ray (1486.6 eV) as the excitation source and choosing C1s as the reference line.

Thermal studies were performed using a WRT-2 thermogravimetric analyzer in N_2 atmosphere and approximately 10 mg of each sample were analyzed from $20 \text{ }^\circ\text{C}$ to $1100 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. Results disclose the weight ratio of gold nanoparticles at 62.6 %, which is higher than that of 44.4 % calculated from initial raw materials. As HAuCl_4 is almost transferred to gold nanoparticles as determined by AAS, the decreased weight ratio of polymer in product may be caused by two factors: (1) un-reacted monomers, and (2) low molecular weight polymer wasted during post-procedures.

The molecular weights of PATP dissolved in *N, N'*-dimethylformamide (DMF) were measured with gel permeation chromatography (GPC, Agilent1100, Agilent Co.).¹ Before analysis, the sample was filtered through a $0.45 \text{ }\mu\text{m}$ syringe filter, and DMF was used as the eluent with the flow rate of 1.0 mL min^{-1} at $25 \text{ }^\circ\text{C}$. Calibration was accomplished with monodisperse polystyrene standards. The number-average molecular weight is 3.94×10^4 with the polydispersity 4.4.

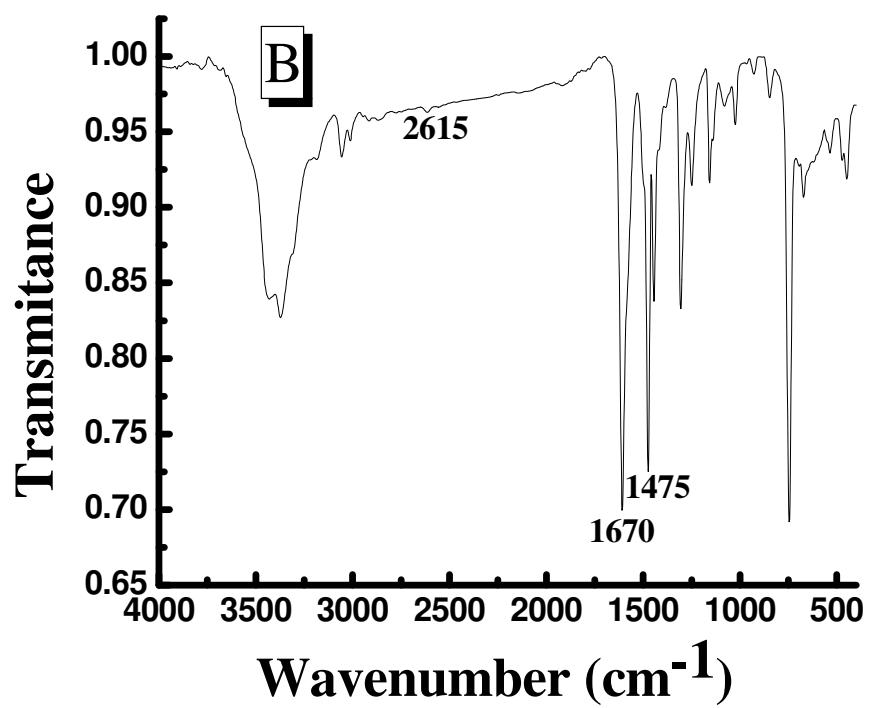
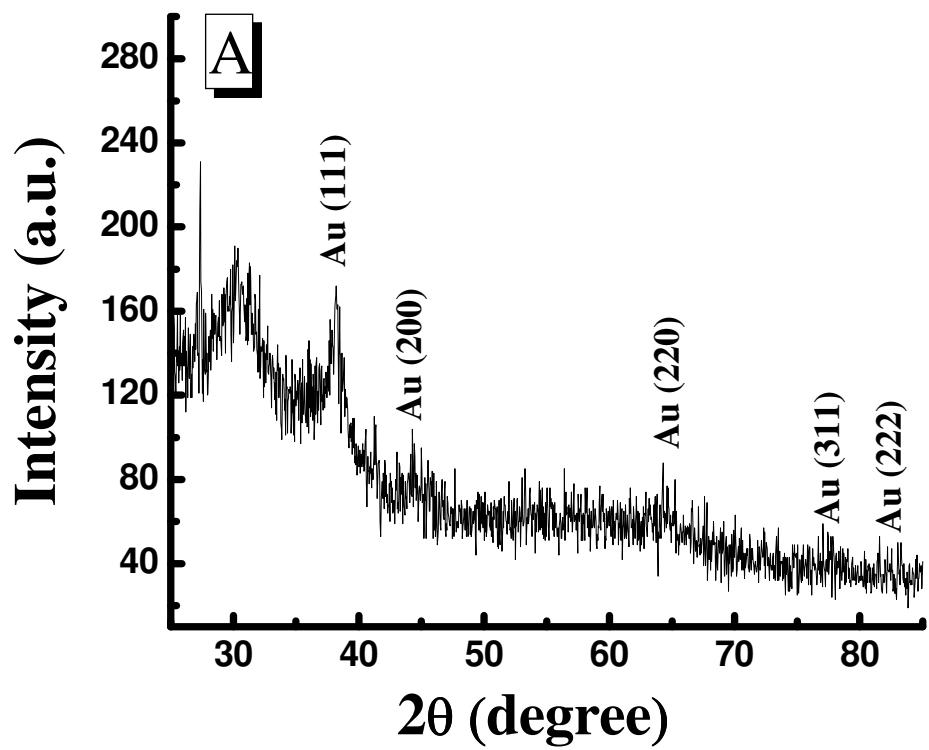
The gold contents in aqueous phase were determined by atomic absorption spectroscopy (AAS), using a Japan Hitachi Model Z-5000 atomic absorption spectrometer.

Gas chromatography (GC) analysis were performed on an Agilent DB-1 GC-FID system equipped with a 100 % dimethyl polysiloxane capillary column (length: 30 m, ID: $0.25 \text{ }\mu\text{m}$, film thickness: 0.25

µm). The GC yield was obtained from the calibration curve.

4. General protocol for Suzuki coupling

Aryl halide (225.0 mg, 2.0 mmol), phenylboronic acid (292.6 mg, 2.4 mmol), and NaOH (320.0 mg, 8.0 mmol) were added to 40 ml of deionized water. The solution was stirred at 80 °C until the chemicals are completely dissolved. Then an aqueous solution of Au catalysts (1.0 mM, 1.0 mL, 0.05 mol %) was added to the stirred solution in one portion, and the reaction mixture was stirred for another 4 h. After the mixture had cooled to room temperature, the organic product was extracted with diethyl ether (3 × 20 ml). The organic layer was dried with excessive Na₂SO₄. After filtration, volatile substances were removed under reduced pressure to yield the final product.



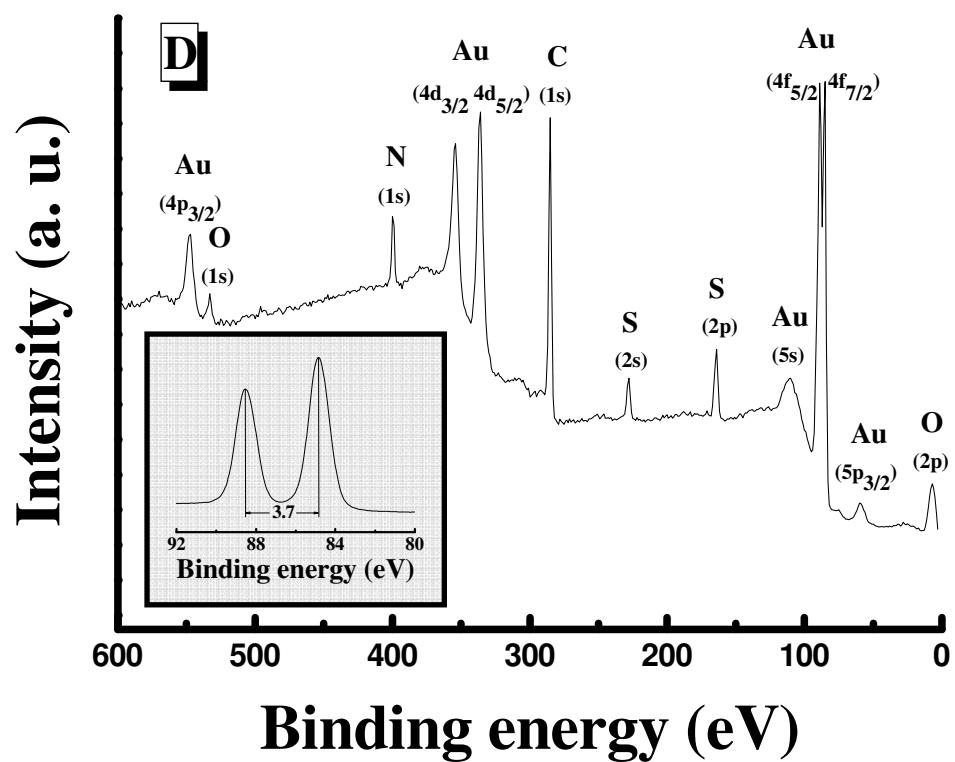
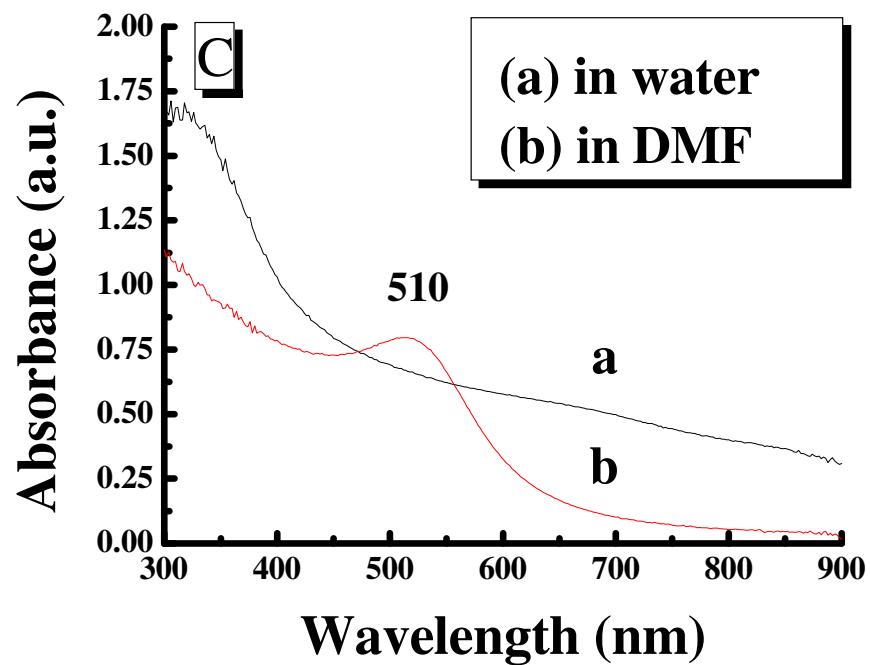


Figure S1. (A) XRD, (B) FTIR, (C) Uv-vis, and (D) XPS spectroscopies of PATP stabilized gold nanoparticles. In the XRD pattern, the five main peaks, which corresponding to (111), (200), (220), (311) and (222) Bragg reflection of Au, indicating the presence of gold nanoparticles in products.² The broad band centered at $2\theta = 15\text{--}30^\circ$ reveals the amorphous feature of polymer PATP. As for FTIR spectrum, the intense peaks in the range of $3200\text{--}3500\text{ cm}^{-1}$ are attributed to the N-H stretching vibrations; the weak absorption band at 2615 cm^{-1} comes from S-H stretching vibrations; the characteristic peaks at 1609 and 1475 cm^{-1} result from the C=C stretching deformation of quinoid and benzenoid rings, respectively. The results confirm the formation of polymer PATP. From XRD and FTIR, we can confirm the successful synthesis of polymer PATP and gold nanoparticles. Curve (a) of Uv-vis spectrum discloses no apparent absorption band for gold nanoparticles because of the low particle size (1.0 nm in average).³ After dissolving polymer with DMF accompanied by aggregation of gold nanoparticles as confirmed by TEM, one obvious surface plasmon band of gold nanoparticles centered at 510 nm is observed as indicated in curve (b).⁴ The measured XPS spectrum shows clearly the signatures of C, N and S for PATP polymer and Au for gold nanoparticles. The inset in figure D represents the XPS signature of the Au 4f doublet ($4f_{7/2}$ and $4f_{5/2}$), which confirms that Au nanoparticles only exist in their metallic state.⁵⁻⁸

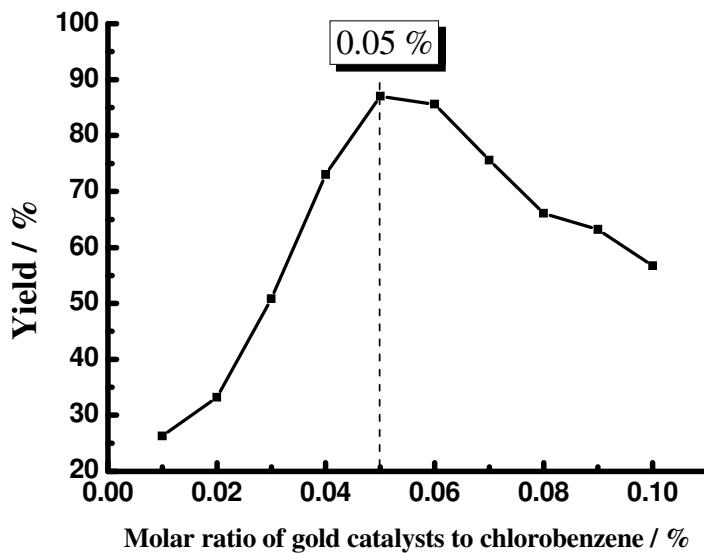


Figure S2. Effect of PATP stabilized gold nanoparticles catalysts concentration on the yield of biphenyl for Suzuki coupling of chlorobenzene and phenylboronic acid. The highest yield is obtained when the gold catalysts used is 0.05 %.

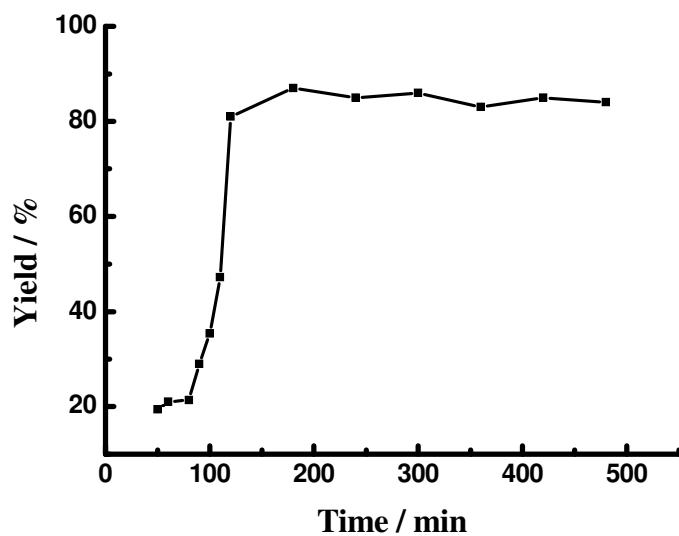


Figure S3. Time course of biphenyl yields for Suzuki coupling of chlorobenzene and phenylboronic acid catalyzed by PATP stabilized gold nanoparticles. After about 2 h, the yield shows the highest and changes little when elonging reaction times.

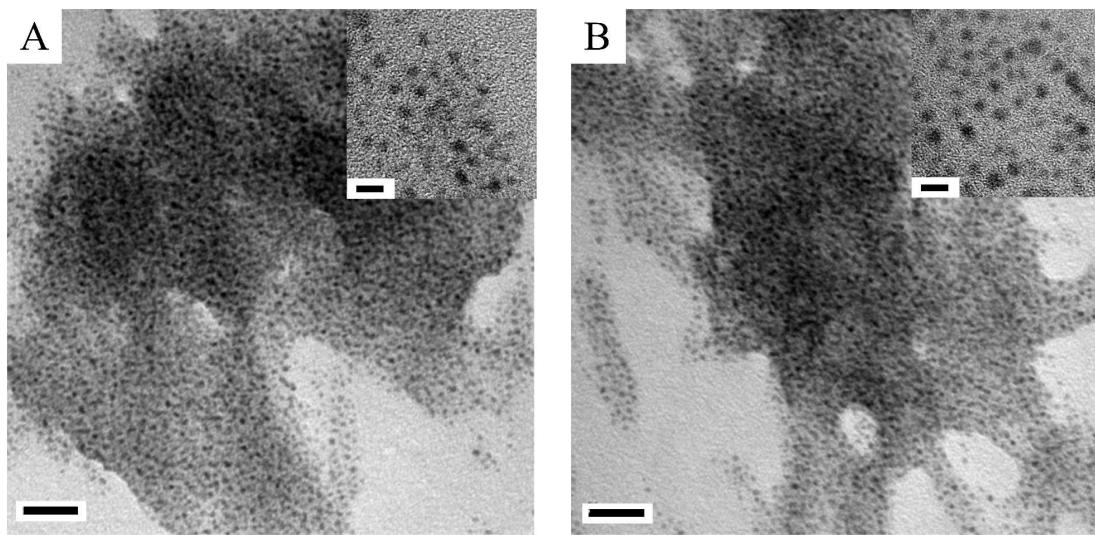


Figure S4. TEM images of PATP stabilized gold nanoparticles (A) before and (B) after 6 runs, scale bar: 20 nm. Insets show corresponding HR-TEM images, scale bar: 4 nm. Comparing with these two figures, we can conclude that the size of gold nanoparticles is almost the same after 6 cycles, from which high stability of gold nanoparticles can be evidenced.

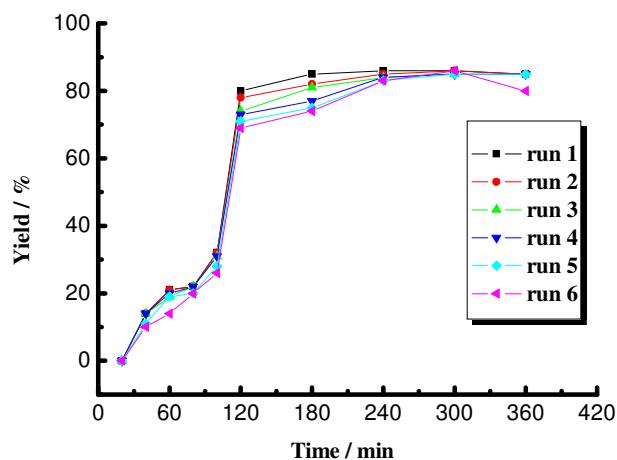


Figure S5. Dependence of product yield on reaction time for the cross-coupling of phenylboronic acid with chlorobenzene to give biphenyl catalyzed by PATP stabilized gold catalysts under different runs. Curves in 0-2 hrs are similar to each other, while steady slight decrease in yield during 2-4 hrs is observed. After 4 h, the yield is almost the same.

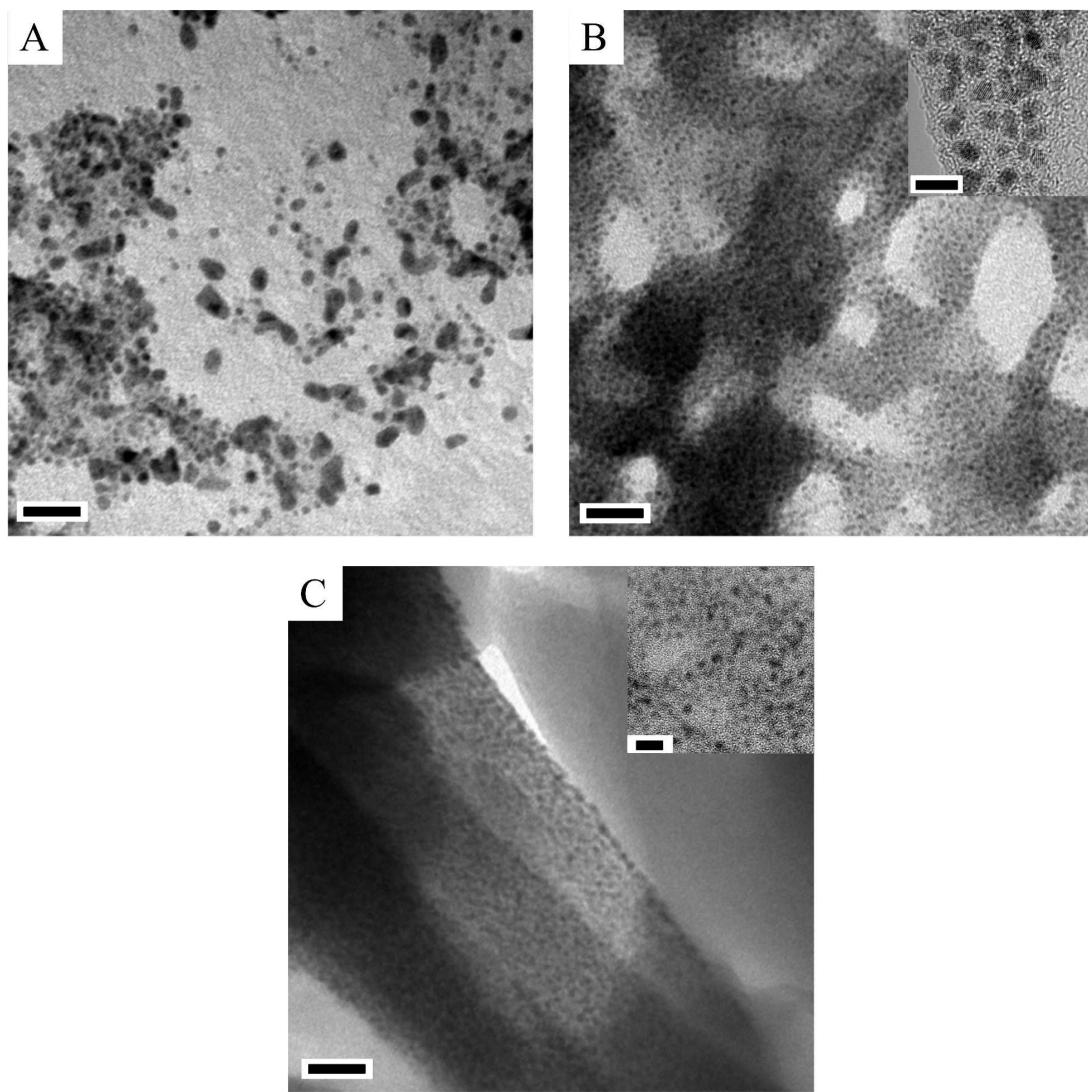
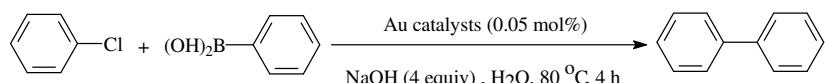


Figure S6. TEM images of PATP stabilized gold nanoparticles synthesized at different molar ratio of HAuCl_4 to 2-aminothiophenol: (A) 1:1, (B) 1:4, and (C) 1:20, scale bar: 20 nm. Insets show the corresponding high resolution (HR)-TEM images, scale bar: 5 nm. The sizes of gold nanoparticles are listed in Table S1.

Table S1. Suzuki coupling of phenyl chloride and phenylboronic acid catalyzed by different PATP stabilized gold nanoparticles^a

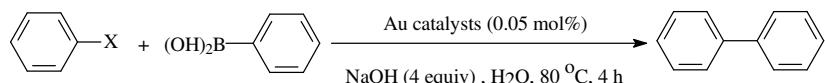


Synthetic conditions for PATP

stabilized gold nanoparticles: [HAuCl ₄]/[2-aminothiophenol]	Size of gold nanoparticles	Yield(%) ^b
1/1	5.0 nm	10
1/2	1.0 nm	87
1/4	2.0 nm	76
1/20	1.0 nm	trace

^a Chlorobenzene (2 mmol), phenylboronic acid (2.4 mmol), Au catalyst (0.05 mol %), NaOH (8 mmol). ^b Isolated yield.

Table S2. Suzuki-Miyaura coupling of aryl halides and phenylboronic acids^a



Entry	X	Yield (%) ^b
1	Cl	87(86) ^c
2	Br	90(89) ^c
3	I	99(99) ^c

^a phenyl halides (2 mmol), phenylboronic acid (2.4 mmol), Au catalyst (0.05 mol %), NaOH (8 mmol). ^b Isolated yield.

^c The values in parentheses refer to scale-up reaction (phenyl halides (5 mmol), phenylboronic acid (6 mmol), Au catalyst (0.05 mol %), NaOH (20 mmol)).

References

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