

Supplementary Materials for:

Unexpected Golden Ullmann Reaction Catalyzed by Au Nanoparticles Supported Periodic Mesoporous Organosilica (PMO)

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Table of Contents

	Page
1. Experimental Procedure	2S
1.1. Preparation of Au Catalysts	2S
1.2. Characterization of PMO and Au@PMO	6S
1.3. General experimental procedure for the Ullmann reaction catalyzed by Au catalysts	9S
1.4. The effect of catalyst loading of Au@PMO in Ullmann coupling of aryl iodides (optimization)	10S
1.5 A brief note to the role of phenylene-containing PMO in activity of Au@PMO	11S
1.6. Spectral data for Table 2	11S
1.7. Copy of ^1H and ^{13}C -NMR spectra of selected biphenyl derivatives	13S

Figures

Figure 1S. Nitrogen adsorption-desorption isotherm of the PMO and Au@PMO	7S
Figure 2S. BJH Pore size distribution of the PMO and Au@PMO	7S
Figure 3S. Thermal gravimetric analysis (TGA) of PMO	8S
Figure 4S. X-ray photoelectron spectra of Au@PMO	8S
Figure 5S. DR-UV spectrum of the Au@PMO catalyst	9S
Figure 6S. Nitrogen adsorption-desorption isotherm of the recovered Au@PMO	9S

Figure 7S. BJH of the recovered Au@PMO	10S
Figure 8S. TEM image of Au@TiO₂	11S
Figure 9S. TEM image of Au@SiO₂	11S
Figure 10S. TEM image of Au@AC	11S
Figure 11S. TEM image of Au@SBA-15	12S
Figure 12S. HRTEM image of a single Au nanoparticle inside the channels of PMO	12S
Figure 13S. TEM image of Au nanoparticles supported in phenylene-containing PMO	
Figure 14S. Reaction progress as a function of time on the Ullman coupling of iodobenzene by using Au@PMO catalyst in the reusability test.	13S
Figure 15S. Recyclability of the Au@PMO in the Ullmann coupling.	13S
Figure 16S. TEM image of Au@PMO after the 5th run.	14S

1. Experimental Procedure:

1.1 Preparation of Au catalyst:

Preparation of Au@PMO:

Preparation of Bifunctional Periodic Mesoporous Organosilica:

The synthesis of Bifunctional Periodic Mesoporous Organosilica has been achieved using known procedure (Eun-Bum Cho, Dukjoon Kim, and Mietek Jaroniec *J. Phys. Chem. C* **2008**, *112*, 4897). This procedure involved a synthetic strategy based on co-condensation of 1,2-bis(triethoxysilyl)ethane (BTEE, Aldrich) and 1,4-bis(triethoxysilyl)benzene (BTEB, Aldrich) in the presence of Pluronic P123 as a structure directing agent. In a typical preparation procedure, 3.3 g of Pluronic P123 (Aldrich, average Mw =5800) was dissolved in 120 g of distilled water and 0.65 g of HCl (37 wt %, Merck) with stirring at room temperature. To this end, 2.43 g of BTEE and 1.38 g of BTEB organosilica precursors were simultaneously added to the mixture, while the stirring was continued for 1.5 h at 40 °C. Then, the mixture was aged at 100 °C for 24 h under static conditions. The template was removed from the as-synthesized material by successive treatment with 300 g of ethanol for 2 h under a static condition and 300 g of acetone at 56 °C under stirring for 5 h. The solid materials were thoroughly washed with distilled water and acetone and dried at 100 °C for 1 day.

Preparation of Au@PMO:

The resulting PMO (0.5 g) was then dispersed in deionized water (7 mL) and gently sonicated to obtain a homogeneous dispersion of PMO particles in water. This uniform slurry was then mixed with (20 mg, 0.05 mmol) of sodium tetra chloroaurate(III) as the gold source in water (5 h) upon which all of the NaAuCl₄ were essentially adsorbed on to PMO materials to give a yellow slurry. To this end, the obtained slurry were then allowed to react with a freshly prepared aqueous solution of stoichiometric amount of NaBH₄ (0.1 M) at room temperature while continues vigorous stirring to obtain the corresponding Au nanoparticles supported PMO (Au@PMO). The color of matrix immediately turned

from yellow to wine red. After filtration, the final material was drying at 100 °C for 12h. The elemental analysis (EA) showed that the loading of Au was 0.08 mmol Au/g solid.

Preparation of Au@SBA-15:

Preparation of SBA-15:

The synthesis of SBA-15 has been achieved using known procedure described by Stucky and his co-workers (D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.*, **1998**, *120*, 6024.). In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw = 5800) was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 35 °C. Then 8.50 g of tetraethoxysilane (TEOS) was added into that solution with stirring at 35 °C for 20 h. The mixture was aged at 80 °C overnight without stirring. The solid was filtered off and washed thoroughly with hot ethanol/water using a Soxhlet apparatus for 18 h to remove the surfactant molecules. It was dried in air at 110 °C overnight.

Preparation of Au@SBA-15:

The resulting SBA-15 (0.5 g) was then dispersed in deionized water (7 mL) and gently sonicated to obtain a homogeneous dispersion of SBA-15 particles in water. This uniform slurry was then mixed with (20 mg, 0.05 mmol) of sodium tetrachloroaurate(III) as the gold source in water (5 h) to give a yellow slurry. To this end, the obtained slurry were then allowed to react with a freshly prepared aqueous solution of stoichiometric amount of NaBH₄ (0.1 M) at room temperature while continues vigorous stirring to obtain the corresponding Au nanoparticles supported SBA-15 (Au@SBA-15). In this case also the color of matrix immediately turned from yellow to red. After filtration, the final material was drying at 100 °C for 12h.

Preparation of Au@TiO₂:

The TiO₂ (Degussa P25) (0.5 g) was dispersed in deionized water (7 mL) and gently sonicated to obtain a homogeneous dispersion of TiO₂ particles in water. This uniform slurry was then mixed with (20

mg, 0.05 mmol) of sodium tetra chloroaurate(III) as the gold source in water (5 h) upon which all of the NaAuCl_4 were essentially adsorbed on to TiO_2 materials to give a yellow slurry. To this end, the obtained slurry were then allowed to react with a freshly prepared aqueous solution of stoichiometric amount of NaBH_4 (0.1 M) at room temperature while continues vigorous stirring to obtain the corresponding Au nanoparticles supported TiO_2 (Au@TiO_2). The color of matrix immediately turned from yellow to purple. After filtration, the final material was drying at 100 °C for 12h.

Preparation of Au@SiO_2 :

The SiO_2 (Merck, 60) (0.5 g) was dispersed in deionized water (7 mL) and gently sonicated to obtain a homogeneous dispersion of SiO_2 particles in water. This uniform slurry was then mixed with (20 mg, 0.05 mmol) of sodium tetra chloroaurate(III) as the gold source in water (5 h) upon which all of the NaAuCl_4 were essentially adsorbed on to SiO_2 materials to give a yellow slurry. To this end, the obtained slurry were then allowed to react with a freshly prepared aqueous solution of stoichiometric amount of NaBH_4 (0.1 M) at room temperature while continues vigorous stirring to obtain the corresponding Au nanoparticles supported SiO_2 (Au@SiO_2). The color of matrix immediately turned from yellow to dark purple. After filtration, the final material was dried at 100 °C for 12h.

Preparation of Au@AC:

The activated carbon (AC, Merck) (0.5 g) was dispersed in deionized water (7 mL) and gently sonicated to obtain a homogeneous dispersion of AC particles in water. This uniform slurry was then mixed with (20 mg, 0.05 mmol) of sodium tetra chloroaurate(III) as the gold source in water (5 h) upon which all of the NaAuCl_4 were essentially adsorbed on to AC materials. To this end, the obtained materials were then allowed to react with a freshly prepared aqueous solution of stoichiometric amount of NaBH_4 (0.1 M) at room temperature while continues vigorous stirring to obtain the corresponding Au nanoparticles supported AC (Au@AC). After filtration, the final material was dried at 100 °C for 12h.

Determination of loading of AuNPs in all supported catalysts

The loading of all studied Au catalysts were measured by Atomic Absorption Spectroscopy (AA) using standard addition method and as can be seen from the data in Table 1 the amount of loaded AuNPs was very close to each other (Table 1S).

Table 1S. Elemental analysis of Au catalysts

Catalyst	Au (mmol)/g solid
Au@TiO ₂	0.084
Au@SiO ₂	0.079
Au@AC	0.080
Au@SBA-15	0.078

1.2 Characterization of PMO and Au@PMO:

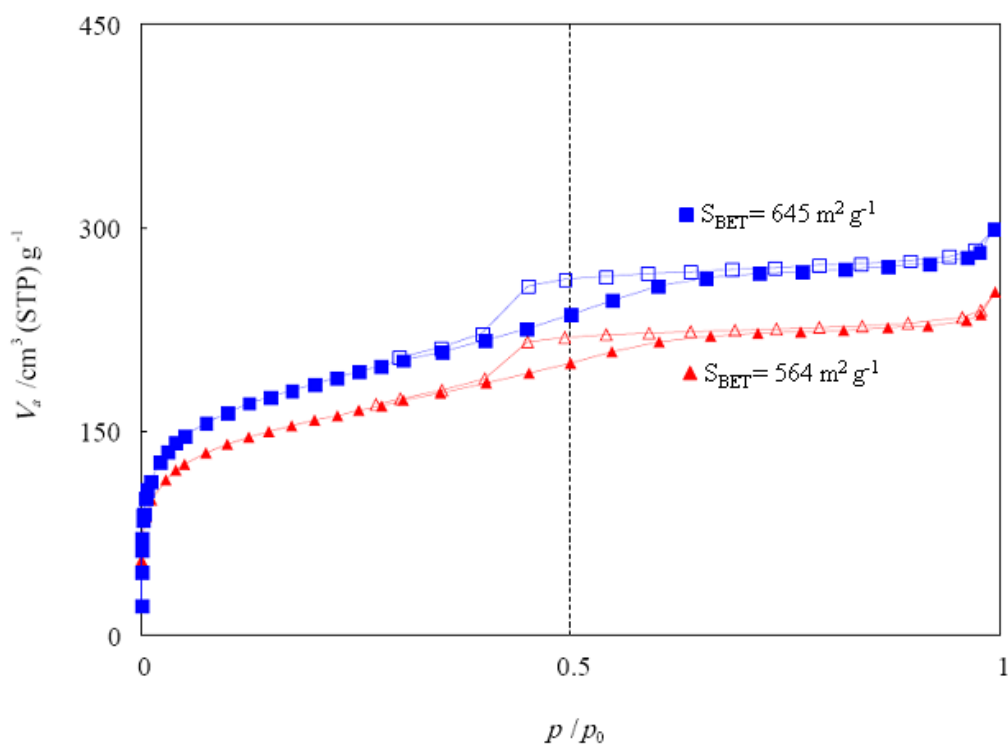


Figure 1S. Nitrogen adsorption-desorption isotherm of the PMO(■) and Au@PMO(▲). The isotherms shows a type IV with a H2 hysteresis loop, which is the characteristic of ordered mesoporous materials indicate that the pore size of PMO sample is in the mesoporous feature with two dimensional hexagonal structure.

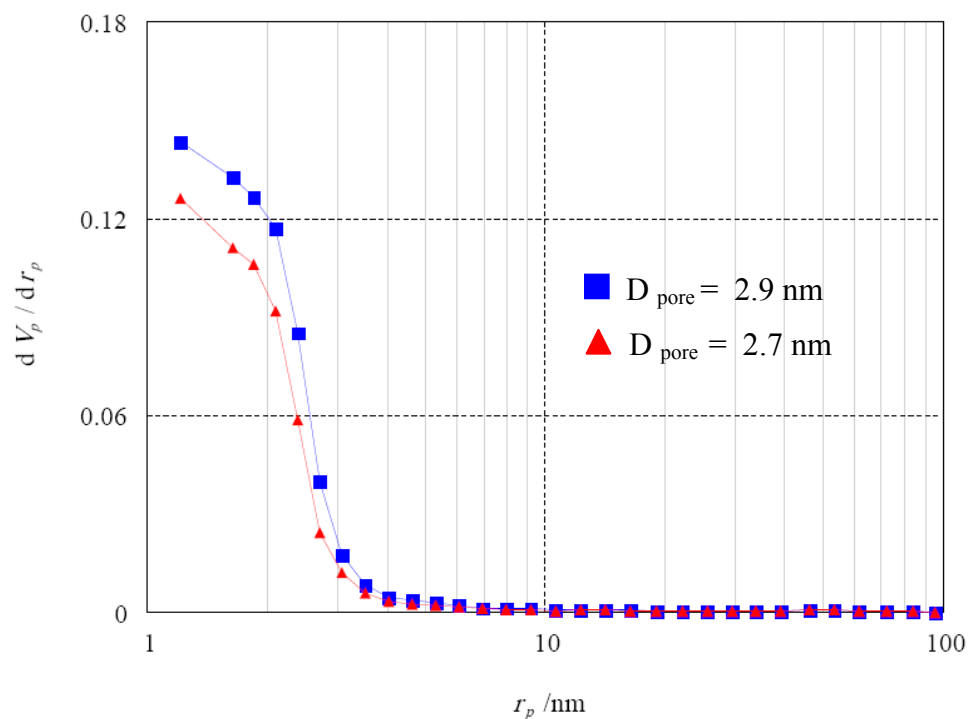


Figure 2S. BJH Pore size distribution of the PMO(■) and Au@PMO(▲).

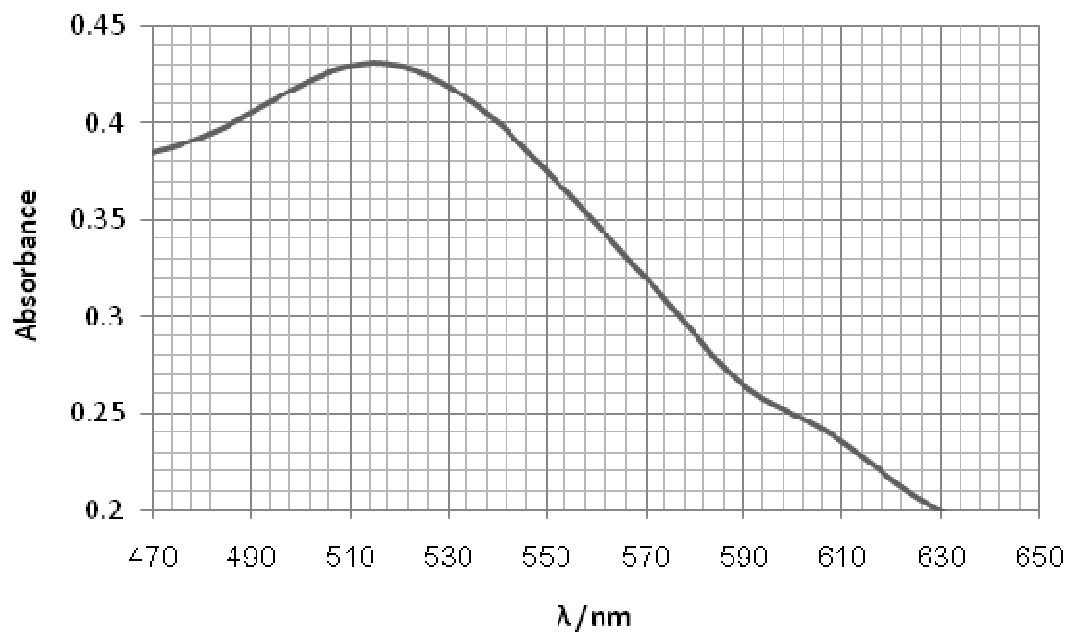


Figure 5S. DR-UV spectrum of the Au@PMO 1 catalyst.

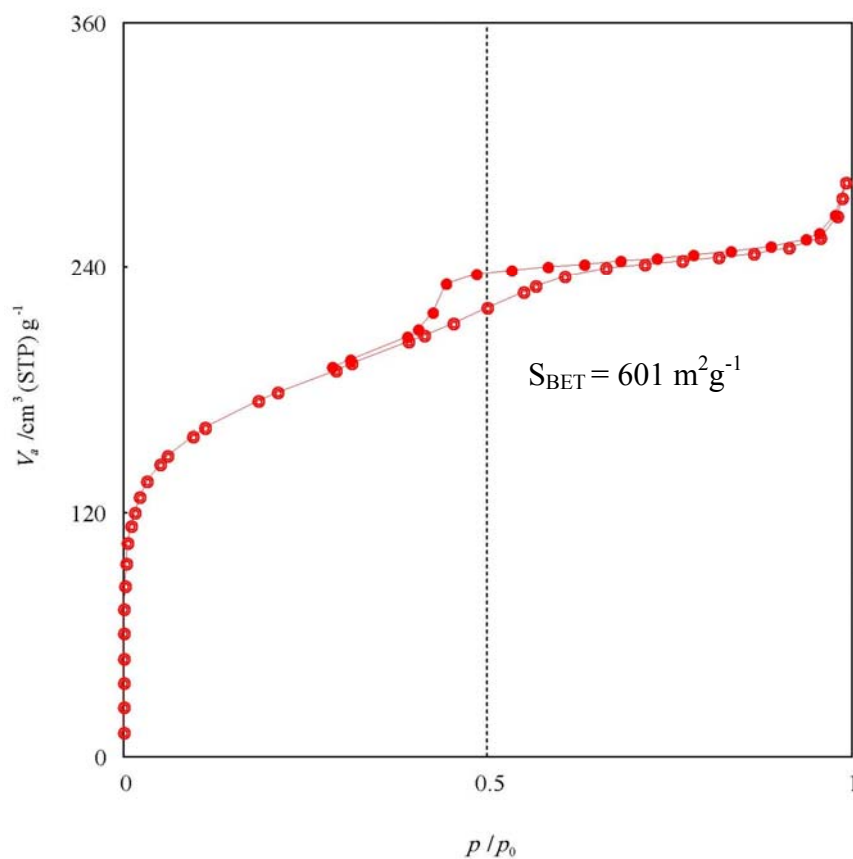


Figure 6S. Nitrogen adsorption-desorption isotherm of the recovered Au@PMO

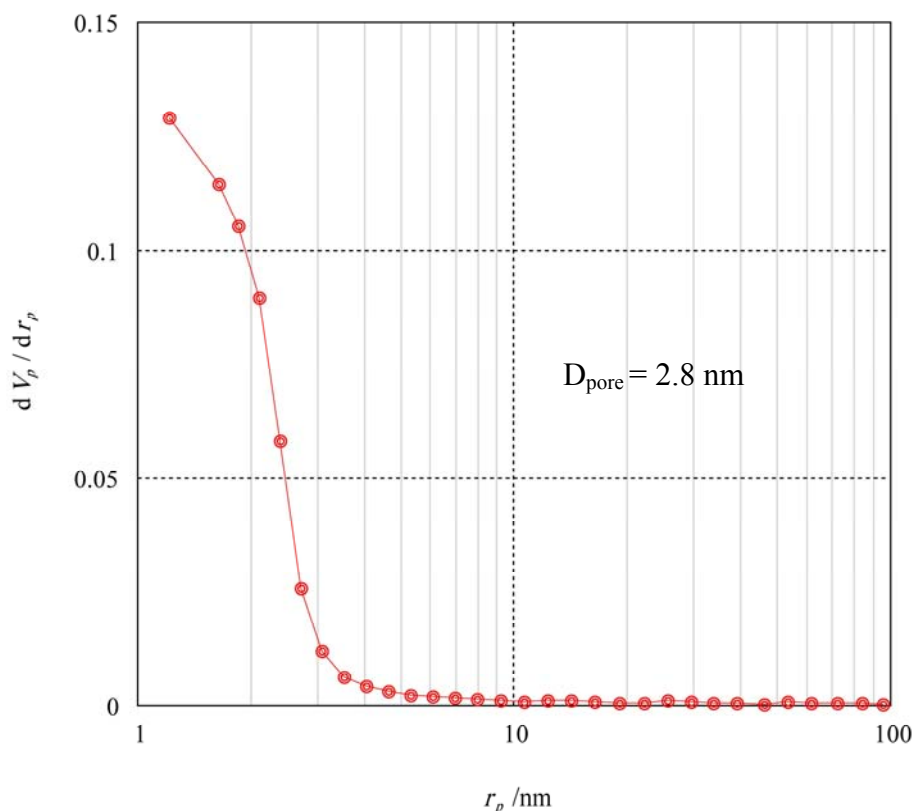


Figure 7S. BJH of the recovered Au@PMO

1.3 General experimental procedure for the Ullmann reaction catalyzed by Au catalysts:

In a schlenk flask (10 ml) equipped with a condenser and magnetic stirrer bar, iodobenzene (1 mmol), was mixed with catalyst (0.1 g, 1 mol %) in NMP (5 mL) under air. The resulting mixture was stirred at 100 °C for 16 h with vigorous stirring. The progress of the reaction was determined by GC-MS (n-decane used as internal standard). The resulting mixer was filtered through a pad of celite and the filtrate was concentrated to yield the product, which was purified by silica gel chromatography (hexane) to yield biphenyls. The identity of the product was confirmed by ^1H and ^{13}C NMR spectroscopy.

1.4 The effect of catalyst loading of Au@PMO in Ullmann coupling of aryl iodides (optimization)

The Effect of the Au@PMO loading was also investigated in the coupling reaction of iodobenzene under the condition outlined in procedure 1.3. The results of this study showed that the amount of gold used in this reaction progress has an important influence (Table 2S). As can be seen, the optimum value for Au loading is certainly 1 mol%

Table 2S. The effect of Au@PMO loading in Ullmann coupling

Entry	Au@PMO (mol%)	Yield (%)
1	0.5	65
2	1	95
3	1.5	95
4	2	95

Reaction conditions: iodobenzene (1 mmol), Au@PMO (X mol%),

1.5 A brief note to the role of phenylene-containing PMO in activity of Au@PMO

We have performed a careful study on all prepared catalysts (Au@PMO, Au@SBA-15, Au@SiO₂, Au@TiO₂, and Au@AC) using transmission electron microscopy (TEM, Figure 8S-13S) Although, we believe and it is well known that (as we have already mentioned in the manuscript) (refereces 2b, 13, 14) the catalytic activity of AuNPs is highly dependent on their size, however, it seems that in the present protocol, the size of AuNPs is not the only reason responsible for the observed catalysis and the synergistic effect between support and nanoparticles is a very important issue that must be considered. As can be interestingly seen, for example, the size distribution of AuNPs supported on activated carbon (Au@AC) seems to be even smaller than that obtained in our Au@PMO catalyst system. Therefore, if we only take the AuNPs size into account for the observed catalysis, we may expect that Au@AC should be even more reactive than our Au@PMO in Ullman homocoupling of aryl iodides. However, this is in sharp contrast to our observations. Therefore, we believe the fact that Au@PMO consistently shows higher activity than those observed for Au@AC (and of course other studied AuNP supported systems) most likely highlight the notion that the large differences between the various gold based catalysts caused greatly by surface properties of PMO, most probably originated from the interaction of phenylene-group embedding inside the silica frameworks with AuNPs.

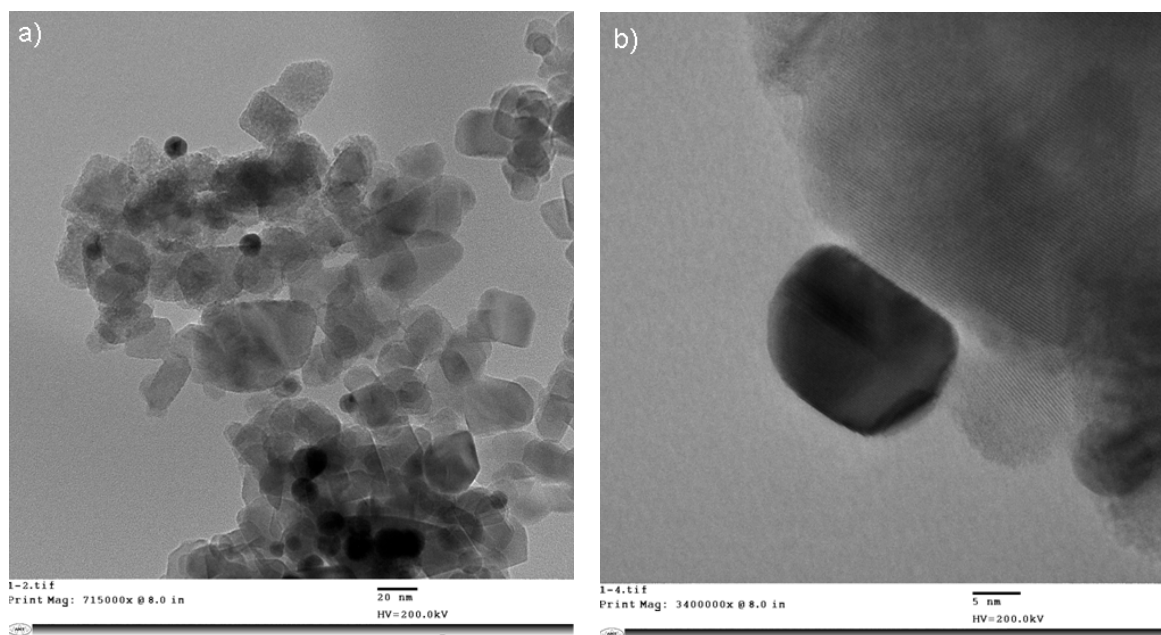


Figure 8S. TEM (a), and HRTEM (b) of Au@TiO₂

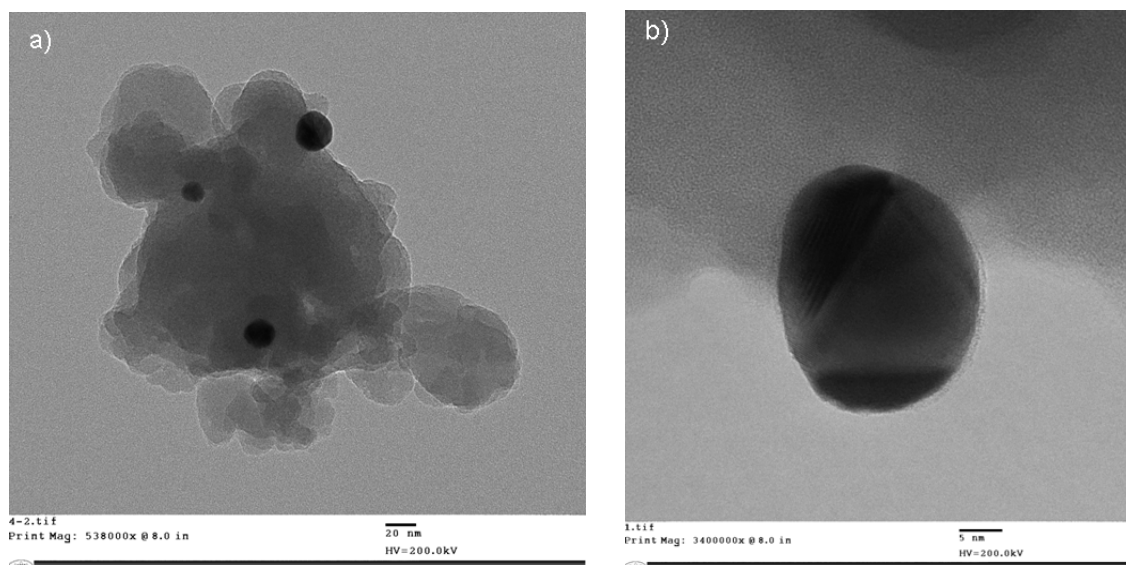


Figure 9S. TEM (a), and HRTEM (b) of Au@SiO₂

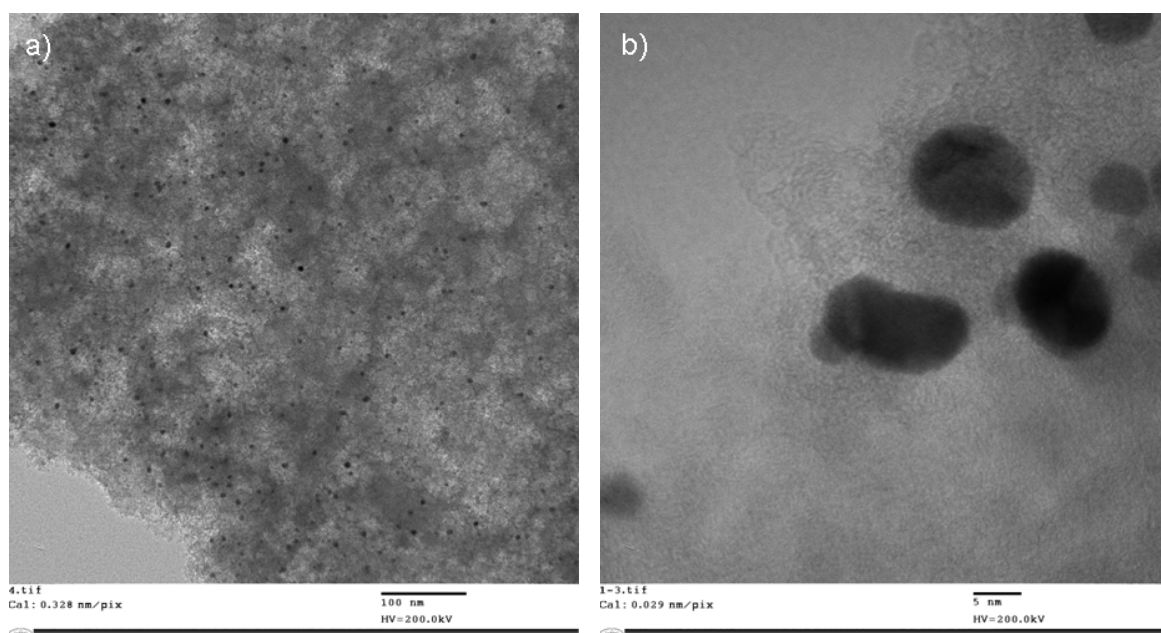


Figure 10S. TEM (a), and HRTEM (b) of Au@AC

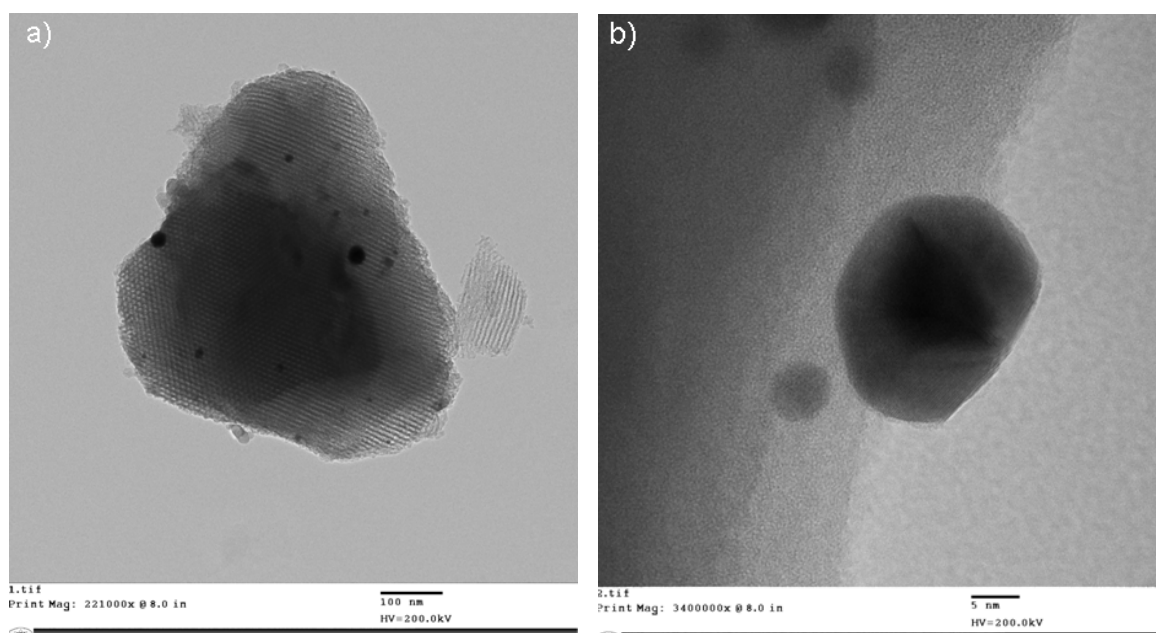


Figure 11S. TEM (a), and HRTEM (b) of Au@SBA-15

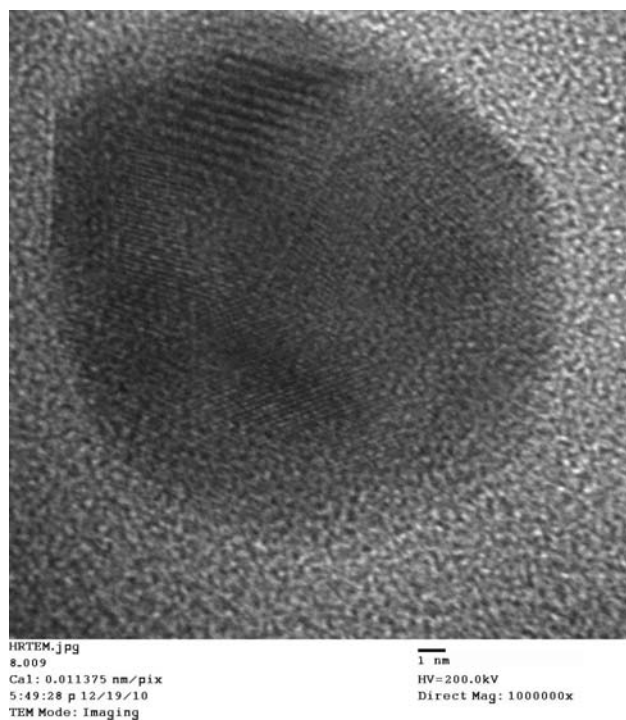


Figure 12S. High Resolution Transmission Electron Microscopy (HRTEM) image of a single Au nanoparticle inside the channels of PMO

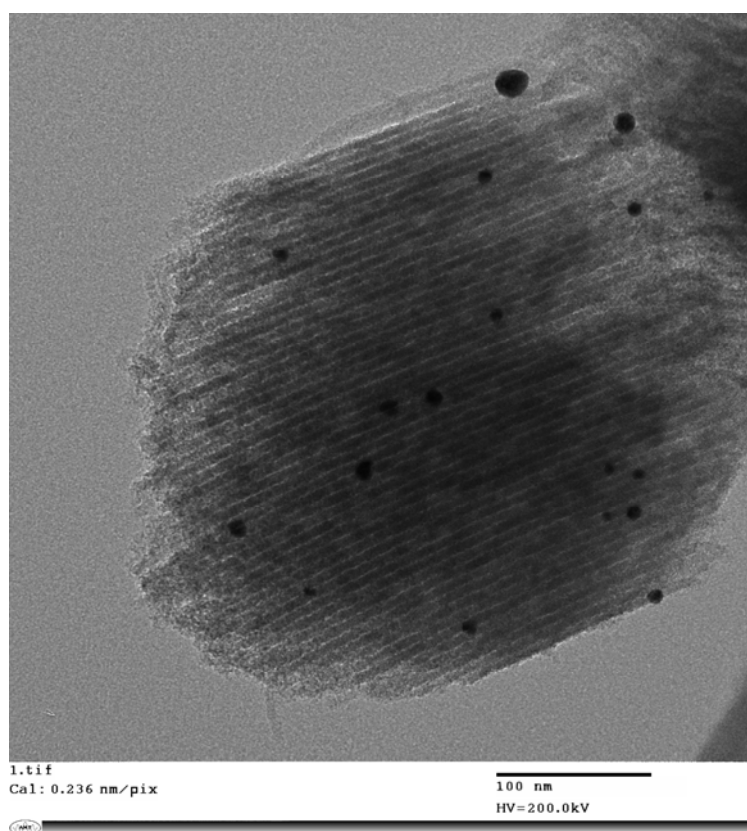


Figure 13S. TEM image of Au nanoparticles supported in phenylene-containing PMO.

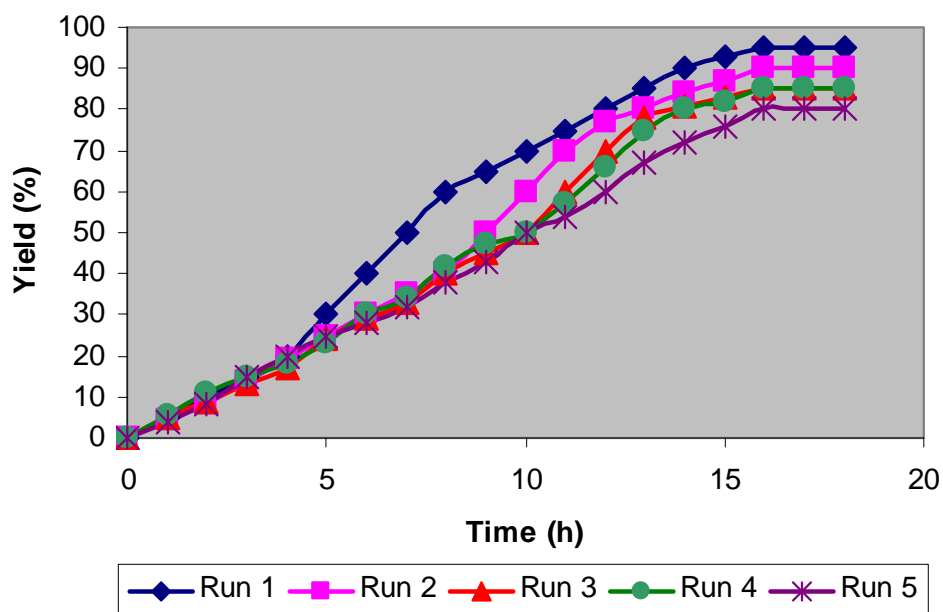


Figure 14S. Reaction progress as a function of time on the Ullmann coupling of iodobenzene by using Au@PMO catalyst in the reusability test.

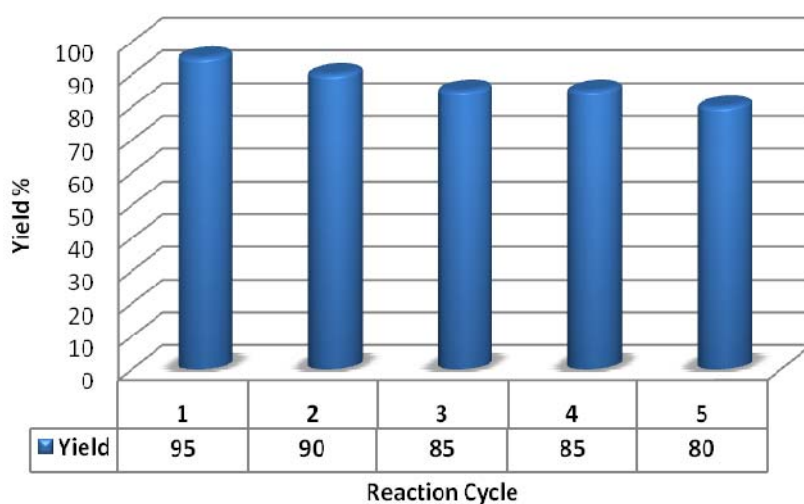


Figure 15S. Recyclability of the Au@PMO in the Ullmann coupling.

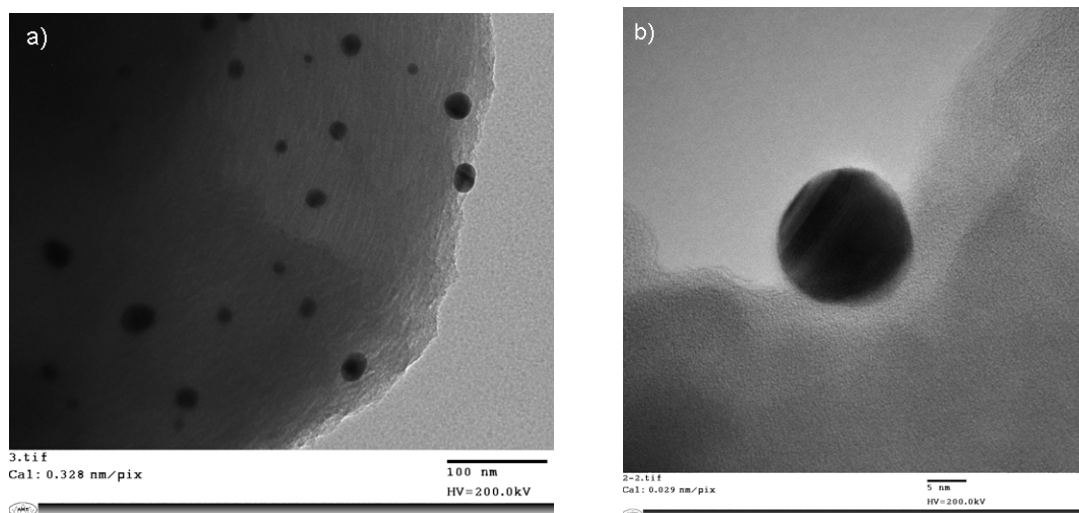
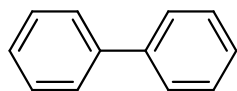
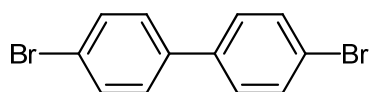


Figure 16S. TEM (a), and HRTEM (b) of Au@PMO after the 5th run.

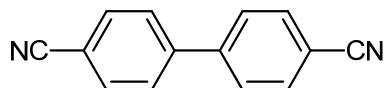
1.6. Spectral data for Table 2



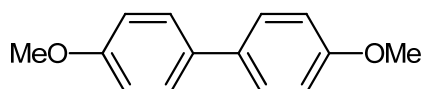
Biphenyl: $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.37\text{-}7.41$ (t, $J = 7.6$ Hz, 2H), $7.47\text{-}7.50$ (t, $J = 7.6$, 4H), $7.39\text{-}7.44$ (d, $J = 6.8$ Hz, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C, TMS): 127.2, 127.3, 128.8, 141.3.



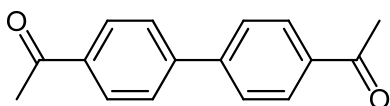
4,4'-dibromo-1,1'-biphenyl: $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.43\text{-}7.45$ (d, $J = 8.4$, 4H), $7.58\text{-}7.60$ (d, $J = 8.8$, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C, TMS): 121.9, 128.5, 132.1, 138.9.



4,4'-biphenyldicarbonitrile: $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.71\text{-}7.73$ (d, $J = 8$, 4H), $7.80\text{-}7.82$ (d, $J = 7.6$, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C, TMS): 112.5, 118.4, 127.9, 132.9, 143.5.



4,4'-dimethoxy-1,1'-biphenyl: $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 3.87$ (s, 6H), $6.98\text{-}7.00$ (d, $J = 8.8$ Hz, 4H), $7.50\text{-}7.52$ (d, $J = 8.8$ Hz, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C, TMS): 55.4, 114.2, 127.7, 133.5, 158.7.



1,1'-([1,1'-biphenyl]-4,4'-diyl)diethanone: $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 2.68 (s, 6H), 7.74-7.76 (d, J = 8.4Hz, 4H), 8.08-8.10 (d, J = 8.4Hz, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C, TMS): 26.7, 127.5, 129.1, 136.6, 144.4, 197.7.

1.7. Copy of ^1H and ^{13}C -NMR spectra of selected biphenyl derivatives

