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Designed Synthesis of Au/Ag/Pd Trimetallic Nanoparticle-Based Catalysts for Sonogashira Coupling Reactions

P. Venkatesan and J. Santhanalakshmi*

Department of Physical Chemistry, University of Madras, Guindy Campus, Chennai-600 025, Tamilnadu, India

Received March 22, 2010. Revised Manuscript Received April 16, 2010

Pdnp and Pd containing trimetallic nanoparticles (tnp) are synthesized by chemical method with cetyltrimethylammonium bromide as the capping agent. Compositionally, four different tnp are prepared and the particle sizes are characterized by UV-vis spectra, HR-TEM, and XRD measurements. The catalytic activities of Pdnp and tnp are tested using the Sonogashira C-C coupling reaction. The product yield and recyclability of the recovered catalysts are studied. tnp (1:1:1) exhibited better catalysis than Pdnp, which may be due to the concerted electronic effects of the Au-Ag core onto the Pd shell atoms.

The use of transition metal nanoparticles of Pt, Pd, Ru, Au, Cu, Ag, and so forth as catalysts in organic C–C coupling reactions has placed nanometal catalysis, an important frontier of research in recent years.¹ For this purpose, mono, bi, tri, and multimetallic nanoparticles in solutions are prepared with appreciable stability using a variety of capping agents such as surfactant micelles, functional polymers, dendrimers, and so forth.² The use of nanometal catalysts in many cases has simplified the reaction procedures and has shown versatilities like product specificity, recyclability of catalysts, high turnover, and so forth.³ Of late, there have been many reports on the use of phosphine-free Pd nanoparticles (Pdnp) as successful replacements of air and moisture sensitive and inert atmosphere requiring conditions of Sonogashira C–C coupling reactions⁴ (Scheme 1).

Palladium nanoparticles have been tested as catalysts for various reactions,^{5,6} because catalytic reactions occur on the surface of the nanoparticles. This issue becomes very important

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Scheme 1. Sonogashitra C-C Coupling Reaction



for the nanoparticles of expensive noble metals such as palladium and platinum. In view of "atom economy", the synthesis of core/ shell nanoparticles having a cheap metal core and a noble metal shell is desirable. Several palladium-containing bi- and trimetallic nanoparticles including core/shell structures have been synthesized.7 In most of these core/shell nanoparticles, however, palladium is in the core and the other metal such as gold and or silver covers the surface of palladium, which is not useful for the catalytic reactions involving palladium as an active catalytic species.⁸ Luis M. Liz Marzan et al. synthesized core/shell Au-Ag nanoparticles from the consecutive reduction of HAuCl₄ and AgNO3; Murali Sastry et al. synthesized core/shell Ag-Pd nanoparticles from the consecutive reduction of AgNO3 and H2PdCl4 through the chemical method. In this study, the authors claimed that palladium nanoparticles catalyzed the reduction of gold and silver precursors and induced the deposition of Au-Ag atoms on the surface of Pd nanoparticles. Herein, we report on the synthesis of Au-Ag-Pd trimetallic nanoparticles (tnp) with Au-Ag rich core/Pd-rich shell structure from the chemical method of gold, silver, and palladium precursors.

The current synthetic procedure is a modified version of the method developed for the synthesis of various nanoparticles of metals, which employs the chemical method of metal–surfactant complexes.⁹ The colloidal dispersions of CTAB protected Au–Ag bimetallic nanoparticles were prepared by refluxing of the aqueous solution of HAuCl₄ and AgNO₃ in the presence of CTAB.¹⁰ The molar ratio of Au–Ag was 1/1, and the molar ratio

^{*}jslakshmi@yahoo.co.in (J. Santhanalakshmi) and venkatesanorg@ gmail.com (P. Venkatesan).

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Figure 1. UV-vis absorption spectra of CTAB stabilized monometallic Pdnp and trimetallic Au-Ag-Pd colloidal nanoparticles at different time intervals in aqueous medium at 25 °C.

of monomer unit of CTAB against total metal (*R*) was kept 40 in the present experiments. The colloidal dispersions of Pd nanoparticles are separately prepared by refluxing a $H_2O/EtOH$ (1/1, v/v) solution of PdCl₂ in the presence of CTAB.¹¹ The colloidal dispersion of CTAB-protected Au-Ag (1/1) nanoparticle and that of CTAB-protected Pd nanoparticles are mixed at room temperature in the designated ratio. The mixed dispersions are kept stirring at least for a 24 h at room temperature to complete the self-organization reaction. The tnp with different molar ratios of the precursor metal salts of gold, silver, and palladium could be prepared without any precipitation. The solutions of all the compositions are very stable over extended periods of time.

The completion of formation reactions of monometallic Pd, bimetallic Au-Ag, and tnp was followed by UV-vis spectroscopy as a function of time (Figure 1). The absorption spectra of the mixtures changed as the duration time was increased, the surface plasmon resonance (spr) bands moved closer to one another and merged into a single peak over the course of the time intervals. The bimetallic Au-Ag nanoparticles as conformed after 45 min, further increased the time duration resulted in a continuous decrease in the absorption band until, eventually, no absorption peak was apparent after 60 min exposure. As the duration of the time was increased up to 24 h (overnight), there is no distinct change in the shape or magnitude of the absorbance. Finally, the color of the colloidal nanoparticles is dark brown, confirming formation of palladiumcoated trimetallic nanoparticles. The Pd nanoparticle shows that a sharp absorbance peak cannot be observed over the entire range due to the brown color of the solution.

Successive reduction strategies are an effective method to prepare core-shell structure bi- and multimetallic nanoparticles. One of the metal salts is reduced first to form the core, and then a second metal is deposited on the surface of preformed monometallic nanoparticles to form the shell. The XRD patterns of the 1:1:1, 0.5:1:1, 1:0.5:1, and 1:1:0.5 stoichometric tnp fcc structures are shown in Figure 2. This is in agreement with the electron diffraction results shown, the presence of well-mixed Au-Ag-Pd trimetallic nanoparticles. Also, the Palladium is present in the shell region of tnp.

Figure 3a shows a typical TEM image of tnp (1:1:1) nanoparticles, and the particles are monodispersed with an average diameter of 4.2 ± 0.2 nm and a narrow size distribution. Figure 3b shows the electron diffraction pattern obtained from a selected area of Figure 3a. The bright rings with occasional bright spots are due to the presence of polycrystals. Regarding the variation of particle sizes of tnp with different compositions, there is no appreciable change in the size and the size growth is only within 10% of the 1:1:1 tnp.



Figure 2. X-ray diffraction (XRD) spectra of the CTAB stabilized trimetallic Au–Ag–Pd colloidal nanoparticles at different mole ratios of a = 0.5:1:1, b = 1:0.5:1, c = 1:1:1, and d = 1:1:0.5, respectively at 25 °C.



Figure 3. Transmission electron microphotographs (HRTEM) of the CTAB-stabilized trimetallic Au–Ag–Pd colloidal nanoparticles solution. (a) HRTEM (bar indicates 20 nm) and (b) electron diffraction pattern spectra in aqueous medium at 25 °C.



Figure 4. Scanning electron microscopy EDX spectra of CTAB stabilized trimetallic Au–Ag–Pd nanoparticles at 25 °C.

 Table 1. EDX Spectral Data of Trimetallic Nanoparticles in 1:1:0.5,

 1:0.5:1, 0.5:1:1, and 1:1:1 Catalysis, Respectively

initial atomic composition Au:Ag:Pd	structure of nanoparticle	atomic composition in nanoparticles Au:Ag:Pd	
0.5:1:1	fcc	0.42:0.90:0.94	
1:0.5:1	fcc	0.98:0.48:0.96	
1:1:1	fcc	0.94:0.96:0.98	
1:1:0.5	fcc	0.96:0.98:0.48	

Energy-dispersive X-ray analyses are also conducted by focusing the electron beam on several different selected regions on each sample (each region area 1 μ m × 1 μ m) of the unsupported Au-Ag-Pd nanoparticles. An EDX spectrum of Au-Ag-Pd nanoparticles is shown in Figure 4. The compositions of Au-Ag-Pd trimetallic nanoparticles in different regions are in close agreement and no significant deviations (Table 1).

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Figure 5. FTIR spectra of CO adsorbed on the CTAB-stabilized monometallic palladium (a = Pdnp) and trimetallic (b = 1:1:0.5, c = 1:1:1) nanoparticles, respectively, at 25 °C.

Infrared spectroscopy has been widely used to study the surface chemistry of small, adsorbed molecules. The vibrational frequency of adsorbed CO changes with the metal substrate and binding structure. Hence, IR spectroscopy of CO on the surface of trimetallic nanoparticles is expected to give information about the surface of the nanoparticle. On gold nanoparticles, however, CO is known to be very weakly and reversibly adsorbed.^{12,13} The adsorbed CO is generally observed only at low temperatures.^{12,13} Gold and silver have fully occupied d-orbitals (5d¹⁰6s¹, 4d¹⁰5s¹, respectively) and exhibit weak coordination ability toward CO. It is reported that only weak Raman and IR bands are observed for CO on gold and silver surfaces.^{12,13} The monometallic Pd particle IR spectra are reported by Toshima and co-workers.¹⁴ The IR spectra of CO adsorbed on mono- and trimetallic nanoparticles stabilized in CTAB is shown in Figure 5. A broad peak is seen at 2030 cm^{-1} and another strong absorption band is observed at 1910 cm⁻¹. The former band can be assigned to the CO adsorbed on the Pd surface at the terminal site (linear adsorption site) and the latter to CO adsorbed at the bridging site (bridging adsorption site).¹⁴ The relative intensities of these two peaks have been reported to vary depending on the particle size¹⁵ constituted of three distinct metals. Such compounds often showed better activity and selectivity compared to mono- and bimetallic colloids.¹⁶ In the present work, the catalytic activity of the Au/ Ag/Pd trimetallic nanoparticles and similarly sized monometallic palladium nanoparticle for Sonogashira coupling reactions using an equal amount of palladium in the reaction mixtures.¹⁷

We initially studied the reaction of iodobenzene with phenyl acetylene in DMF-water (3:1) as a model reaction under gradual heating from 20 to 120 °C in the presence of 0.5 mol % of trimetallic Au-Ag-Pd nanoparticle and 3 equiv of various bases. The results are summarized in Table 2. These results suggested

that the bases used have dramatic effects on the yields of crosscoupling product in the Sonogashira reaction. Among the bases screened, K_2CO_3 and Cs_2CO_3 gave the best results (Table 2, entry 3, 6). In addition, a profound solvent effect on the reaction was observed. DMF-water (3:1) was found to be the best solvents (Table 2, entry 12). Variation in mole percentage of the catalysts for trimetallic Au-Ag-Pd indicates 0.5 mol % catalyst loading produced maximum percentage yield, compared to 0.6 mol % of the catalysts (Table 2, entry 3, 15 to 17). The temperature effects studies show that the optimum reaction temperature is found at 120 °C, since 140 °C reaction temperature also produced the same percentage yield (Table 2, entries 3, 12 to 14).

Under optimized reaction conditions (trimetallic Au–Ag–Pd as catalyst, K_2CO_3 as base and DMF–water), a series of aryl bromides or iodides and phenyl acetylene were tested in the reaction conditions, and results were summarized in Table 3. The catalytic activity of trimetallic Au–Ag–Pd nanoparticle toward the various aryl substituents reacting with phenyl acetylene in the Sonogashira reaction keeping the reactions conditions of entry 3 in Table 2 constant has been performed separately. The results are given in Table 3. It is found that reaction time varied slightly for different substituents.

The reaction occurred exclusively with aryl iodides and bromides but not with aryl chlorides, and produced the corresponding products of biphenyl acetylene with excellent yield (entries 1 to 3, Table 3). Various aryl halides and phenyl acetylene are employed in the Sonogashira reaction under the same catalysts conditions, as shown in Table 3 (entries 4 to 8). The iodobenzene with electron-donating ring substituents proceed with good yield (entry 5, Table 3) unlike the reported yield values. When trimetallic Au-Ag-Pd nanoparticles serve as catalyst in the Sonogashira reaction, better yields crop up.

The turnover frequency of the catalysts in the Sonogashira reaction has been measured by recovering the mono-, bi-, and trimetallic nanoparticle precipitates upon addition of dilute HCl (pH < 3.0) to the reaction mixture remaining after the removal of the product into the CH₂Cl₂ phase. The precipitates are subjected to Sonogashira reaction catalysis. It is found that 99.0%, 92%, 68%, and 46% product yields existed corresponding to fresh and first, second, and third reuses, respectively. Catalyst reuse the fourth time showed that the product yield is low, but in the case of monometallic Pdnp precipitated during the reaction. The catalytic activity of the Pd colloidal solution decreased during the reaction as the metal was precipitated. Similar observations were made by Herrmann and co-workers for the Heck reaction between aryl halides and styrene using palladium colloid as catalyst.¹⁸ This instability of the colloid might be due to the use of high temperatures. We report that the tnp was no formation of any precipitate at the end of the reaction. Therefore, further improvements on the catalyst stability are necessary for practical applications.

The metallic nanoparticles are definitely much less catalytically active during the second cycle of the coupling reaction. The reason is a lower amount of nanoparticles present in the solution if caused by precipitation of larger nanoparticles. Another possibility is that, if the number density has not changed, but only the size is getting smaller, the smaller particles might not be as catalytically active as the larger particles. As a result, the lower catalytic activity observed during the second cycle is due to a lower amount of nanoparticles present in the solution because of larger nanoparticles aggregating and precipitating out of solution. In addition, surface poisoning by the products could be another reason.

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Table 2. Sonogashira Coupling Reaction Using Mono-, Bi-, and Trimetallic Nanoparticles with Various Effects⁴

į	▶ + _ /=\	nano particles	>
		K ₂ CO ₃ , DMF-H ₂ O	

entry	catalyst type	catalysts (mol %)	base	solvent	temp	product yield (%)
1	Pdnp	0.5	K ₂ CO ₃	DMF-H ₂ O	120 °C	94.0
2	Au-Pdnp	0.5	K ₂ CO ₃	DMF-H ₂ O	120 °C	96.0
3	tnp (1:1:1)	0.5	K ₂ CO ₃	DMF-H ₂ O	120 °C	99.5
4	tnp(0.5:1;1)	0.5	K ₂ CO ₃	DMF-H ₂ O	120 °C	99.0
5	tnp (1:1:0.5)	0.5	K ₂ CO ₃	DMF-H ₂ O	120 °C	98.0
6	tnp (1:1:1)	0.5	Cs_2CO_3	DMF-H ₂ O	120 °C	99.0
7	tnp (1:1:1)	0.5	NaOH	$DMF-H_2O$	120 °C	66.0
8	tnp (1:1:1)	0.5	Et ₃ N	DMF-H ₂ O	120 °C	82.0
9	tnp (1:1:1)	0.5	NaOAC	DMF-H ₂ O	120 °C	56.0
10	tnp (1:1:1)	0.5	K_2CO_3	DMF	120 °C	76.0
11	tnp (1:1:1)	0.5	K_2CO_3	CH ₃ CN	120 °C	45.0
12	tnp (1:1:1)	0.5	K_2CO_3	DMF-H ₂ O	140 °C	99.0
13	tnp (1:1:1)	0.5	K ₂ CO ₃	DMF-H ₂ O	100 °C	94.0
14	tnp (1:1:1)	0.5	K ₂ CO ₃	DMF-H ₂ O	80 °C	92.0
15	tnp (1:1:1)	0.2	K ₂ CO ₃	DMF-H ₂ O	120 °C	88.0
16	tnp (1:1:1)	0.3	K ₂ CO ₃	DMF-H ₂ O	120 °C	90.0
17	tnp (1:1:1)	0.6	K ₂ CO ₃	DMF-H ₂ O	120 °C	99.0
18		without cat	K_2CO_3	DMF-H ₂ O	120 °C	46.0
19		without cat	Na ₂ CO ₃	DMF-H ₂ O	120 °C	

^a [Phenyl acetylene] = 1.05 mmol, [Iodobenzene] = 1.00 mmol, 3:1 molar ratio of DMF-water, and 0.5 mol % catalyst at 2 h period.

Table 3. Catalytic Activity of Mono- and Trimetallic Nanoparticles for Sonogashira Reaction^a

X	* =-{	nano particles K ₂ CO ₃ , DMF-H ₂ O	R	
entry	catalysts	R	Х	yield (%) ^b
1	tnp (1:1:1)	Н	Ι	99.0
2	tnp (1:1:1)	Н	Br	95.0
3	Tnp (1:1:1)	Н	Cl	30.0
4	Tnp (1:1:1)	$4 - NO_{2}$	Ι	92.0
5	Tnp (1:1:1)	$4 - OCH_3$	Ι	96.0
6	Tnp (1:1:1)	$4 - CH_3$	Ι	70.0
7	Tnp (1:1:1)	$2 - OCH_3$	Ι	86.0
8	Tnp (1:1:1)	$4 - \text{COCH}_3$	Br	92.0

^{*a*} Reaction conditions: Phenyl acetylene (1.05 mmol), iodobenzene (1.00 mmol), K_2CO_3 (3.00 mmol), and 0.5 mol % catalysis, DMF-H₂O (3:1 v/v) 120 °C, for 2 h. ^{*b*} Isolated yield. All compounds were fully characterized (see Supporting Information).

Recovery and Recycling of Nanoparticle Catalysts

After the completion of the reaction, 0.1 M HCl solution and 3-fold excess of dichloromethane (CH₂Cl₂) are added so that the trimetallic nanoparticle (Au-Ag-Pd) catalyst and the products are correspondingly separated into the pH-responsive aqueous and organic phases, respectively. The precipitate of pH-responsive metallic nanoparticle catalyst was collected by ultracentrifugation. The collected catalyst is dried and reused for the next cycle of reaction. When the recovered catalyst is UV-visible spectra recoated, the spr peaks are not as prominent as in the first cycle.

The same reaction mixture solution was used for recycling after the addition of fresh amounts of the reactants. For recycling, iodobenzene (1 mmol), phenyl acetylene (1.05 mmol), and potassium carbonate (3 mmol) were added without addition of any nanoparticle. The reaction mixture was then refluxed for another 2 h to complete the second cycle.

As clearly shown in Table 2, the trimetallic nanoparticles (tnp) showed much better catalytic activity than mono- and bimetallic nanoparticles, which resulted from the larger number of



Figure 6. Comparison of the catalytic activity of 4.2 nm Au/Ag/Pd trimetallic nanoparticles (a = first cycle, b = third cycle) and 4.0 nm monometallic Pd nanoparticles (c = first cycle). Reaction conditions: Phenyl acetylene (1.05 mmol), iodobenzene (1.00 mmol), K₂CO₃ (3.00 mmol), and 0.5 mol % catalysis, DMF-H₂O (3:1 v/v) 120 °C, for 2 h.

nanoparticles derived from the core/shell structure (an equal amount of nanoparticles was used). The nanoparticle catalyst can be recycled and reused at least three times without losing the catalytic activity (entry 3 in Table 2).

The product yields were determined by gas chromatography. Each catalytic reaction was carried out in at least two runs. Both plots reveal that using 0.5 mol % Au-Ag-Pd (1:1:1) was sufficient to catalyze the coupling with conversion and product yield of \geq 95%. We have successfully fabricated the first example of a Au-Ag-Pd trimetallic nanoparticle using wet chemical method of mixtures consisting of Au, Ag, and Pd colloids. Figure 6 shows that the present Au-Ag-Pd trimetallic nanoparticles demonstrated good catalytic properties on the product formation test platform, performing better than a traditional Pd containing monometallic catalyst.

In conclusion, we have synthesized a novel family of Au– Ag–Pd core/shell trimetallic nanoparticles from the wet chemical method of metal–surfactant complexes. Surface plasmon peaks

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in UV-vis spectroscopy have confirmed the formation of mono-, bi-, and trimetallic nanoparticles. The HRTEM photographs of trimetallic nanoparticles showed the sizes as 4.2 ± 0.5 nm. The particle size results from HRTEM and XRD agree well with each other. SEM-EDX spectra confirmed the presence of the three metals. Their catalytic activities were tested in the Sonogashira coupling reactions. These novel palladium-containing trimetallic nanoparticles are air- and moisture-stable, and the reaction can be readily conducted under aerobic conditions. Trimetallic Au-Ag-Pd nanoparticle catalysis of Sonogashira reaction produced better results than mono- and bimetallic catalysts. In fact, the presence of metal nanoparticles as catalysts replaces environmentally detrimental catalytic strong bases being used in Sonogashira reaction. Metal nanoparticles as catalysts also gave appreciably high yield of the products. The high catalytic activity of trimetallic nanoparticles is probably due to the sequential electronic effect between elements in a particle. More detailed investigations of nanoparticle structure effects on the catalytic activity and their applicability in other synthetic transformations are currently underway.

Acknowledgment. The author thank to IIT Madras, India, for recording TEM of samples recovered from different stage of preparations. Financial support to the Department from DST-FIST is also acknowledged.

Supporting Information Available: Experimental procedures of Sonogashira reaction and ¹H and ¹³C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.