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Bimetallic quantum dots (Cu-Pd, Ni-Pd) catalyzed reaction of bromo arenes with alkenes and aryl boronic acids

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Bimetallic quantum dots (Cu-Pd and Ni-Pd) are active ligand-free catalysts for the alkenylation and arylation of aryl bromides. The catalysts are easy to synthesize by benign green protocols and characterized by various techniques. The bimetallic QD catalysts synthesized thus are superior to $Pd(OAc)_2$ or other Pd NP catalysis of alkenylation reactions of aryl bromides with similar E-selectivity. The reaction of aryl bromide with aryl boronic acid is facile with high yields.

Keywords: Bimetallic QDs catalysis, Mizoroki-Heck, Suzuki coupling, Aryl bromides, Cu-Pd, Ni-Pd

Bimetallic NP alloys show different catalytic properties than individual metal NP[1-12.] Bimetallic Cu-Pd quantum dots (2 - 5 nm) exhibit enhanced surface property and catalysis[13,14]. Such nanoclusters efficiently catalyze the various well-known cross-coupling reactions[15,16]. Few reports show the green synthetic protocol for nanoparticles, and the development of sustainable eco-friendly methods is of great importance[18-23]. Some examples include the reduction of inorganic nanomaterials by using microorganisms, plant extracts, *etc.*[24–27] By using plant and leaf extracts, different morphology for the surface of nanoparticles can be tailored. Because of their high tunable properties, quantum dots (QD's) are of great interest[1].

Bimetallic catalysts are extensively studied and efficient in several reactions[1]. The cost of Pd catalyst is quite prohibitive for many industrial processes where Pd/C and other catalysts are used. Bimetallic catalysts with a low percentage of noble metal combined with a higher content of earth-abundant metal might be an excellent strategy to circumvent this problem. In addition, this might lead to different and better catalysis of desired reactions while opening up new catalytic pathways[28].

Bimetallic catalysis permits the smaller loading of noble metals, and the reaction benefits from the synergism of the second metal catalyst. Ni-Pd nanoparticles successfully catalyze the well-known cross-coupling reactions[13,14].

Several methods are now available for the activation of atom economical aryl halides, and require special PPh_4Cl additives, reagents (dimethylglycine), bulky tBu_3P ligands, NHC, palladacycles and nanoparticle catalysts with PEG as solvent[17]. Pd and Au on nanoporous CeO_2 exhibit a profound effect on the catalysis of the Suzuki coupling[29]. Pd NPs actively catalyze these cross couplings[30-33]. But there are very few reports on using bimetallic QD catalysts in these reactions[15,16,34,35,45-47]. The bimetallic combination of $Pd(OAc)_2$ with $NiBr_2$ and stoichiometric excess NaI activates even aryl chlorides in the Mizoroki-Heck reactions[36]. The Ni-Pd bimetallic NP on CWNTS is a dynamic catalyst system[30-33,37]. The synergism of bimetallic catalysts has been demonstrated in several reaction systems[34,35]. Pd nanoclusters supported on PVP are promising catalysts for the alkenylation or arylation reactions[38].

Alkenylation or arylation of the atom economical aryl bromides is a challenging task[36,39-44]. Various additives and unique ligands are utilized for the activation of bromo-arenes. A binary Ni-Pd nano alloy catalyzes the reaction of hindered bromides with aryl boronic acids[48]. Bimetallic nanoalloys of Ni-Pd and Cu-Pd supported on ABPBI (polybenzimidazole) polymer successfully catalyze the cross-coupling reaction of aryl halides with alkenes and aryl boronic acids[49]. The PVP (poly(N-vinyl-2-pyrrolidone)-supported dual $PdCl_2$-$NiCl_2$ system efficiently catalyzes the hydro esterification of styrene[50]. Ni-Pd bimetallic catalysts exhibit synergism for the thermal coupling of bromo-arenes with alkenes and aryl boronic acids[51]. This work achieves the surface property of bimetallic Cu-Pd and Ni-Pd alloyed semiconductor QDs catalysts.

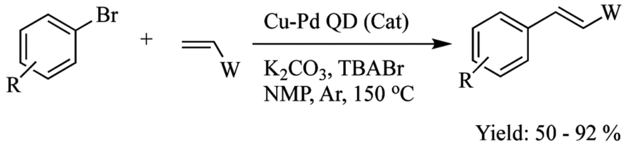
Results and Discussion

Cu-Pd and Ni-Pd bimetallic quantum dots were prepared using a green approach with neem powder extract and sonication for 30 minutes at RT. After 24 h at *p*H 8, quantum dots were separated by a centrifuge machine (400 rpm for 10 minutes) and dried under vacuum.

We then explored the Cu-Pd and Ni-Pd catalysis for alkenylation and arylation of various aryl bromides. These bimetallic QD catalysts gave moderate to high yielding Mizoroki-Heck reactions with aryl iodides. The QD's are readily prepared by a simple green protocol.

The Cu-Pd catalyst showed excellent reactivity for bromo-arenes with ethyl acrylate and styrene under standard Mizoroki-Heck reaction conditions (Scheme 1). The rection of aryl iodides was relatively fast and gave very high yields. On the other hand, Ni-Pd catalysts were adequate only for aryl iodides, while bromides gave moderate gains (Table 1). A random 10:1 ratio of Cu-Pd and 5:1 ratio of Ni-Pd were used as catalysts. The comparative experiments with monometallic Pd QDs are in Table 2. The reaction of bromobenzene with ethyl acrylate or styrene gave low yields (17, 26%) catalyzed by Pd NP.

The Cu-Pd, Ni-Pd bimetallic QDs were analyzed and characterized by various techniques. TEM data shows images of bimetallic Cu-Pd quantum dots with polycrystalline nature. The size of QD's varies from 3.5 nm to 5.7 nm and confirm their bimetallic nature. EDS data supports the presence of Cu-Pd in the ratio 10:1 and Ni-Pd in the ratio 5:1, where the salts were mixed in a 10:1 ratio. Similarly, Ni-Pd showed polycrystalline bimetallic QD nature with size variation from 3.4 nm to 6.8 nm. SEM studies show different morphology for Cu-Pd and Ni-Pd. Cu-Pd shows coral-like clusters with porous structures while



R: 4-CH_3O, 4-Cl, 1-BrNap, 4-CH_3

W: $COOC_2H_5$, C_6H_5

Scheme 1 — Alkenylation of aryl bromides catalyzed by Cu-Pd QDs

Table 1 — Alkenylation of aryl bromides catalyzed by Cu-Pd QDs

S. No.	Aryl Bromide	Alkene	Product, E:Z Ratio	Time (h)	Yield (%)
1	C_6H_5Br **1a**	EA	$C_6H_5.CH{=}CH.COOC_2H_5$, (E) **4a**	2	72
2	C_6H_5Br **1a**	Styrene	$C_6H_5.CH{=}CH.C_6H_5$, (E) **4b**	4	92
3	4-$CH_3O.C_6H_4Br$ **1b**	EA	4-$CH_3O.C_6H_4.CH{=}CH.COOC_2H_5$, (E) **4c**	25	50
4	4-$CH_3O.C_6H_4Br$ **1b**	Styrene	4-$CH_3O.C_6H_4.CH{=}CH.C_6H_5$, (E) **4d**	5	79
5	C_6H_5Br **1a**	EA	$C_6H_5.CH{=}CH.COOC_2H_5$, (E) **4a**	4.5	17^c
6	4-$CH_3O.C_6H_4Br$ **1b**	Styrene	4-$CH_3O.C_6H_4.CH{=}CH.C_6H_5$, (E) **4d**	72	62^c
8	4-$Cl.C_6H_4Br$ **1c**	Styrene	4-$Cl.C_6H_4.CH{=}CH.C_6H_5$, (E) **4e**	4	86
9	1-Br.Nap **1d**	EA	1-$Nap.CH{=}CH.COOC_2H_5$, (E) **4f**	6	50
10	1-Br.Nap **1d**	Styrene	1-$Nap.CH{=}CH.C_6H_5$, (E) **4g**	5	63
11	4-$CH_3C_6H_4.Br$ **1e**	EA	4-$CH_3.C_6H_4.CH{=}CH.COOC_2H_5$, (E) **4h**	5	56

[a] Reaction conditions: ArBr (1 mmol), Alkene (1-2 mmol), K_2CO_3 (1.2 mmol), TBABr (1 mmol), Cu-Pd QD (0.010 g, 0.06 mmol), NMP (5 mL), Argon, 150°C; EA – Ethyl acrylate (**2a**), Styrene – **2b**,**c**: catalyst Ni-Pd QD

Table 2 — Comparison of Pd QD catalyzed reaction of bromobenzene

S.No.	Aryl Bromide	Alkene	Product, E:Z Ratio	Time (h)	Yield (%)
1	C_6H_5Br **1a**	**2a**	$C_6H_5.CH{=}CH.COOC_2H_5$, (E) **4a**	1.5	26
2	C_6H_5Br **1a**	**2b**	$C_6H_5.CH{=}CH.C_6H_5$, (E) **4b**	2	17

[a] Reaction conditions: ArBr (1 mmol), Alkene (1-2 mmol), K_2CO_3 (1.2 mmol), TBABr (1 mmol), Cat: Pd QD (0.003 g, 0.06 mmol), NMP (5 mL), Argon, 150°C; **2a**: Ethyl acrylate, **2b**: Styrene, **2c**: catalyst: Pd QD

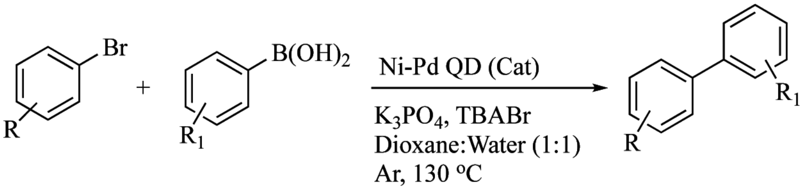
Ni-Pd is small independent pellets (See Supporting Information for bimetallic QD Characterization data).

Ni-Pd QDs was a superior catalyst for the arylation of aryl bromides (Scheme 2) compared to the Cu-Pd catalyzed reaction with alkenes. A (1:1) dioxane: water was an optimum solvent system for the arylation reactions. These reactions progressed in very short reaction times with various aryl bromides in high yields (Table 3). Comparative Suzuki coupling experiments catalyzed by Pd QD with bromo anisole gave a lower 23% yield (Table 4).

The reactivity of the bimetallic QD catalyst is rationalized thus: The bimetallic QD Ni-Pd or Cu-Pd form a redox couple facilitating electron transfer from Ni to Pd or Cu to Pd and increasing its activity. Thus, the QDs readily activate aryl bromides for both the couplings with alkenes and aryl boronic acids. Bimetallic QDs catalyze the Mizoroki-Heck reaction and Suzuki coupling due to their unique electronic and structural features. The following is the probable mechanism:

(i) Activation of the Pd-Cu quantum dots: The Pd-Cu quantum dots are activated by donation of electrons to the Pd and Cu atoms on the surface of the quantum dots.

(ii) Oxidative addition: The aryl or vinyl halide is activated by the Pd-Cu QD through oxidative addition, which involves the insertion of the aryl halide into the Pd-Cu bond.



R: 4-CH_3O, 1-BrNap, CH_3, 4-Cl, 4-BrPh, 2-BrPy

Yield: 68 - 96 %

R_1: 4-Cl, 4-OCH_3, 1-Nap, 2-Nap

Scheme 2 — Arylation reaction catalyzed by Ni-Pd Bimetallic QDs

Table 3 — Arylation reaction catalyzed by Ni-Pd Bimetallic QD[a]

S. No.	Aryl Halide	Aryl Boronic acid	Product	Time (h)	Yield (%)
1	C_6H_5I **1g**	$C_6H_5B(OH)_2$ **3a**	Biphenyl	1.5	71[b]
2	4-$CH_3O.C_6H_4I$ **2b**	4-$CH_3O.C_6H_4B(OH)_2$ **3b**	4,4’-Dimethoxybiphenyl	2.5	92
3	C_6H_4Br **1a**	$C_6H_5B(OH)_2$ **3a**	Biphenyl	2.5	25[b]
4	C_6H_4Br **1a**	$C_6H_5B(OH)_2$ **3a**	Biphenyl	1.5	73
5	4-$CH_3O.C_6H_4Br$ **1b**	$C_6H_5B(OH)_2$ **3a**	4-Methoxybiphenyl	6.5	90
6	1-Nap.Br **1d**	$C_6H_5B(OH)_2$ **3a**	1-phenyl naphthyl	2.5	96
7	4-$CH_3C_6H_4Br$ **1e**	4-$ClC_6H_4B(OH)_2$ **3c**	4,4’-Methylchlorobiphenyl	3	68
8	1-Nap.Br **1d**	4-$CH_3OC_6H_4B(OH)_2$ **3b**	4-Methoxyphenyl-1-naphthyl	3	96
9	1-Nap.Br **1d**	1-Nap.$B(OH)_2$ **3d**	1,1’-Binaphthyl.	6	85
10	4-ClC_6H_4Br **1c**	$C_6H_5B(OH)_2$ **3a**	4-Chlorobiphenyl	2	95
11	4-Br.$C_6H_4C_6H_5$ **1f**	2-Nap.$B(OH)_2$ **3e**	2-Napthyl-4-Biphenyl	6	69
12	2-PyBr **1g**	$C_6H_5B(OH)_2$ **3a**	NR	–	NR

[a] Reaction conditions: ArBr (0.5 mmol), Aryl boronic acid (0.6 mmol), K_3PO_4 (0.6 mmol), TBABr (0.5 mmol), Ni-Pd QD (0.005 g, 0.03 mmol), Dioxane:Water (1:1. 10 mL), Argon, 130°C

[b] Catalyst: Cu-Pd QD

Table 4 — Comparison of arylation catalyzed by Pd QD and $Pd(OAc)_2$[a]

S. No.	Aryl Halide	Aryl Boronic acid	Product	Time (h)	Yield (%)
1	4-$CH_3O.C_6H_4I$ **2b**	$C_6H_5B(OH)_2$ **3b**	4-$CH_3O.C_6H_4.C_6H_5$ **5c**	4	34[a]
2	4-$CH_3O.C_6H_4Br$ **1b**	$C_6H_5B(OH)_2$ **3a**	4-$CH_3O.C_6H_4.C_6H_5$ **5c**	6.5	23[b]

[a] Reaction conditions: ArX (0.5 mmol), Aryl boronic acid (0.6 mmol), K_3PO_4 (0.6 mmol), TBABr (0.5 mmol), Cat : Pd QD (0.003 g, 0.03 mmol),
Dioxane:Water (1:1. 10 mL), Argon, 130°C, a: $Pd(OAc)_2$ b: Pd QD

(iii) Transmetalation: The alkene reacts with the Pd-Cu complex to form a Pd-alkene complex.

(iv) Reductive elimination: The Pd alkene complex undergoes reductive elimination to form the new carbon-carbon double bond.

The Suzuki coupling is reaction between an aryl halide and an aryl boronic acid to form a C-C bond through similar mechanism.

In both reactions, the bimetallic nature of the QDs enhances the catalytic activity and selectivity compared to monometallic catalysts due to the synergism between the two metals.

QDs are nanoscale particles typically ranging from 1 to 10 nm in diameter. The unique structure provides a high surface area to volume ratio. QDs have unique electronic properties such as quantum confinement, which tune their electronic structure and energy levels. This allows for the precise control of the electronic properties of the catalyst, enhancing catalytic activity and selectivity. The surface chemistry of QDs is also precisely controlled, allowing for the functionalization of surface with ligands or other chemical groups. This enhances the stability and selectivity of the catalyst, as well as control the size and shape of the nano particles. In contrast other catalysts may not have the same level of control over their size, structure and electronic properties, surface chemistry or optical properties.

The energy levels of the metal atoms in the QD can be modulated by the presence of the second metal atom, leading to a shift in the electron density and energy levels. The interaction between the two metal atoms lead to increased electronic delocalization, resulting in a more efficient electron transfer and faster catalytic reaction rates. The presence of the second metal atom alters the surface chemistry of the QD, leading to changes in the adsorption and desorption properties of the catalyst.

The bimetallic nature of QDs affect the electron transfer and reactivity of the catalyst by altering the energy levels, electronic delocalization, surface chemistry, and enabling synergistic effects.

Bimetallic quantum dots exhibit enhanced reactivity towards aryl bromides by providing a high surface area and unique electronic properties, which improve the adsorption of aryl bromides onto the catalytic surface. The presence of the second metal in the alloy enhance the adsorption of the reactants onto the catalyst surface and facilitate the oxidative addition and reductive elimination steps of the catalytic cycle. The synergistic interaction between the two metal atoms promotes the formation of the aryl-metal bond.

Bimetallic QDs have a high surface area to-volume ratio, providing a large number of active sites for catalytic reactions. This is because the atoms in the QDs are located on the surface, which allows for greater exposure to the reactants. The size and shape of bimetallic quantum dots is precisely controlled during synthesis, which lead to better control over the catalytic properties. The close packing of atoms in the QD structure leads to a higher degree of structural order and stability. The combination of two different metals lead to new electronic and geometric properties that are not present in either metal alone.

Bimetallic quantum dots are often alloys, homogeneously mixed at the nanoscale level. This has a significant impact on their electronic and catalytic properties. The alloy composition also affects the redox properties of the bimetallic quantum dots, which influence their ability to participate in oxidation-reduction reactions.

In cross-coupling reactions, bimetallic nano alloys exhibit improved reactivity and selectivity compared to monometallic catalysts. The resistance of bimetallic QDs to halogen acids indeed improve their catalysis ability. Halogen acids, liberated during the cross-coupling reaction of the aryl halides, cause corrosion and leaching of the mono metal catalysts, which lead to a decrease in catalytic activity and selectivity. Bimetallic QDs, on the other hand, exhibit improved resistance to halogen acids compared to monometallic catalysts. The combination of two different metals in the QD lead to a material that is more stable and less susceptible to corrosion and leaching. The alloying of the two metals at the nano scale, also lead to the formation of a passivation layer that protect the catalyst from further leaching. Overall, the resistance of bimetallic alloys to halogen acids improves their catalysis ability by enhancing their stability and preventing corrosion and leaching of the metal catalysts. Further work on the mechanism and applications of such redox couple QDs is in progress.

Experimental Section

(a) Synthesis of CuPd quantum dots (10:1)

10 mmol (0.24 mg for 100 mL) solution of copper (II) nitrate trihydrate and one mmol (0.017 g for 100 mL) palladium (II) chloride were prepared in distilled water. Then 100 mL of each solution was

taken into two separate flasks. Then 5 mL of neem extract was added to each flask of a metal solution, and the flasks were sonicated for 30 minutes, at RT individually. After sonication, both solutions of Cu $(NO_3)_2$ & $PdCl_2$ were mixed and again sonicated for 30 minutes. The solution was sonicated and then adjusted to *p*H 8 with 1 M NaOH and stored overnight. After one day, Cu-Pd (10:1 ratio) quantum dots were formed and characterized by UV, XRD, TEM-EDAX (See Supporting Information) and further used for catalyzing coupling reactions.

(b) Common Procedure for the Bimetallic Cu-Pd QDs catalyzed alkenylation

0.157 g of aryl halide was taken in 5 mL of NMP and added 0.2 g of styrene, 0.322 g of TBABr, 0.165 g K_2CO_3 followed by 0.010 g Cu-Pd QDs in a round bottom flask and heated to 150°C for 2-6 h under argon atmosphere. The reaction was TLC monitored, and after completion, quenched by adding water. Usual workup by extraction with ethyl acetate gave the crude product. The crude product was purified by column chromatography on silica gel (100-200 mesh, Petroleum Ether: 2% Ethyl acetate). The compounds were completely characterized, and information provided in the Supporting Information.

(c) General procedure for the arylation catalyzed by Bimetallic Ni-Pd QDs

To 10 mL of solvent dioxane:water (1:1) in a round bottomed flask, was added (0.5 mmol) of aryl bromide, aryl boronic acid (0.6 mmol), TBABr (0.5 mmol) and K_3PO_4 (0.6 mmol) followed by Ni-Pd QDs (0.03 mmol). Refluxing at 130°C for 2-6 h under argon gave after standard extractive workup followed by chromatographic purification over silica gel (100–200 mesh, 2% Ethyl acetate: petroleum ether) gave the pure product in high yields. Characterization data are provided in the Supplementary Information.

Conclusion

Bimetallic Cu-Pd and Ni-Pd quantum dots are readily synthesized following green protocols using neem leaf extract. These are efficient ligand-free catalysts and activate aryl bromides for the coupling with alkenes and aryl boronic acids. Bimetallic QDs are better catalysts than monometallic Pd for both the cross-coupling reactions.

Supplementary Information

Catalyst characterization and spectral data for all compounds are available in the Supplementary Information. Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

Conflicts of interest

There are no conflicts to declare.

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