

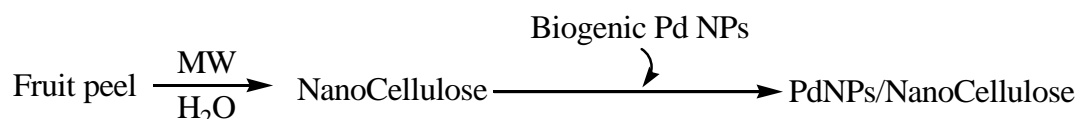
## PROJECT COMPLETION REPORT

- 1. Title of the Project:** *“Development of catalytic reaction strategies for the synthesis and functionalization of potential bioactive heterocyclic molecules”*
- 2. Principal Investigator :** Dr. Anindita Dewan
- 3. Mentor:** Professor A. J. Thakur
- 4. Implementing Institution and other collaborating Institution(s):** Tezpur University,
- 5. Date of Commencement:** 04/10/2019
- 6. Planned Date of Completion:** 03/10/2022
- 7. Actual Date of Completion:** 03/10/2022
- 8. Objectives as stated in the project proposal:**
  1. Development of new transition metal based (Pd, Cu & Rh) homogeneous and heterogeneous catalyst for the synthesis and functionalization of bioactive heterocyclic molecules. NOSE approach will be employed to get better yield, selectivity and reusability. Bio-based support will be developed for synthesis of heterogeneous catalyst.

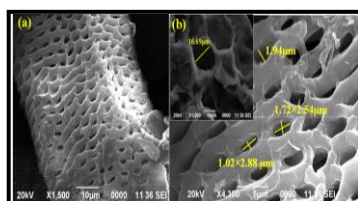
Following relations will be carried out using newly developed catalyst systems

2. Sequential synthesis of carbazoles from aryl and heteroarylboronic acids via C-H activation
3. Sequential synthesis of acridones from aryl and heteroarylboronic acids via Oxidative C–H/C–H Carbonylation
4. Synthesis of chromone or quinolone and indole derivatives via tandem Sonogashira coupling and cyclization reaction
5. Synthesis of isocoumarins via tandem coupling and cyclization reaction of o-iodobenzoic acid with terminal alkynes.

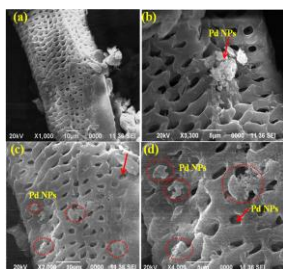
6. Functionalization of heteroaromatic compounds by cross coupling strategies
  7. Newly synthesized catalyst and heterocyclic molecules will be characterized by modern analytical and spectroscopic tools such as TEM, SEM, EDX, PXRD, FTIR, UV-Vis,  $^1\text{H}$  &  $^{13}\text{C}$ NMR, and HRMS
- 9. Deviation made from original objectives if any, while implementing the project and reasons thereof:** There is no deviation from the original objectives.
- 10. Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs:**



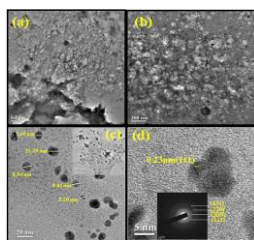
We have try to develop a renewable, recyclable, nature benign bionanocellulose based honey comb like heterogeneous surface from waste fruits peel by simple microwave technique in pure water without using any other external chemicals within very short reaction time under neutral reaction conditions. The Pd nanoparticles are loaded on the bionanocellulose surface by simple stirring at room temperature and characterized by several sophisticated analytical tools like XRD, SEM, TEM, FTIR, BET etc.



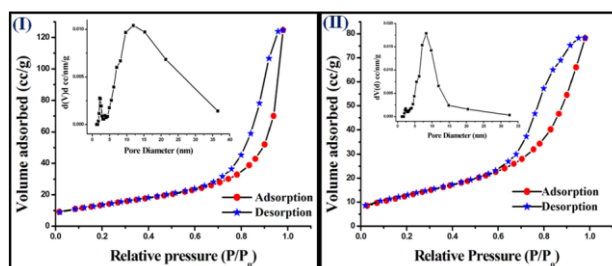
**Fig. 1 (a) and (b)** SEM image of bionanocellulose



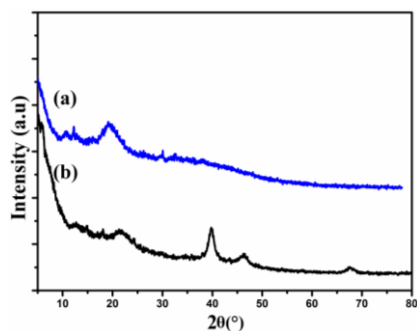
**Figure 2(a-d)** SEM images of Pd NP supported NanoCellulose



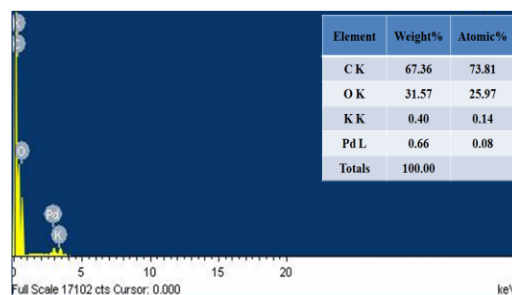
**Figure 3** TEM images of (a) NanoCellulose (b) and (c) Pd NP@ NanoCellulose; (d) HRTEM image and SAED pattern of Pd NP@ NanoCellulose



**Figure 4** N<sub>2</sub> adsorption/desorption isotherm of (I) NanoCellulose and (II) Pd NP@ NanoCellulose and inset in (I) & (II) are the pore size distribution curves

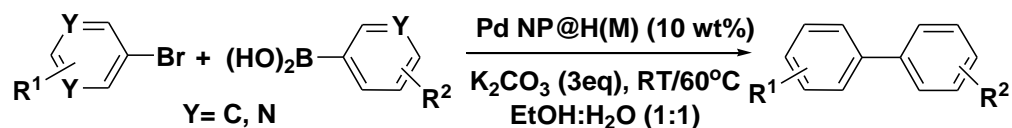


**Figure 5** Powder XRD spectra of (a) NanoCellulose and (b) PdNP@NanoCellulose



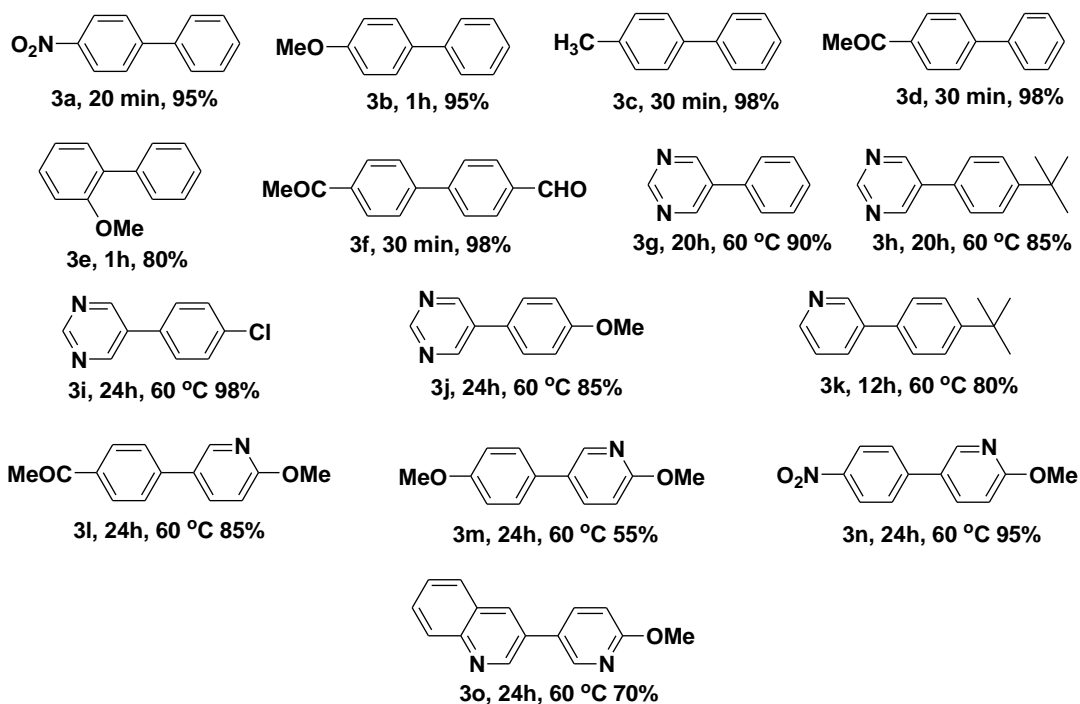
**Figure 6** EDX images of Pd NP@NanoCellulose

The newly developed heterogeneous nanocomposite material has been utilized as efficient heterogeneous catalyst PdNPs@NanoCellulose (PdNP@H(M)) for the synthesis of potential bioactive biaryl/heterobiaryl up to 98% yield via Suzuki-Miyaura reaction (**Scheme 1**). The catalyst is reusable up to six catalytic circles without significant loss of its catalytic activity.



**Scheme 1:** PdNP@NanoCellulose catalyzed Suzuki-Miyaura reaction

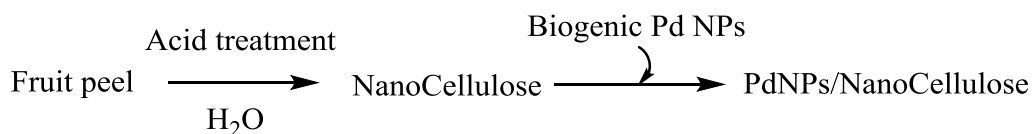
**Table 1:** Substrate scope for Suzuki–Miyaura reaction



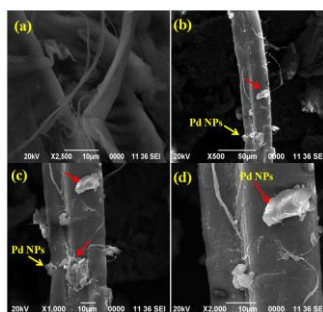
The same heterogeneous catalyst PdNPs@NanoCellulose (PdNP@H(M)) has been applied for the synthesis of potential bioactive alkynyl/heteroalkynyl derivatives via Sonogashira reaction in excellent yield (**Scheme 2**).



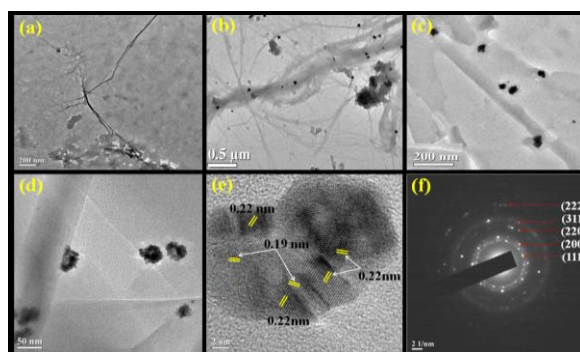
Next, here we have try to reports the design, synthesis and application of naturally occurring cellulose, generated from agro waste pomegranate peel, as novel supports for active biogenic Pd(0) nanoparticles (NPs) (**Scheme 3**) for room temperature Suzuki-Miyaura and Sonogashira cross-coupling reactions. The Pd nanoparticles are loaded on the bionanocellulose surface by simple stirring at room temperature and characterized by several sophisticated analytical tools like XRD, SEM, TEM, FTIR, BET etc.



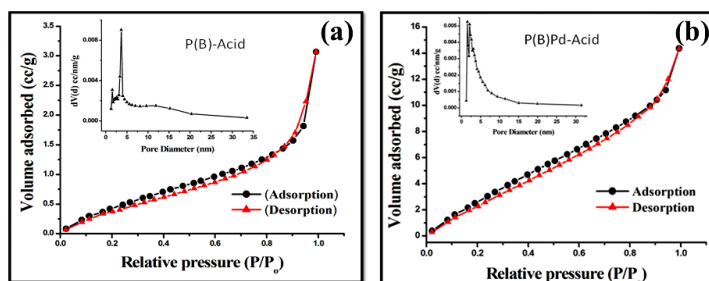
**Scheme 3:** Synthesis of bio-based surface and immobilization of Pd NPs on it



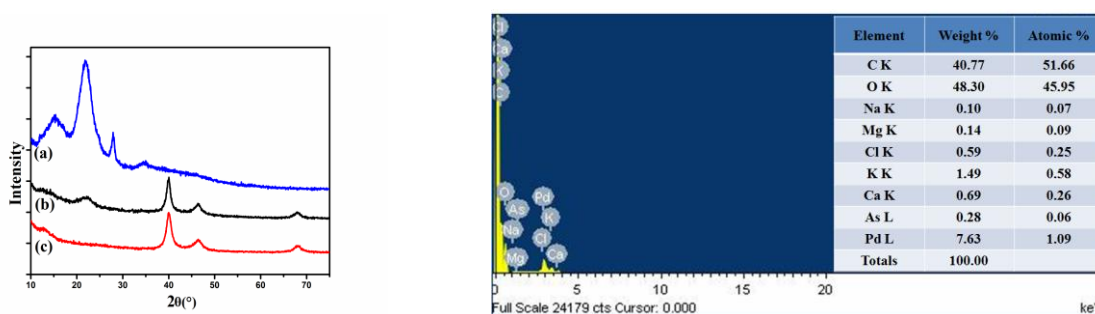
**Figure 7:** SEM images of (a) CNF and (b), (c) & (d) of Pd@CNF



**Figure 8:** TEM images of (a) CNF, (b), (c) and (d) Pd@CNF; (e) HRTEM image and (f) SAED pattern of Pd@CNF



**Figure 9:** N<sub>2</sub> adsorption/desorption isotherms of (a) CNF (b) Pd@CNF, and inset in (3a) & (3b) are the pore size distribution curves

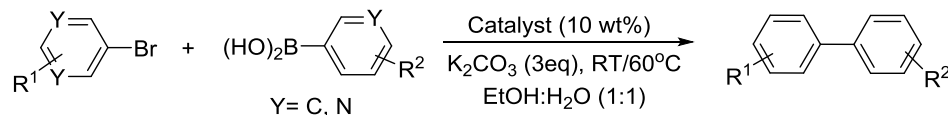


**Figure 10:** Powder XRD spectra of (a) CNF (b) Pd@CNF and (c) PdNP

**Figure 11:** EDX image of Pd@CNF

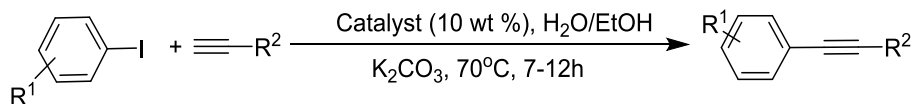
In order to reveal the incorporation in Pd NPs in CNF, ICP-OES analysis of Pd@CNF was performed, and it was found that 1 gram of solid Pd@CNF contains 15 mg palladium.

The catalytic reactivity of this newly developed heterogeneous biodegradable catalyst (Pd@CNF) has been utilised for the synthesis of potential bioactive biaryl up to 98% yield via Suzuki-Miyaura cross-coupling reaction.



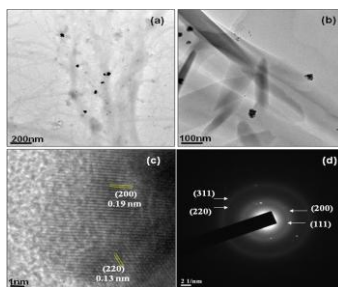
**Scheme 4:** Pd@CNF catalysed Suzuki–Miyaura reaction

The same heterogeneous catalyst Pd@CNF has been applied for the synthesis of potential bioactive alkynyl derivatives via Sonogashira reaction in excellent yield



**Scheme 5:** Pd@CNF catalysed Sonogashira coupling of aryl iodides and terminal acetylene

The catalyst is reusable up to fifth catalytic circles without significant loss of its catalytic activity.



**Figure 12:** (a,b) TEM and (c) HRTEM images of Pd@CNF after 5<sup>th</sup> reuse, and (d) SAED pattern of Pd@CNF.

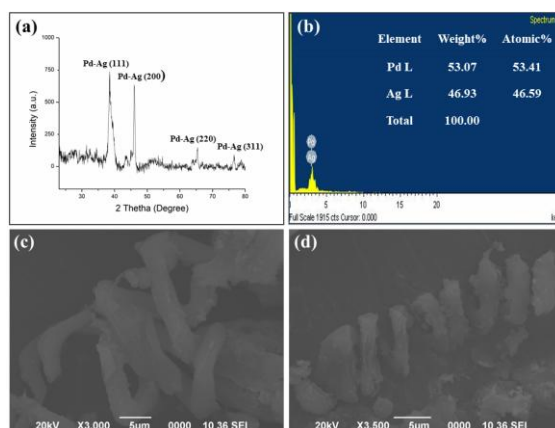
This work presents the utilization of natural organic waste for the synthesis of stable, renewable, recyclable cellulosic nanofibers and Pd-anchored heterogeneous nanofibers. The *in-situ* generation and immobilization of biogenic PdNPs to cellulosic nanofibers demonstrated outstanding catalytic effectiveness in promoting Suzuki-Miyaura and Sonogashira cross-coupling reaction under ligand-free and mild reaction conditions. The newly developed bio-based heterogeneous catalyst Pd@CNF is reusable up to five catalytic cycles without significant loss of catalytic activity.

[This work is published in *Sustainable Chemistry and Pharmacy*, 2021, 23, 100502]

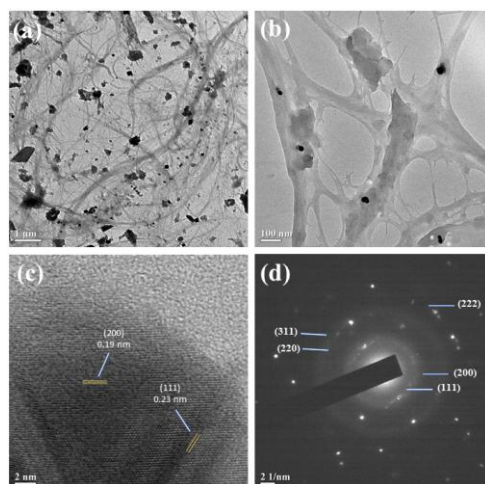
Next, we have utilized a potent natural organic waste material in the synthesis of stable bimetallic Pd/Ag nanoparticles in a cost-effective and environmental approach.



The formation of bimetallic nano hybrid was confirmed by standard analytical techniques such as TEM, SEM, EDX, PXRD and ICP-AES analysis. The synthesized nanoparticles demonstrated outstanding catalytic effectiveness in promoting Suzuki-Miyaura cross coupling of heteroaryl compounds. The protocol enabled the preparation of a range of *N*-heterocyclic biaryl compounds under ambient conditions with a low catalyst loading. The synergic interactions between the two metals existing adjacent to each other in the nano hybrid resulted in its catalytic enhancement for the cross-coupling reaction. The methodology opens the opportunity for the large-scale synthesis of active biological targets in a green and economical manner.



**Figure 13.** (a) PXRD pattern, (b) EDX pattern, and (c,d) SEM images of bimetallic Pd/Ag NPs.



**Figure 14** (a,b) TEM images, (c) HRTEM image, and (d) SAED image of bimetallic Pd/Ag NPs.

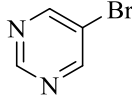
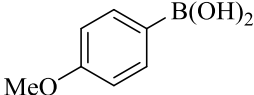
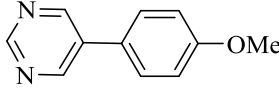
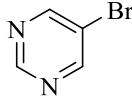
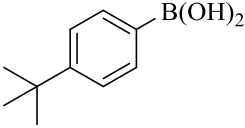
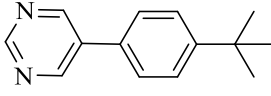
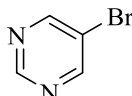
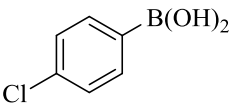
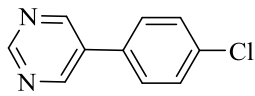
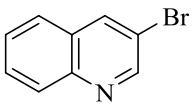
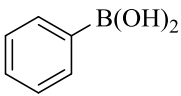
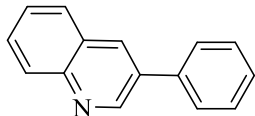
The reactivity of waste-derived bimetallic Pd/Ag NPs in heterocyclic series is unknown and the reaction condition must be improved in terms of green chemistry (solvent, reaction parameters and recycling). To determine the efficiency of the synthesized Pd/Ag NPs towards the Suzuki-Miyaura cross-coupling reaction, we considered 3-bromopyridine and phenylboronic acid as the model substrates in the presence of  $K_2CO_3$  as base.

To determine the usefulness of bimetallic Pd/Ag NPs in the current methodology, we performed a reaction with monometallic Pd NPs synthesized by same bio-reduction technique in our laboratory and observed 78% yield of the desired product in 8 h. The result indicates the synergic ability of AgNPs in assisting PdNPs in the catalytic enhancement of the cross-coupling reaction.

**Table 3:**

Suzuki-Miyaura coupling of *N*-heteroaryl halides and arylboronic acids<sup>a</sup>

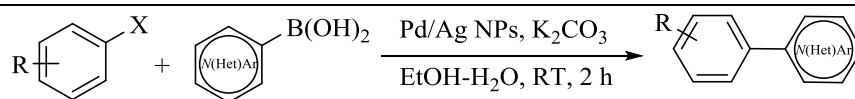
Entry	Heteroaryl halides	Arylboronic acids	Product	Yield <sup>b</sup> (%)
1				92
2				88
3				89
4				81
5				85

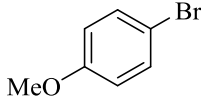
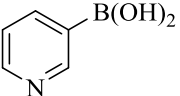
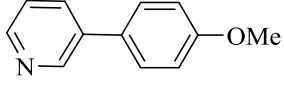
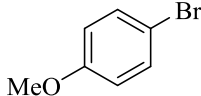
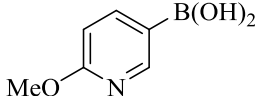
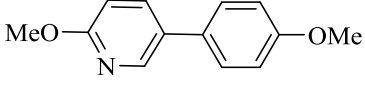
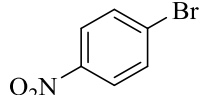
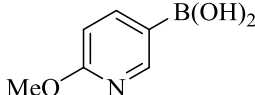
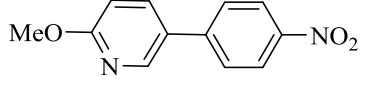
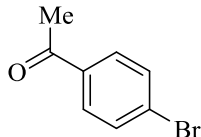
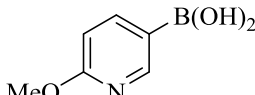
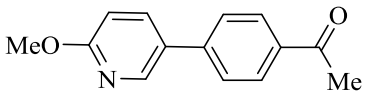
6				83
7				85
8				79
9				72

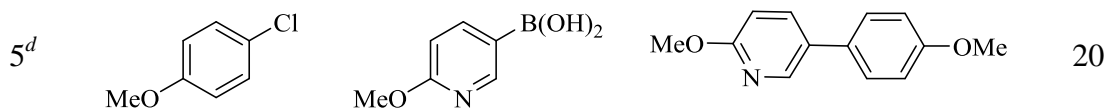
<sup>a</sup>Reaction conditions: heteroaryl halide (0.5 mmol), arylboronic acid (0.6 mmol), Pd/Ag NPs (0.01 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), H<sub>2</sub>O-EtOH (4 ml), RT, 2 h, air; <sup>b</sup>yield.

**Table 4:**

Suzuki-Miyaura coupling of aryl halides and *N*-heteroarylboronic acids<sup>a</sup>



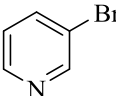
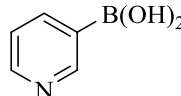
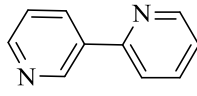
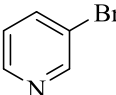
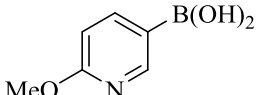
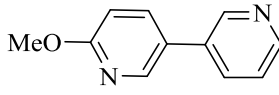
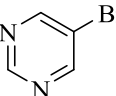
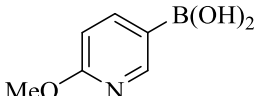
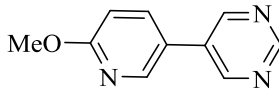
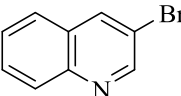
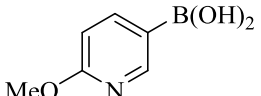
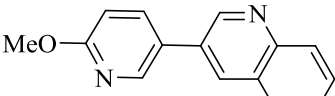
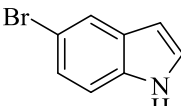
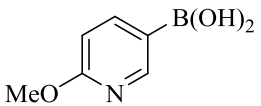
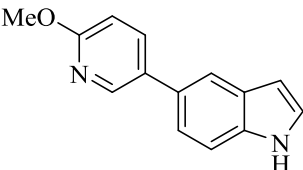
Entry	Aryl halides	Heteroarylboronic acids	Product	Yield <sup>b</sup> (%)
1 <sup>c</sup>				77
2				85
3				82
4				81



<sup>a</sup>Reaction conditions: aryl halide (0.5 mmol), heteroarylboronic acid (0.6 mmol), Pd/Ag NPs (0.01 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), H<sub>2</sub>O-EtOH (4 ml), RT, 2 h, air; <sup>b</sup>yield; <sup>c</sup>reaction time 6 h; <sup>d</sup>reaction time 12 h.

**Table 5:**

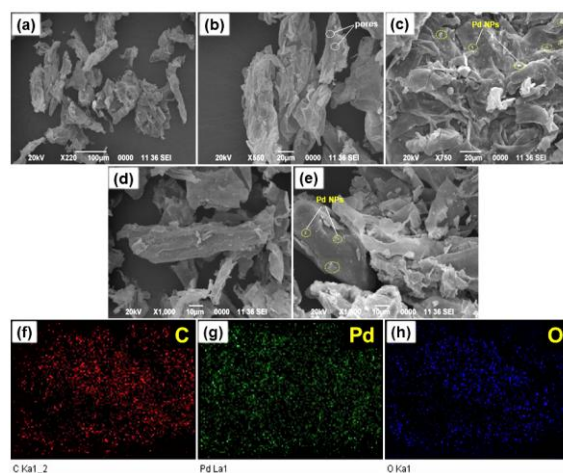
Suzuki-Miyaura coupling of *N*-heteroaryl halides and *N*-heteroarylboronic acids<sup>a</sup>

Entry	Heteroaryl halides	Heteroarylboronic acids	Product	Yield <sup>b</sup> (%)
1 <sup>c</sup>				10
2				84
3				83
4				80
5 <sup>d</sup>				76

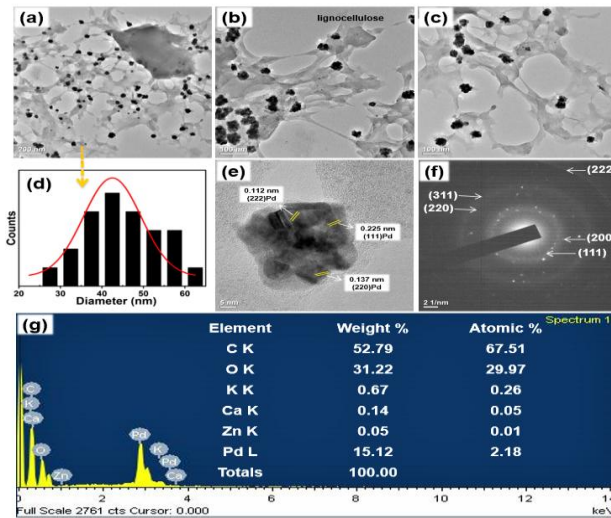
<sup>a</sup>Reaction conditions: heteroaryl halide (0.5 mmol), heteroarylboronic acid (0.6 mmol), Pd/Ag NPs (0.01 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), H<sub>2</sub>O-EtOH (4 ml), RT, 2 h, air; <sup>b</sup>yield; <sup>c</sup>reaction time 12 h; <sup>d</sup>temperature 40 °C, reaction time 5 h.

*This work is published in Green Chem., 2022, 24, 7208-7219.*

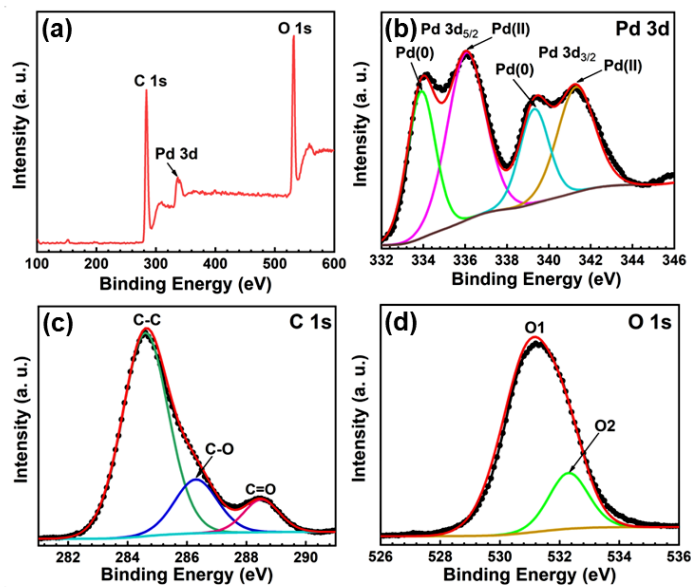
Next, this work demonstrated that lignocellulose derived from pomegranate peels can be utilized as a highly adaptable material for anchoring Pd nanoparticles, both in terms of its production route and material efficiency. The micrographs of lignocellulose-supported Pd nanomaterials showcase the synthesized Pd nanoparticles fairly entangled in the spider-web like 3D bio-network which stabilizes their dispersion. The synthesized Pd NPs@LCpp displayed remarkable catalytic proficiency in site-selective C2-H arylation of *N*-H indoles with arylboronic acids without resorting to directing group instalment on substrate. Compared to our previously developed methodology, the present catalyst system showed remarkable functionality tolerance towards indole bearing free *N*-H group. The presence of lignocellulosic support offers multifunctional features over conventional Pd catalysis, in terms of improved activity, selectivity, free *N*-H functionality tolerance, minimal metal leaching, and reusability for at least five reaction cycles, thus improving the overall efficiency of the process. Optimization of the method revealed the potential for minimizing Ag consumption throughout the re-cyclability course. The new catalyst was also found to be active for selective double functionalization of indole frameworks in a one-pot system. The sustainability profile presented by the process, unfolds a straightforward and scalable route to production of raw biomass-based supported nanomaterials of high potentials.



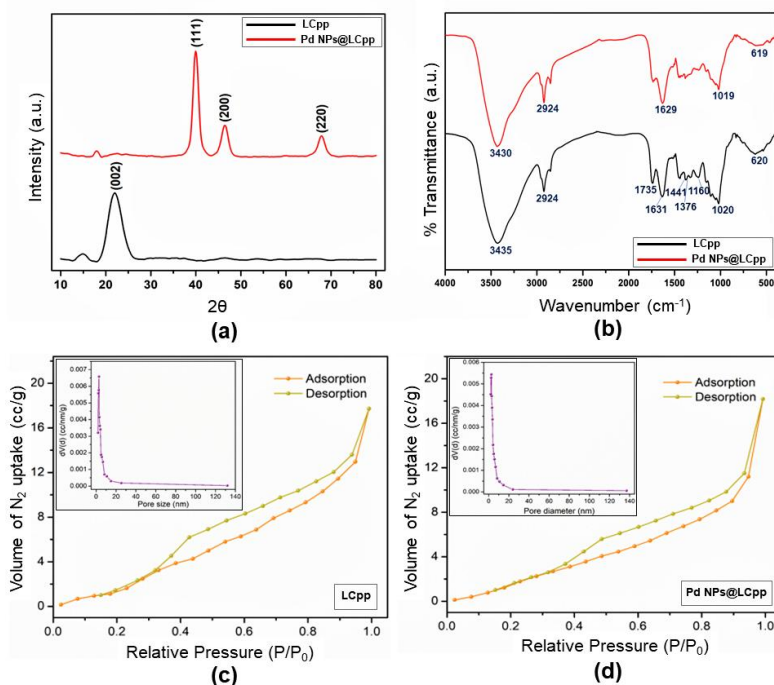
**Figure 15:** SEM micrographs of (a, b) LCpp, (c-e) Pd NPs@LCpp, and corresponding (f-h) EDX elemental mapping images



**Figure 16** (a-c): TEM images, (d) particle size distribution histogram (e) HRTEM image, (f) SAED pattern, and (g) EDX image of Pd NPs@LCpp

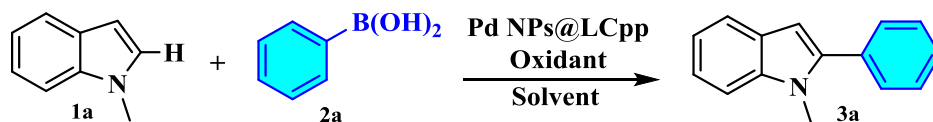


**Figure 17** (a) Survey scans XPS spectrum of Pd NPs@LCpp and corresponding high-resolution XPS spectra of (b) Pd 3d, (c) C 1s and (d) O 1s



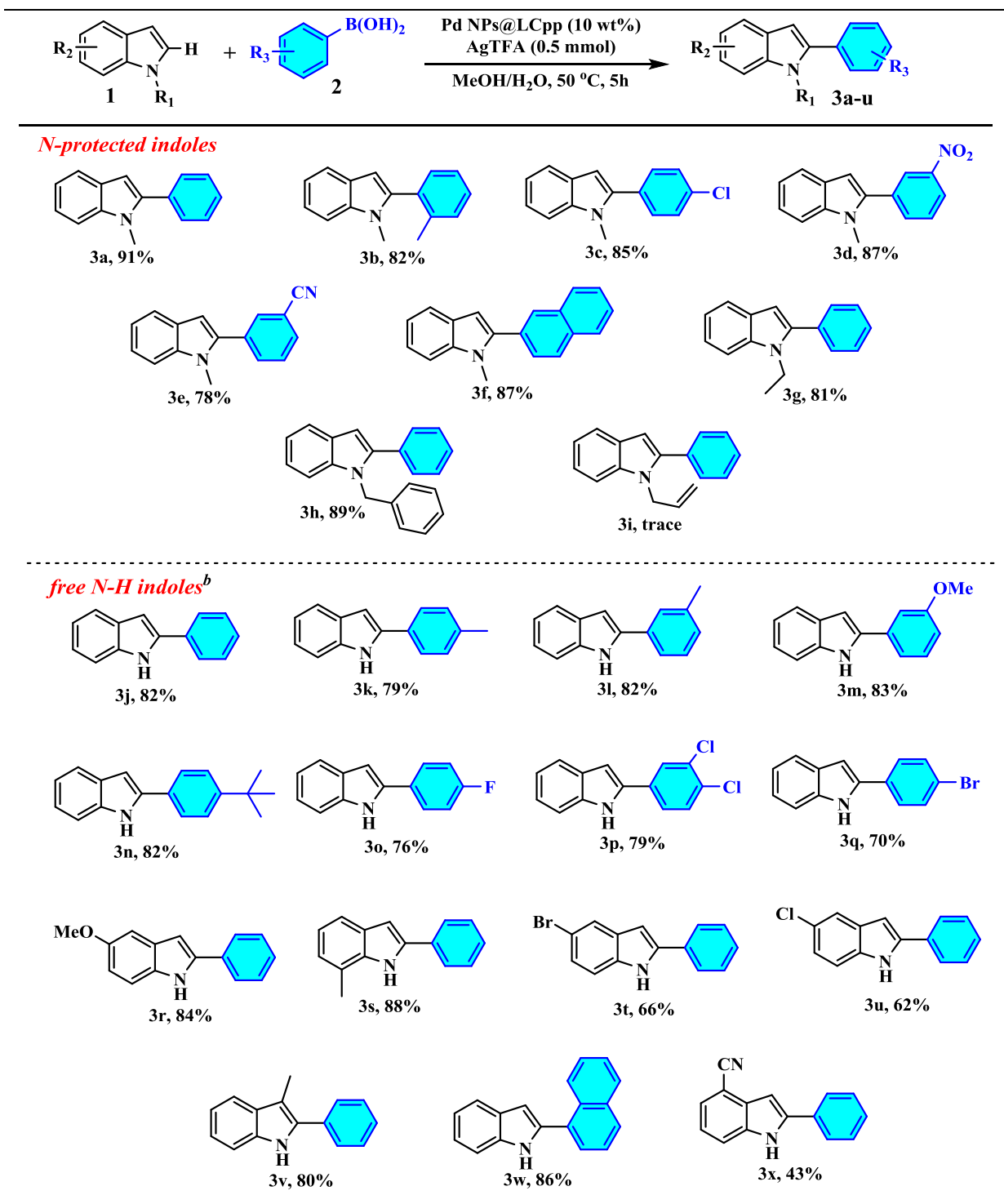
**Figure 18** (a) Powder XRD patterns, (b) FTIR spectra of LCpp and Pd NPs@LCpp, N<sub>2</sub> adsorption/desorption isotherms of (c) LCpp and (d) Pd NPs@LCpp and inset in (c, d) shows the BJH pore size distribution curves

In our desire to appraise the catalytic effectuality of the as-prepare PdNPs@LCpp, we employed it as a catalyst in the C2-H arylation of indoles with arylboronic acids in the absence of any ligands or directing groups.



**Scheme A**

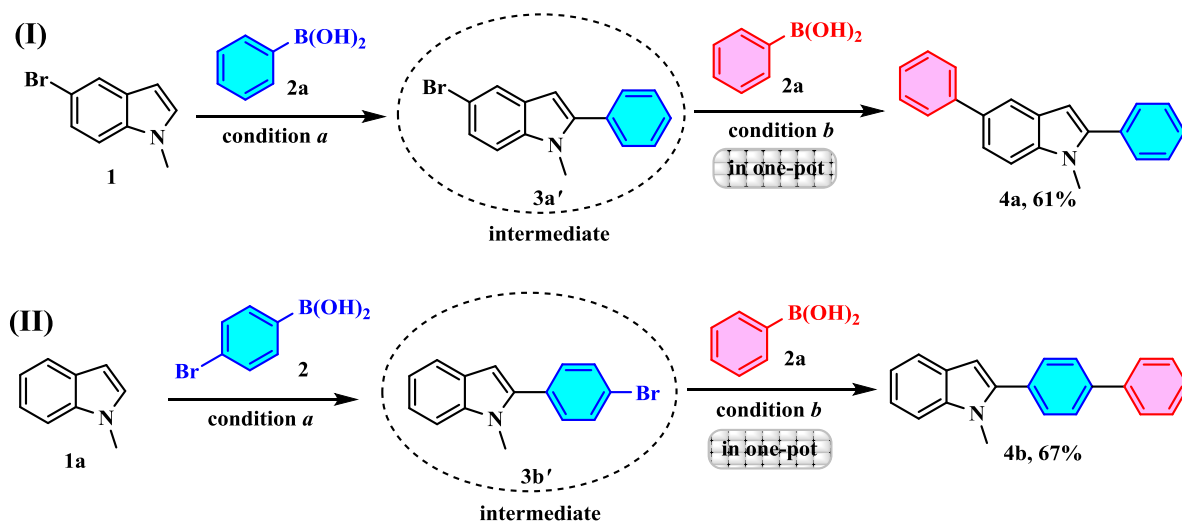
**Table 6:** Substrate scope for C2-H arylation of indoles with arylboronic acids<sup>a</sup>



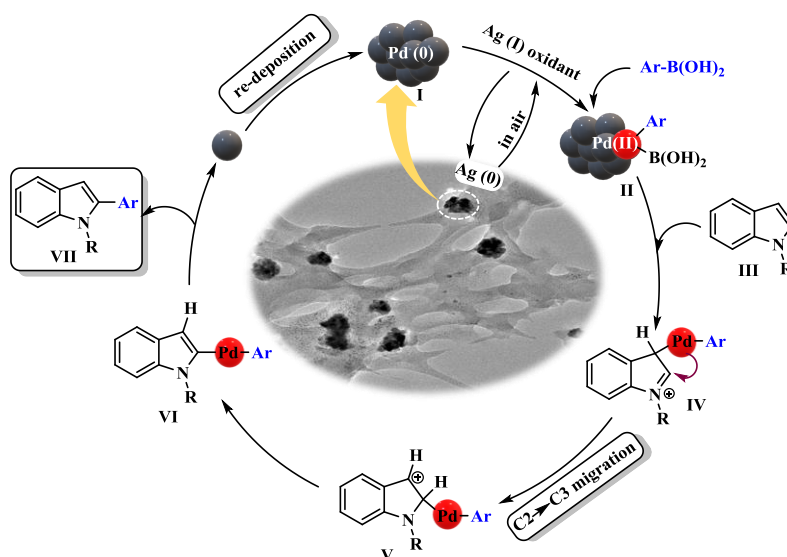
<sup>a</sup>Reaction conditions: indole (1 mmol), boronic acid (1.2 mmol), Pd NPs@LCpp (10 wt %, 0.001 mmol Pd), AgTFA (0.5 mmol), MeOH)/H<sub>2</sub>O (5:1) 2mL, temperature (50 °C), time (5 h), in air; <sup>b</sup> reaction time (12 h)



On a similar line (**Scheme 2(II)**), *N*-methyl indole **1a** was allowed to react with 4-bromophenylboronic acid **2**, where the C2 arylated product **3b'** was double functionalized to 2-([1,1'-biphenyl]-4-yl)-*N*-methyl indole **4b** in one-pot process. Thus, the method extends introduction of additional functionalities in the indole heterocyclic cores, thereby increasing their synthetic value. The Pd NPs@LCpp proved highly effective in both the steps of sequential transformations in a very low Pd loading, avoiding any further addition for the subsequent step.



**Scheme B (I, II)** Sequential one-pot double functionalization of indoles



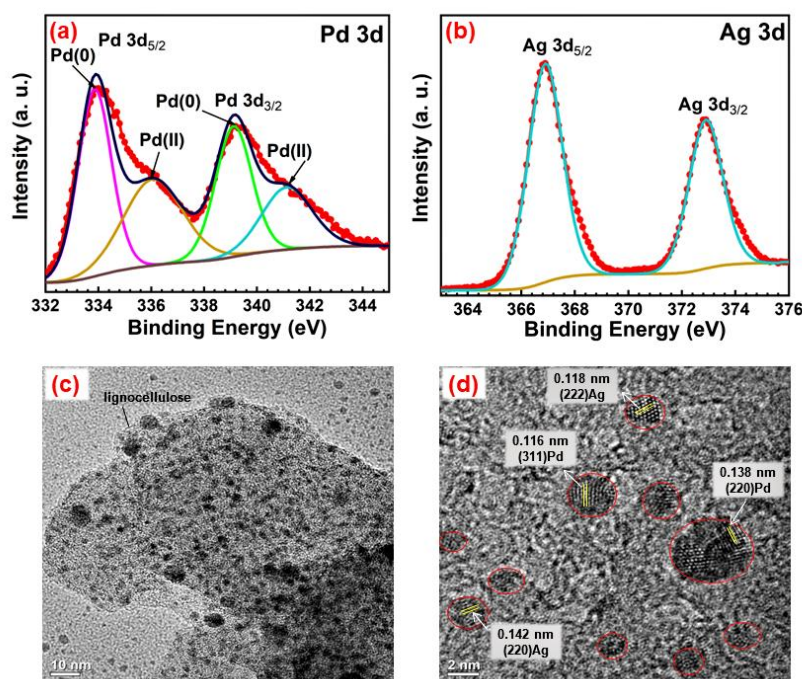
**Scheme :** Plausible mechanism for C2-H arylation of indoles with arylboronic acids

**Recyclability study:**

<p><b>1a</b></p> <p>+</p> <p><b>2a</b></p>	$\xrightarrow{\text{reaction conditions}}$	<b>cycle</b>	<b>1<sup>st</sup> run</b>	<b>2<sup>nd</sup> run</b>	<b>3<sup>rd</sup> run</b>	<b>4<sup>th</sup> run</b>	<b>5<sup>th</sup> run</b>
		Yield (%)	91	91	86	85	80
		Oxidant (eq.)	0.5	0.3	0.2	0.2	0.2

Reaction conditions: indole (1 mmol), boronic acid (1.2 mmol), Pd NPs@LPP (10 wt %, 0.001 mmol Pd), MeOH)/H<sub>2</sub>O (5:1) 2 mL, temperature (50 °C), time (5 h), in air.

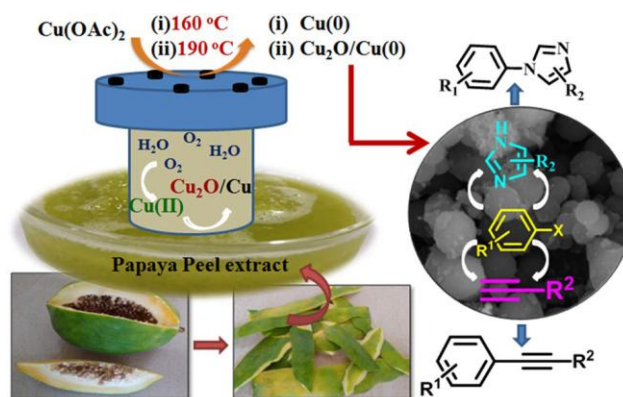
**Table 7:** Reusability test for Pd NPs@LCpp



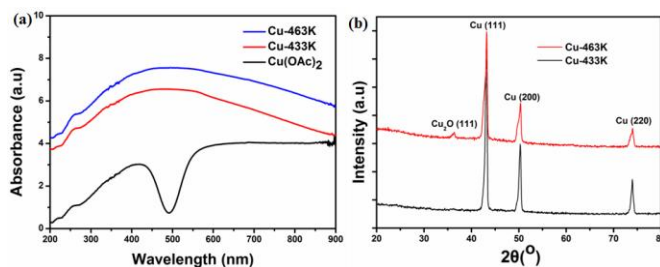
**Figure 19:** High-resolution XPS spectra of (a) Pd 3d and (b) Ag 3d, (c,d) TEM images of recycled Pd NPs@LCpp catalyst

Cu<sub>2</sub>O/Cu nanocatalyst was prepared by simple in situ gas phase H<sub>2</sub>O/O<sub>2</sub> stimulating approach via deposition of Cu<sub>2</sub>O on the surface of Cu nanoparticles (NPs) using aqueous extract of papaya peel. The synthesized hybrid copper catalyst offers an

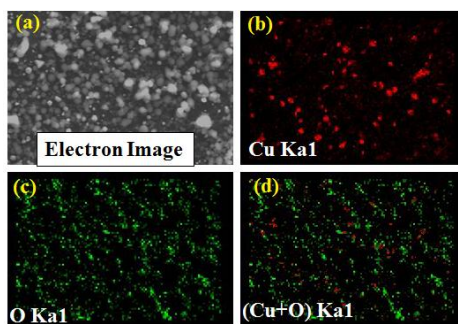
efficient methodology for Pd-free Sonogashira and Chan–Lam cross-coupling reactions. A site-selective type catalytic activity was observed in Sonogashira coupling reaction by performing a controlled experiment using Cu (0) and the hybrid Cu<sub>2</sub>O/ Cu nanocatalyst. It is characterized by solid UV-visible spectroscopy, Fourier transform infrared (FTIR spectroscopy), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). XRD and XPS analysis confirmed the formation of the Cu (0) and Cu<sub>2</sub>O NPs. The Cu<sub>2</sub>O/ Cu NPs appear two different phases distributed like a lamellar sheet stacked one above the other. The presence of Cu<sub>2</sub>O phase in hybrid nano catalyst provides an attractive advantage highlighting a Cu (I)-Cu (0) synergistic interaction in the respective cross-coupling reaction.



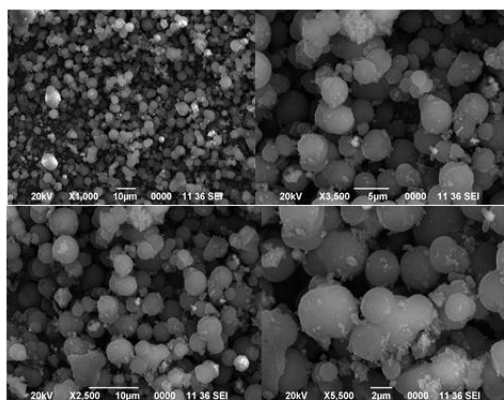
Scheme A



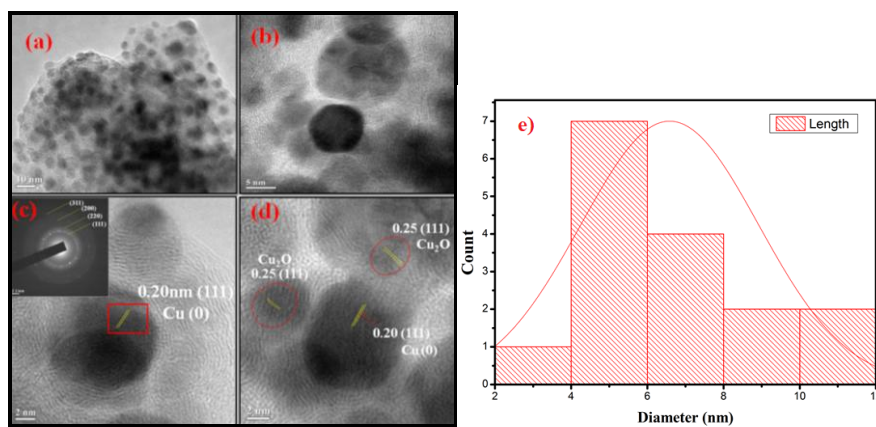
**Figure 2** (a) Solid state UV/Vis spectra of Cu-433K and Cu-463K (b) Powder XRD pattern of Cu(OAc)<sub>2</sub>, Cu-433K and Cu-463K.



**Figure 5** EDS maps (a) electron image (b) Cu distribution (c) O distribution (d) Cu and O distribution of Cu-463K



**Figure 6** The SEM images of Cu-463K



**Figure 7** TEM and HRTEM images and inset in (c) is the SAED pattern of the Cu-463K NPs; e) Particle size distribution histogram

Initially, the catalytic activities of the copper NPs were investigated for Sonogashira cross-coupling reaction considering 4-iodoanisole and phenylacetylene as the model substrate. The reaction was performed under a  $N_2$  atmosphere using  $K_2CO_3$  as a base in

DMF as the reaction medium. A significant difference in catalytic activity for both the copper NPs was observed with Cu-463K being more competent than Cu-433K (**Scheme 1**).

**Table 2** Sonogashira cross-coupling of aryl iodides and phenylacetylene

Entry	R <sup>1</sup>	R <sup>2</sup>	Time(h)	Yield (%) <sup>[b]</sup>
1	4-NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	12	90
2	4-COMe	C <sub>6</sub> H <sub>5</sub>	12	91
3	4-Br	C <sub>6</sub> H <sub>5</sub>	24	70
4	4-OMe	C <sub>6</sub> H <sub>5</sub>	24	80
5	3-NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	12	85
6	3-CHO	C <sub>6</sub> H <sub>5</sub>	24	80
7	4-NO <sub>2</sub>	4-MeC <sub>6</sub> H <sub>5</sub>	12	90
8	4-COMe	3-MeC <sub>6</sub> H <sub>5</sub>	24	80
9	3-	C <sub>6</sub> H <sub>5</sub>	12	60

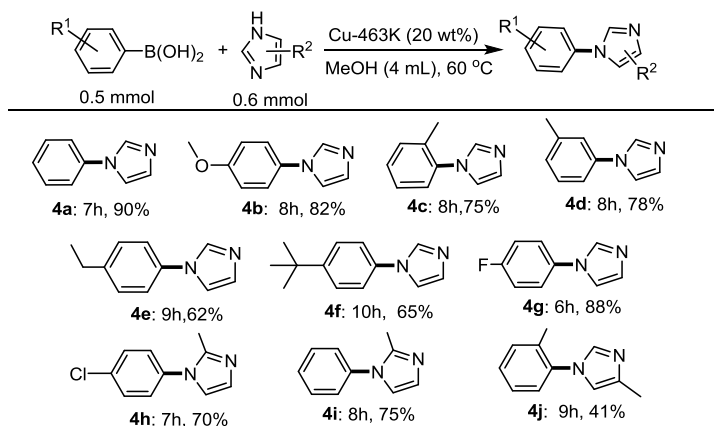
Iodopyridine

<sup>[a]</sup> Reaction conditions: aryl iodide (0.5mmol), phenylacetylene (0.6 mmol), Cu-463K (10 wt%), K<sub>2</sub>CO<sub>3</sub> (2 mmol), DMF (4 mL), N<sub>2</sub> atm;

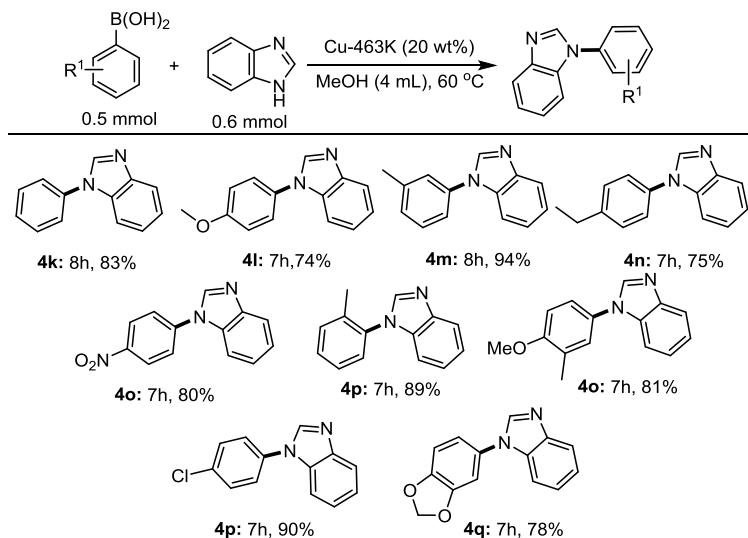
<sup>[b]</sup> Isolated yield

Next, the catalytic efficiency of the Cu/Cu<sub>2</sub>O NPs (Cu-463K) was examined towards C-N cross-coupling of aryl boronic acids with imidazoles.

**Table 4a.** Substrate scope for C-N cross coupling reaction for Imidazole(s) and arylboronic acids.



**Table 4b.** Substrate scope for C-N cross coupling reaction for Benzimidazole and arylboronic acids.



The present methodology highlights an economical alternative strategy for the synthesis of copper NPs using agro-waste material. The *in-situ* fabrication of Cu<sub>2</sub>O particles on the Cu surface *via* gas phase H<sub>2</sub>O/O<sub>2</sub> stimulation without the assistance of conventional reducing agents opens up a newer perspective for the generation of metal NPs. Moreover, the system highlights an efficient palladium free-Sonogashira coupling

reaction avoiding any undesired side product. In addition diverse N-arylated imidazole/benzimidazole could be synthesised using the hybrid Cu<sub>2</sub>O/Cu NPs. The synergistic action between the biphasic Cu(0) and Cu(I) surface shows excellent activity in and C-C/C-N coupling of arylboronic acid with reusability of C-N coupling without significant loss in its activity. Moreover, as future scope, this synthetic methodology can be extended to the synthesis of tri-phasic Cu/Cu<sub>2</sub>O/CuO NPs or bi/trimetallic heterogeneous catalytic system, which might be effective in different catalytic organic transformations.

### **11. Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject:**

Recently, there is a renewed interest in using green chemistry principles in the field of research addressing current requirements in synthetic chemistry and catalysis. Green chemistry is the design, development and implementation of chemical products and processes to reduce the use and generation of substances hazardous to human health and the environment. The extraction and isolation of nanocellulose (as support for metal nano particles) from biomass involve some vigorous pre-treatment processes, directing the elimination of non-cellulosic components, such as polymers of free sugar, fatty acids, flavonoids, terpenoids, hemicellulose and lignin, carried out in a number of chemical, mechanical, and combined methods. Also, the use of harsh chemicals for cellulose extraction is not considered as “green”, negatively interrupting the process through the generation of toxic and hazardous wastes, material contamination, degradation, and overall environmental stress. Recently, a variety of advanced methods such as ionic liquid treatments, use of deep eutectic solvents, microwave and ultrasonic treatments, have also been explored. In this regard, development of a simple extraction method to isolate cellulose fibers from waste fruit peels without using sophisticated chemical pre-treatments or techniques goes in line with environmental preservations and sustainability. Cellulose is an important biopolymer and has received attention as a renewable, nontoxic, inexpensive, and biodegradable plant-derived material. Micro- and nanocrystalline cellulose exhibits unique properties such as high surface area, availability of a large

number of unsaturated hanging bonds on their surfaces, and tenability which make it an appropriate candidate for a wide range of applications such as biomedical products, nanocomposite materials, textiles, heterogeneous surfaces, and so on.

Moreover, the development of the field of green chemistry through organic reactions conducted in aqueous solvent has become one of the most exciting research endeavours for organic chemists. Actually, water is an attractive alternative to traditional organic solvents because it is inexpensive, non-flammable, non-toxic, and environmentally sustainable by alleviating the problem of pollution by organic solvents. Also, water is an attractive solvent for metal-catalyzed reactions, such as C-C couplings and C-N couplings. Furthermore, from the commercial point of view, lack of possibility of reuse of such costly homogeneous catalysts makes their widespread or industrial use less viable. So by using supported or impregnated heterogeneous catalyst will obviously be a better alternative.

## **12. Conclusions summarising the achievements and indication of scope for future work:**

- a) Here we have synthesised a renewable, recyclable, environmental benign bio-nanocellulosebased honeycomb-like heterogeneous surface from waste pomegranate peel using a simple microwave technique in pure water without using any other external chemicals within a very short reaction time under neutral reaction conditions. In situ generation and immobilization of biogenic PdNPs onto NCmw make it an effective heterogeneous catalyst for biaryls and alkynyl derivative synthesis via the Suzuki–Miyaura and Sonogashira cross-coupling reaction. This method is extremel important from the green and sustainable chemistry point of view by utilizing waste materials as renewable sources for a reusable catalyst.
- b) We have also utilized natural agro waste for the synthesis of stable, renewable, recyclable cellulosic nanofibers and Pd-anchored heterogeneous nanofibers. The *in-situ* generation and immobilization of biogenic PdNPs to cellulosic nanofibers demonstrated outstanding catalytic effectiveness in promoting Suzuki-Miyaura



- and Sonogashira cross-coupling reaction under ligand-free and mild reaction conditions. The newly developed bio-based heterogeneous catalyst Pd@CNF is reusable up to five catalytic cycles without significant loss of catalytic activity.
- c) Again we have developed a novel micro-dimensional cellulose fibers from biomass waste using a simple ethanol-water filtration technique. The pomegranate peel derived cellulose micro-fibers presented as an admirable support matrix for bimetallic Pd-Ag nanoparticles. The synergistic visible-light harvesting and electronically interacting centres developed a novel plasmon-enhanced photocatalyst in promoting Suzuki-Miyaura coupling in exciting nitrogen heterocycles at room temperature under visible light.
- d) We have also synthesized lignocellulose derived from pomegranate peels can be utilized as a highly adaptable material for anchoring Pd nanoparticles, both in terms of its production route and material efficiency. The micrographs of lignocellulose-supported Pd nanomaterials showcase the synthesized Pd nanoparticles fairly entangled in the spider-web like 3D bio-network which stabilizes their dispersion. The synthesized Pd NPs@LCpp displayed remarkable catalytic proficiency in site-selective C2-H arylation of *N*-H indoles with arylboronic acids without resorting to directing group instalment on substrate. Compared to our previously developed methodology, the present catalyst system showed remarkable functionality tolerance towards indole bearing free *N*-H group. The presence of lignocellulosic support offers multifunctional features over conventional Pd catalysis, in terms of improved activity, selectivity, free *N*-H functionality tolerance, minimal metal leaching, and reusability for at least five reaction cycles, thus improving the overall efficiency of the process. Optimization of the method revealed the potential for minimizing Ag consumption throughout the re-cyclability course. The new catalyst was also found to be active for selective double functionalization of indole frameworks in a one-pot system. The sustainability profile presented by the process, unfolds a straightforward and scalable route to production of raw biomass-based supported nanomaterials of high potentials.
- e) We have also developed a methodology for the synthesis of copper NPs using agro-waste material. The *in-situ* fabrication of Cu<sub>2</sub>O particles on the Cu surface

*via* gas phase H<sub>2</sub>O/O<sub>2</sub> stimulation without the assistance of conventional reducing agents opens up a newer perspective for the generation of metal NPs. Moreover, the system highlights an efficient palladium free-Sonogashira coupling reaction avoiding any undesired side product. In addition diverse N-arylated imidazole/benzimidazole could be synthesised using the hybrid Cu<sub>2</sub>O/Cu NPs. The synergistic action between the biphasic Cu(0) and Cu(I) surface shows excellent activity in and C-C/C-N coupling of arylboronic acid with reusability of C-N coupling without significant loss in its activity. Moreover, as future scope, this synthetic methodology can be extended to the synthesis of tri-phasic Cu/Cu<sub>2</sub>O/CuO NPs or bi/trimetallic heterogeneous catalytic system, which might be effective in different catalytic organic transformations.

### **13. New Observations:**

- a) These heterogeneous nano-catalysts can be easily synthesized at room temperature.
- b) It is efficient catalyst for Suzuki-Miyaura, Sonogashira and Chan-Lam type cross-coupling reaction under mild reaction condition.
- c) We have developed a novel heterogeneous Pd-Ag bimetallic nanoclusters as catalyst which has interfacial electron-transfer from plasmonic metal Ag to Pd makes suitable for room temperature Suzuki-Miyaura coupling of nitrogen-rich heterocycles (74-93 %) under visible light condition.
- d) We have also developed Pd based lignocellulose supported catalytic proficiency in site-selective C<sub>2</sub>-H arylation of *N*-H indoles with arylboronic acids without resorting to directing group instalment on substrate.
- e) We have also synthesised heterogeneous Cu<sub>2</sub>O/Cu nanocatalysts and used it for N-arylated imidazole/benzimidazole and Pd-free Sonogashira coupling reaction.

#### 14. Innovations:

We have developed some renewable, recyclable, environmental benign bio-nanocellulose based heterogeneous surface and catalyst from waste fruits peel using a simple easy and green technique. The Suzuki-Miyaura, Sonogashira type cross-coupling, site-selective C2-H arylation of *N*-H indoles with arylboronic acids without resorting to directing group has been carried out at room temperature using green solvent and green methods. Also developed a novel heterogeneous Pd-Ag nanoparticles as catalyst and utilized for Suzuki-Miyaura cross-coupling reaction of nitrogen-rich heteroaromatics using visible light condition under the framework of green chemistry principles. We have also synthesised Cu based heterogeneous nanocatalysts and used it for *N*-arylated imidazole/benzimidazole and Pd-free Sonogashira coupling reaction.

#### 15. Application Potential:

- a. Immediate: Developed some renewable, recyclable, environmental benign heterogeneous catalyst using natural agro waste and utilized these catalyst for Suzuki-Miyaura, Sonogashira cross-coupling, Chan-Lam type and Indol functionalization reaction under green condition
- b. Long Term: A remarkable amount of progress can be achieved toward solving the long-standing challenge of developing readily available and additives for cross coupling reactions using appropriate choice of catalyst.

#### 16. S&T benefits accrued:

##### a. List of Research publications

S No	Authors	Title of paper	Name of the Journal	Volume	Pages	Year
1.	Anindita Dewan, *	Pd	ACS	9	954-966	2021

	Manashi Sarmah, Pankaj Bharali, Ashim J. Thakur, Purna K. Boruah, Manash R. Das, and Utpal Bora	Nanoparticles- Loaded Honeycomb- Structured Bio- nanocellulose as a Heterogeneous Catalyst for Heteroaryl Cross-Coupling Reaction	Sustainabl e Chem. Eng.			
2	<b>Anindita Dewan</b> *, Manashi Sarmah, Prantika Bhattacharjee, Pankaj Bharali, Ashim J. Thakur, Utpal Bora	Sustainable nano fibrillated cellulose supported <i>in situ</i> biogenic Pd nanoparticles as heterogeneous catalyst for C–C cross coupling reactions	Sustainabl e Chemistry and Pharmacy	23	100502	2021
3	Prantika Bhattacharjee, <b>Anindita Dewan</b> *, Purna K. Boruah, Manash R. Das, Sanjeev P. Mahanta, Ashim J. Thakur, Utpal Bora*	Bimetallic Pd- Ag nanoclusters decorated micro-cellulose bio-template towards efficient catalytic Suzuki- Miyaura coupling	Green Chem.	24	7208- 7219	2022

		reaction of nitrogen-rich heterocycles				
4	P. Bora,; D. Konwar,; <b>A. Dewan.</b> ; M. R Das; U. Bora,	Bio-Carbon Layered CuO Catalysed Decarboxylative Alkenylation of Cyclic Ethers	<i>New J. Chem.</i>	46	12551-12557	2022
5	Manashi Sarmah · Debasish Sarmah · <b>Anindita Dewan</b> · Porag Bora · Purna K. Boruah · Manash R. Das · Pankaj Bharali · Utpal Bora	Dual Responsive Sustainable Cu <sub>2</sub> O/Cu Nanocatalyst for Sonogashira and Chan-Lam Cross-Coupling Reactions	Catalysis Letters		<a href="https://doi.org/10.1007/s10562-022-04060-w">https://doi.org/10.1007/s10562-022-04060-w</a>	2022
6	Sameeran Kumar Das, <b>Anindita Dewan</b> , Pangkita Deka , Rakhee Saikia , Sanjib Thakuria, R.C. Deka , Ashim J. Thakur , Utpal Bora ,*	Biogenic palladium nanostructures for Suzuki-Miyaura and Sonogashira cross-coupling reaction under mild reaction conditions	Current Research in Green and Sustainable Chemistry	5	100301	2022

**b. Manpower trained on the project**

i) **Ph.D. produced:** No

ii) **Other Technical Personnel trained:** Ph.D and MSc student trained.

c. **Patents taken, if any:** No

**17. Financial Position:**

<b>S No</b>	<b>Financial Position/ Budget Head</b>	<b>Funds Sanctioned</b>	<b>Expenditure</b>	<b>% of Total cost</b>
1.	Salaries/ Manpower costs	1st Year:	19,80,000/-	
2.	Equipment	9,45,000/-	1,77,215/-	
3.	Supplies & Materials	2 <sup>nd</sup> Year:	3,99,883/-	
4.	Contingencies	9,15,000/-	74,092/-	
5.	Travel	3 <sup>rd</sup> Year:	-	
6.	Overhead Expenses	7,00,000/-	1,72,851/-	
	Others, if any	27,40,000/-		
	<b>Total</b>		28,04,041/-	<b>100%</b>

**18. Procurement/ Usage of Equipment**

a)


<b>S No</b>	<b>Name of Equipment</b>	<b>Make/ Model</b>	<b>Cost (FE/ Rs)</b>	<b>Date of Installation</b>	<b>Utilisation Rate (%)</b>	<b>Remarks regarding maintenance/ breakdown</b>
1	Laboratory Electrical Muffle Furnace	IIC-106A	49900/-	09/03/20	100%	They are all in good condition
2	LED Digital Magnetic Stirrer With Hot Plate (2 nos.)	Tarsons	49950/-	09/03/20		
3	Laboratory Centrifuge	R8M Plus	29880/-	09/03/20		
4	Computer, Printer	acer & HL-L2321D	47,485/	29/01/21		

**b) Plans for utilising the equipment facilities in future:**

Currently research scholars are using these equipments. Again, I will apply another new project and so for this I will use these equipment.

Name and Signature with Date

a. Anindita Dewan  
(Principal Investigator)

b.  07-02-23  
(Mentor)

**Dr. Ashim Jyoti Thakur**  
Professor  
Dept. of Chemical Sciences  
JNU University, Napam-784028

## STATEMENT OF EXPENDITURE

1. Sanction Order No and Date: SR/WOS-A/ CS-86/2018
2. Total Project Cost: **29,45,000/-**
3. Revised Project Cost (if applicable): **29,45,000/-**
4. Date of Commencement: 04/10/2019
5. Grant received in each year:
  - a. 1<sup>st</sup> Year: **1, 80,000/-** (Non-Recurring Grant) + **9, 45,000/-** (Recurring Grant) = **11, 25,000/-** (Grand Total)
  - b. 2<sup>nd</sup> Year: 9,15,000/-
  - c. 3<sup>rd</sup> Year: 7,00,000/-
  - d. 4<sup>th</sup> Year: 1,50,000/-
  - e. Interest, if any: **6891/- + 1128/- + 3849/-**
  - f. **Total (a+b+c+d): 28,90,000/-**



## STATEMENT OF EXPENDITURE

For the financial year wise (1<sup>st</sup> April 2022 to 4<sup>th</sup> Oct 2022)

S No	Sanctioned Heads	Sanctioned Cost (1 <sup>st</sup> Year + 2 <sup>nd</sup> Year + 3 <sup>rd</sup> Year)	Grant Received (A)	Expenditure Incurred				Total Expenditure IV + V + VI + [VI(a)] (VII)	Balance as on (date) (VIII)	Requirement of Funds for Last year	Remarks (if any)
				1 <sup>st</sup> Year (4 <sup>th</sup> Oct 2019 to 31 <sup>st</sup> March 2020) (IV)	2 <sup>nd</sup> Year (1 <sup>st</sup> April 2020 to 31 <sup>st</sup> March 2021) (V)	3 <sup>rd</sup> Year & so on (1 <sup>st</sup> April 2021 to 31 <sup>st</sup> March 2022) (VI)	(1 <sup>st</sup> April 2022 to 4 <sup>th</sup> October 2022) [VI(a)]				
1.	Fellowship	19,80,000/-	9,45,000/- (1 <sup>st</sup> year)	2,69,677/-	7,15,000/-	6,60,000/-	335,323/-	19,80,000/-			2,785/- (refunded on 9/11/2021)  +  3,200/- (refunded on 2/5/2023)
2.	Consumables	4,00,000/-	+ 9,15,000/- (2 <sup>nd</sup> year)	1,06,647/-	24,914/-	2,03,597/-	64,725/-	399,883/-			
3.	Travel	60,000/-	+ 7,00,000/- (3 <sup>rd</sup> year)+	-	-	-	-	-			
4.	Contingencies	75,000/-	(4 <sup>th</sup> year)	-	29,360/-	20,000/-	24,732/-	74,092/-			
5.	Others, if any	-	150,000/-	-	-	-	-	-			
6.	Overhead expenses	2,50,000/-		56,250/-	51,963/-	64,638/-	77,144/-	2,49,995/-			
7.	Total(without equipment)	2765000/-	27,10,000/-	432574/-	821237/-	948235/-	5,01,924/-	27,03,970/-			
8.	Equipment	1,80,000/-	180,000/-	1,29,730/-	47,485/-	-	-	1,77,215/-			
9.	Total(with equipment)	29,45,000/-	28,90,000	5,62,304/-	868722/-	9,48,235/-	5,01,924/-	28,81,185/-	2,830/-		

*Anindita Dewan*

(Dr. Anindita Dewan)

Name and Signature of Principal Investigator

Date 3/10/23

Signature of Competent financial authority: \_\_\_\_\_

(with seal) *Finance Officer* Date: \_\_\_\_\_

*222pur University*

\* DOS – 4<sup>th</sup> October 2019

Note :

- Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of DST i.e. Figures in Column (VIII) should not exceed corresponding figures in Column (III)
- Utilisation Certificate for each financial year ending 31<sup>st</sup> March has to be enclosed along with request for carry-forward permission to the next financial year.

## GFR-12 – A

[(See Rule 238 (1)]

### FORM OF UTILIZATION CERTIFICATE

#### FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR 1<sup>st</sup> April 2022 to 4<sup>th</sup> October 2022 in respect of **recurring** GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme : **Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No: **SR/WOS-A/CS-86/2018 (C)**
3. Principal Investigator: **Dr. Anindita Dewan**
4. Whether recurring or non-recurring grants: **Recurring Grant**
5. Grants position at the beginning of the Financial year  
(i) Cash in Hand/Bank: **3,57,954/-**  
(ii) Unadjusted advances:  
(iii) Total: **3,57,954/-**
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl. No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Government	Grant received during the year			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
			Sanction No. (i)	Date (ii)	Amount (iii)			
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
3,57,954/-	0	-	SR/WOS-A/CS-86/2018 (C)	14/3/2023	1,50,000	5,07,954/-	5,01,924/-	6,030/-

Component wise utilization of grants:

Grant-in-aid- General	Grant-in-aid- Salary	Total
1,66,601/-	3,35,323/-	5,01,924/-

Details of grants position at the end of the year

- (i) Cash in Hand/Bank: 2830/-
- (ii) Unadjusted Advances: (Refunded 3,200/- to CAN on 2/5/2023)
- (iii) Total: 6,030/-

*Anindita Dewan*  
Signature of PI  
Date 3/10/23

*[Signature]*  
Signature  
Name: *[Signature]*  
(Head of the Finance)/ (With seal)  
Date *Finance Officer*  
*Tezpur University*

*[Signature]*  
Signature  
Name: *[Signature]*  
(Head of the Organisation)/ (With seal)  
Date *Registrar*  
*Tezpur University*



Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

- (i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.
- (ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.
- (iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.
- (iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.
- (v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.
- (vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.
- (vii) It has been ensured that the physical and financial performance under WOS-A (name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.
- (viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)
- (ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date:

Place:

Signature

Name.....

Chief Finance Officer

(Head of the Finance)

*Finance Officer*

*Tezpur University*

(Strike out inapplicable terms)

Signature

Name.....

Head of the Organisation

*Registrar*

*Tezpur University*