

Electronic Supplementary Material (ESI)

for

First report on the utility of organotellurium compound as stabilizer in the colloidal synthesis of applied nanocatalytic system having transition metal: application in O-arylation of phenol

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S1. General Experimental Section

For carrying out HR-TEM studies, JEM 3200FS Electron Microscope operating at 300kV was used. A dispersion of powdered sample in methanol was dropped onto a porous, copper grid supported carbon film and dried under IR-lamp overnight. A JNM ECX-500 NMR spectrometer working at a frequency of 500 MHz was used for recording NMR spectra. FEI-Quanta FEG 200F SEM-EDX system was used for the study of surface morphology and elemental composition. A 9kW SmartLab rotating anode X-ray diffractometer (XRD) was used for PXRD studies. X-ray photoelectron spectroscopic (XPS) studies were carried out using Nexsa base (ThermoFisher) spectrometer. Nitrogen gas was used to create inert atmosphere, wherever required, using Schenk technique. All reactions were carried out in glassware (dried in an oven) under ambient conditions. The ^1H NMR spectroscopy was used to assess the % conversions of the reactants into products in the C–O coupling reaction.

S2. Starting materials, syntheses of ligand L1 and nanoparticles N1-N3

Bromooctadecane and sodium borohydride were obtained from ThermoFisher Scientific. Diphenyl ditelluride and sodium tetrachloropalladate(II) were obtained from Merck Group. Other chemicals and solvents were procured from local suppliers.

S2.1 Synthesis of Ligand (L1)

Diphenyl ditelluride (0.409 g, 1.0 mmol) was stirred in 10 mL of ethanol at 40°C for 30 minutes in a sealed Schlenk tube. The nitrogen gas was purged into the assembly and a solution of NaBH_4 (0.100 g, 2.6 mmol) in 15 mL of ethanol was added using a syringe, followed by the addition of a solution of 1-bromooctadecane (0.666 g, 2.0 mmol) in 10 mL ethanol using a syringe. The reaction was stirred for another two hours at room temperature. The flaky white colored solid (**L1**) was obtained. It was filtered and dried in air.

S2.2 Synthesis of Nanoparticles N1

Ligand **L1** (0.229 g, 0.5 mmol) was dissolved in DCM and subjected to stirring. A solution of Na_2PdCl_4 (0.147 g, 0.5 mmol) in methanol was added to the stirring solution of the ligand. Stirring was continued for 20 minutes. Thereafter, nitrogen gas was purged and solution of NaBH_4 (0.039 g, 1.0 mmol) was added to the solution followed by continuous stirring for 2 hours. Black precipitate of **N1** appeared. The black particles were then extracted and washed with methanol in a centrifuge and the resulting residue was dried in vacuo.

S2.3 Synthesis of Nanoparticles N2

Ligand **L1** (0.229 g, 0.5 mmol) was dissolved in DCM and subjected to stirring. A solution of Na_2PdCl_4 (0.589 g, 2.0 mmol) in methanol was added to the stirring solution of the ligand. Stirring was continued for 20 minutes. Thereafter, nitrogen gas was purged and methanolic solution of NaBH_4 (0.156 g, 4.0 mmol) was added to the solution followed by continuous stirring for 2 hours. Black precipitate of **N2** appeared. The black particles were then extracted and washed with methanol in a centrifuge and the resulting residue was dried in vacuo.

S2.4 Synthesis of Nanoparticles N3

Ligand **L1** (0.916 g, 2.0 mmol) was dissolved in DCM and subjected to stirring. A solution of Na₂PdCl₄ (0.147 g, 0.5 mmol) in methanol was prepared and added to the stirring solution of the ligand. Stirring was continued for 20 minutes. Thereafter, nitrogen gas was purged and methanolic solution of NaBH₄ (0.039 g, 1.0 mmol) was added to the solution followed by continuous stirring for 2 hours. Black precipitate of **N3** appeared. The black particles were then extracted and washed with methanol in a centrifuge and the resulting residue was dried *in vacuo*.

S3. General Procedure for O-arylation of phenol catalysed using N1-N3

An oven dried round bottom flask was charged with aryl halide (1.0 mmol), phenol (1.1 mmol), K₂CO₃ (2.0 mmol), DMSO (5 mL) and nanoparticles **N1/N2/N3** (25 mg). The flask was equipped with a reflux condenser and the reaction mixture was refluxed for 16 hours at 110°C. The reaction mixture was then cooled to room temperature. Water (25 mL) was added to the reaction mixture. The product was extracted twice using ethyl acetate and washed three times using distilled water. The solution, obtained after washing, was dried over anhydrous Na₂SO₄, filtered, and the solvent was evaporated off to obtain the crude product. This crude was subjected to ¹H NMR analysis for determination of percentage conversion.

S4. Poisoning and Hot filtration tests

S4.1 Poisoning tests

Mercury and PPh₃ poisoning tests were carried out using all three nanocatalysts (i.e., **N1/N2/N3**) for reaction between 1-bromo-4-nitrobenzene and phenol. An oven dried round bottom flask was charged with DMSO (5mL), 25 mg of the catalyst (**N1/N2/N3**) and 400eq. of poisoning agent (Hg or PPh₃). The mixture was allowed to stirred for 10 minutes. Thereafter, 1-bromo-4-nitrobenzene (1.0 mmol), phenol (1.1 mmol) and K₂CO₃ (2.0 mmol) were added to the system. The reaction mixture was stirred and refluxed at 110 °C for 16 hours. The reaction mixture was then cooled to room temperature and water (25 mL) was added to it. The reaction mixture was decanted in case of mercury poisoning test and normal procedure (as adopted for other reactions) was followed for further workup. The assessment of % conversions was done using ¹H NMR spectroscopic analysis. No significant drop in conversion was observed during these tests.

S4.2. Procedure for Hot filtration test

An oven dried round bottom flask was charged with 1-bromo-4-nitrobenzene (2.0 mmol), phenol (2.2 mmol), K₂CO₃ (4.0 mmol), DMSO (10 mL) and nanoparticles of **N1** (50 mg). The flask was equipped with a reflux condenser and the mixture was refluxed at 110 °C. After 3 hours, the reaction mixture was cooled and centrifuged to extract the catalyst. After separation of the catalyst, the reaction mixture was divided into 3 parts. One part was consumed to assess the % conversion. The catalyst was reintroduced to one of the remaining two parts in the same proportion in which it was added in the original reaction mixture. Both the remaining portions were again placed under refluxion for 8 hours. Reactions in both mixtures were quenched and conversion for estimated using ¹H NMR spectroscopy.

S5. Experiments for catalysts' recyclability

To study the reusability of the catalytic system, five cycles of the catalytic reactions between 4-chloronitrobenzene and phenol were performed in the presence of the nanocatalytic system **N2** and assessment of the conversions was made for every cycle. An oven dried round bottom flask was charged with 4-chloronitrobenzene (1.0 mmol), phenol (1.1 mmol), K_2CO_3 (2.0 mmol), DMSO (5 mL), and nanoparticles **N2** (50 mg). The flask was equipped with a reflux condenser and refluxion was carried out for 16 hours at 110 °C. The reaction mixture was cooled to room temperature and water (25 mL) was added to it. Thereafter, the product was extracted using ethyl acetate and nanoparticles were centrifuged from the aqueous layer. The extracted nanoparticles were the reused in a fresh set of C–O coupling reaction of phenol and 4-chloronitrobenzene. The results obtained have been compiled in [Fig. S23](#).

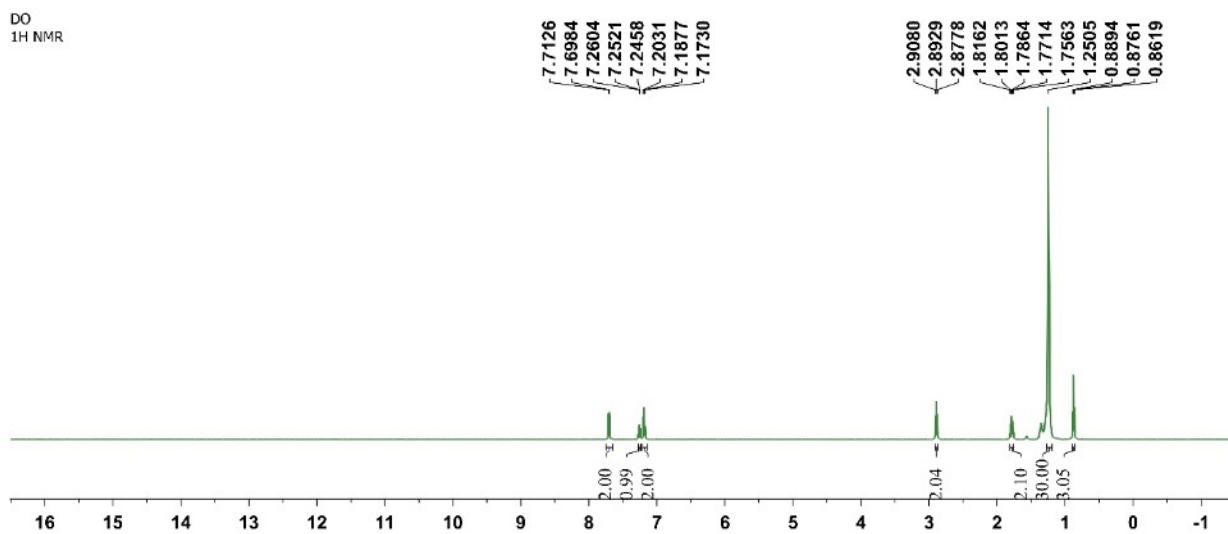


Fig. S1. ^1H NMR of Ligand L1

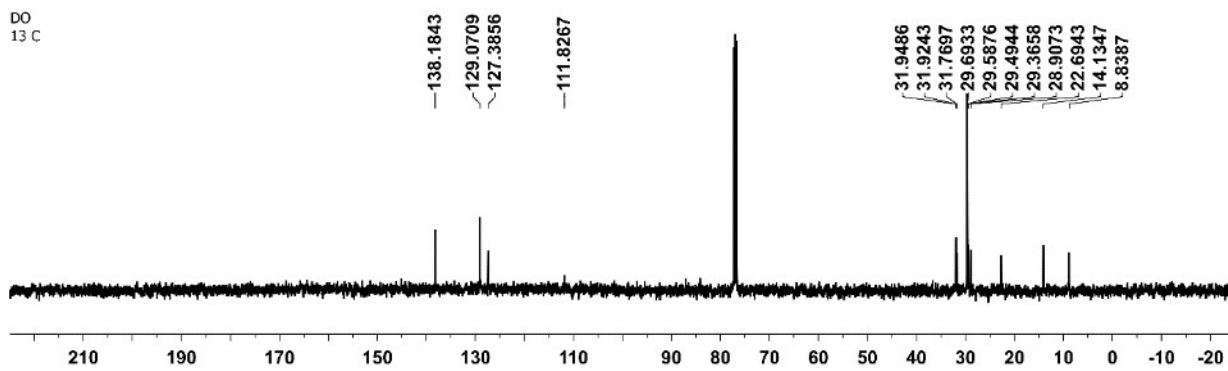


Fig. S2. ^{13}C NMR of Ligand L1

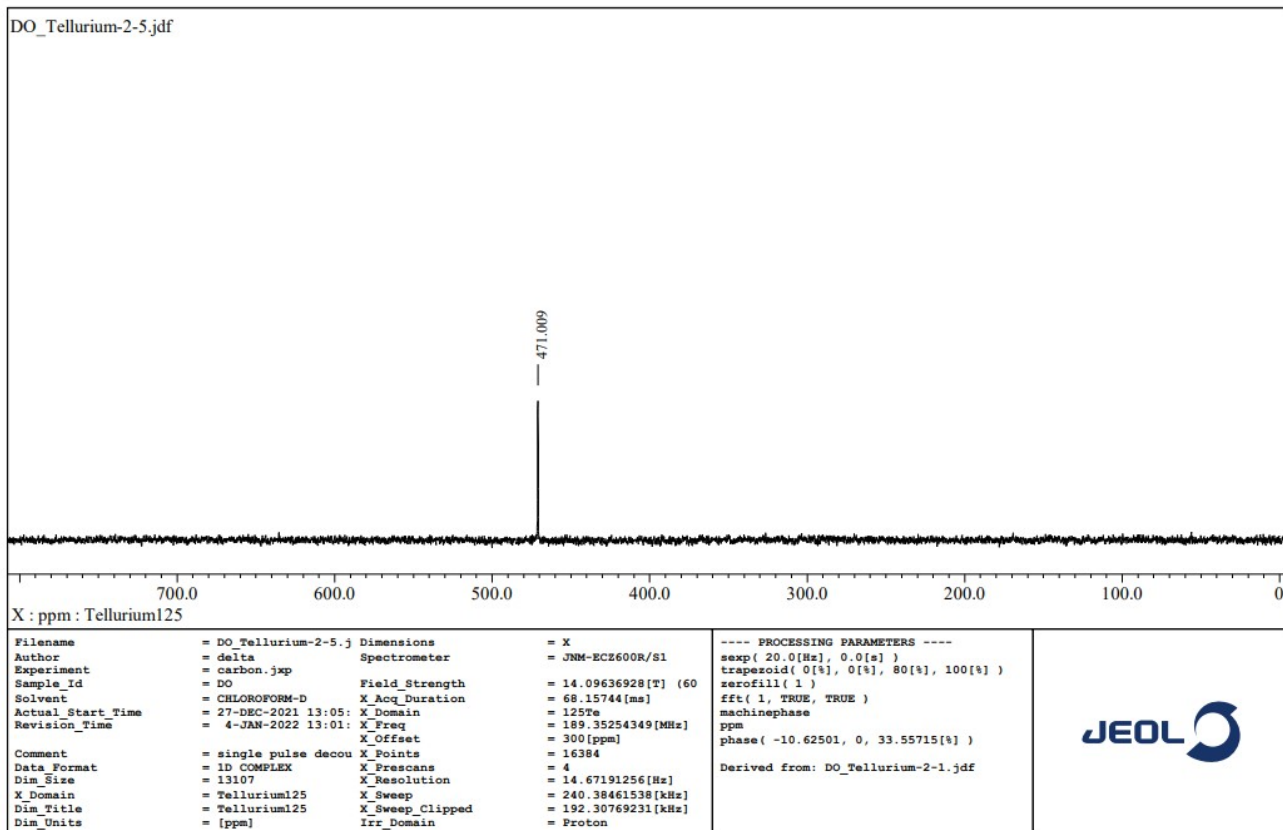


Fig. S3. ^{125}Te NMR of Ligand L1

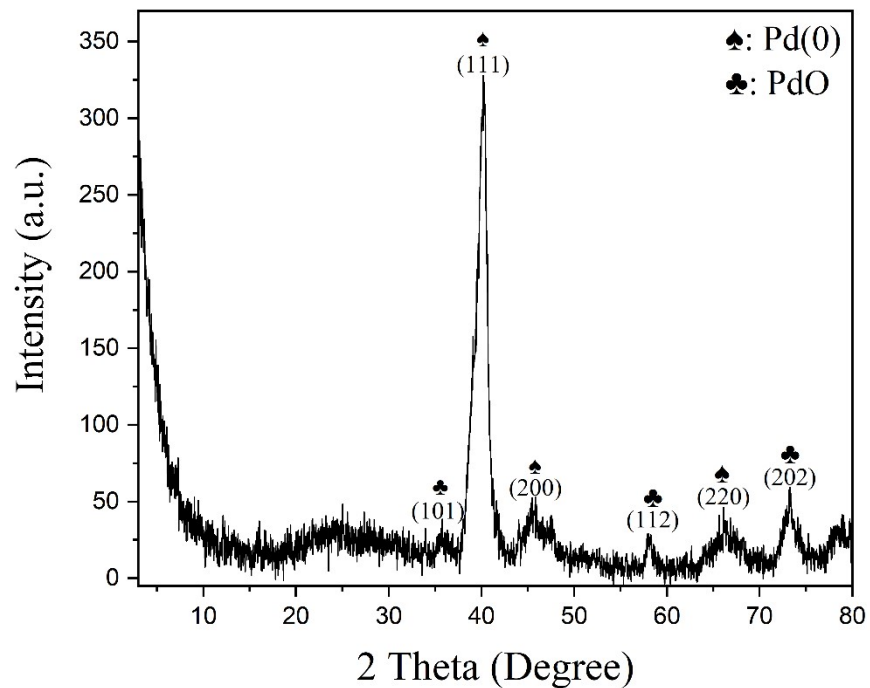


Fig. S4. PXRD pattern of N2

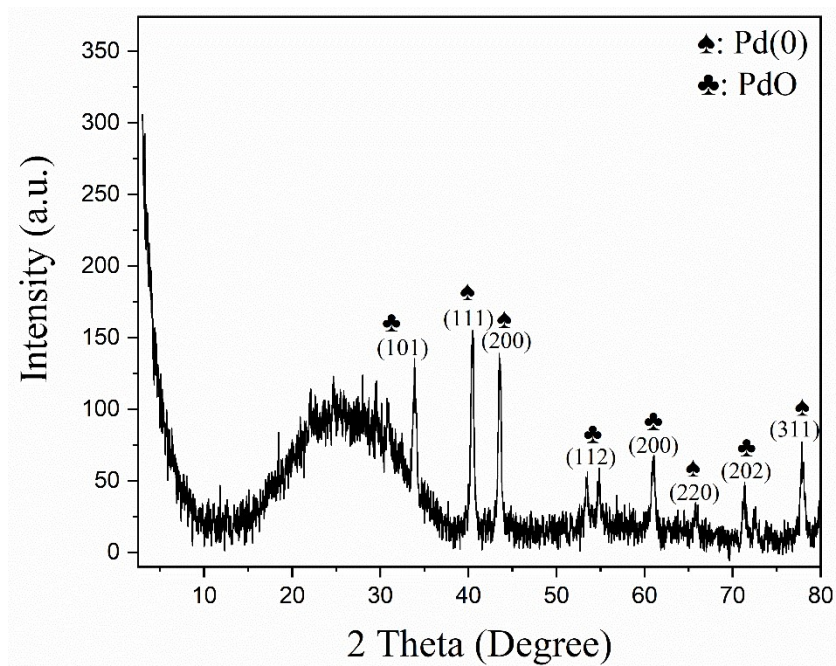


Fig. S5. PXRD pattern of N3

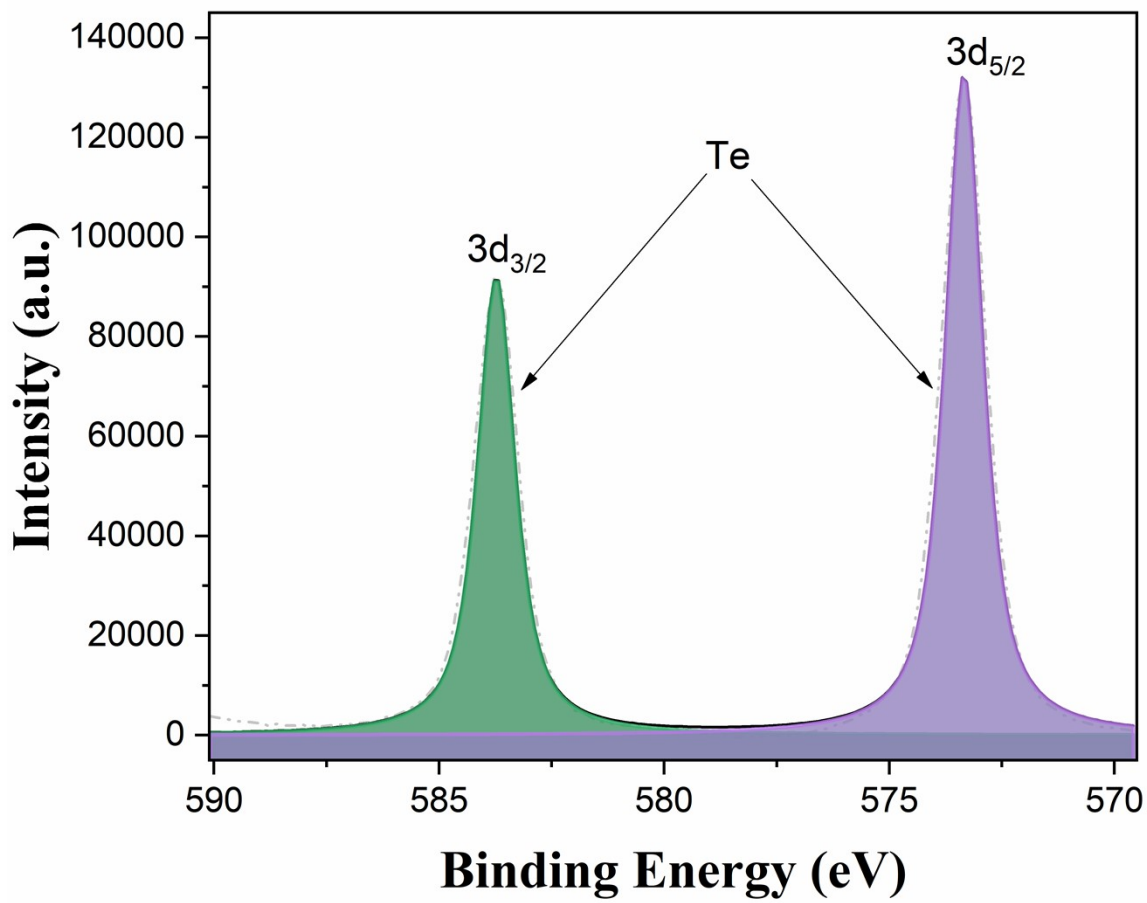


Fig. S6. XPS pattern of Te-3d region of L1

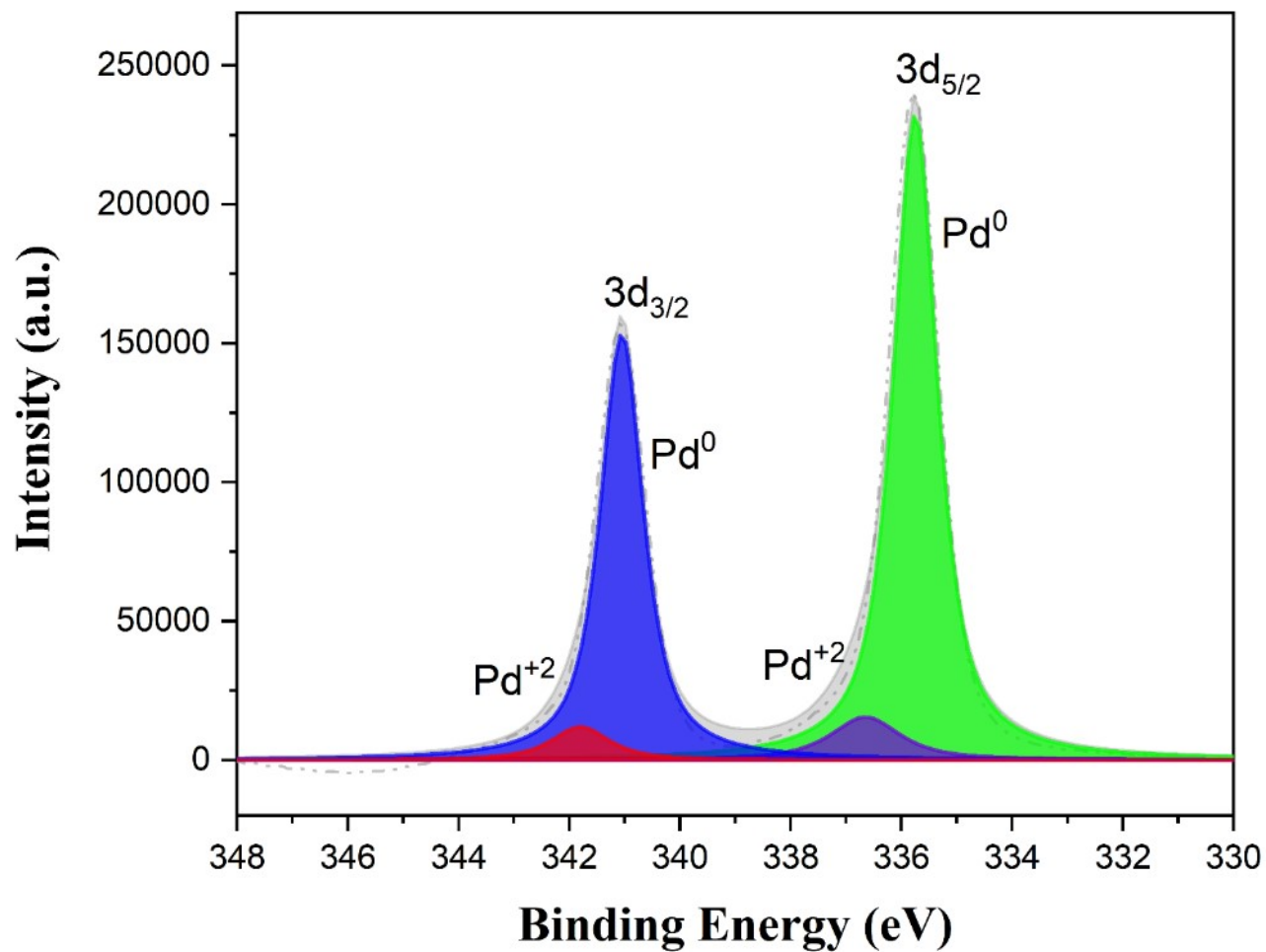


Fig. S7. XPS pattern of Pd-3d region of N₂

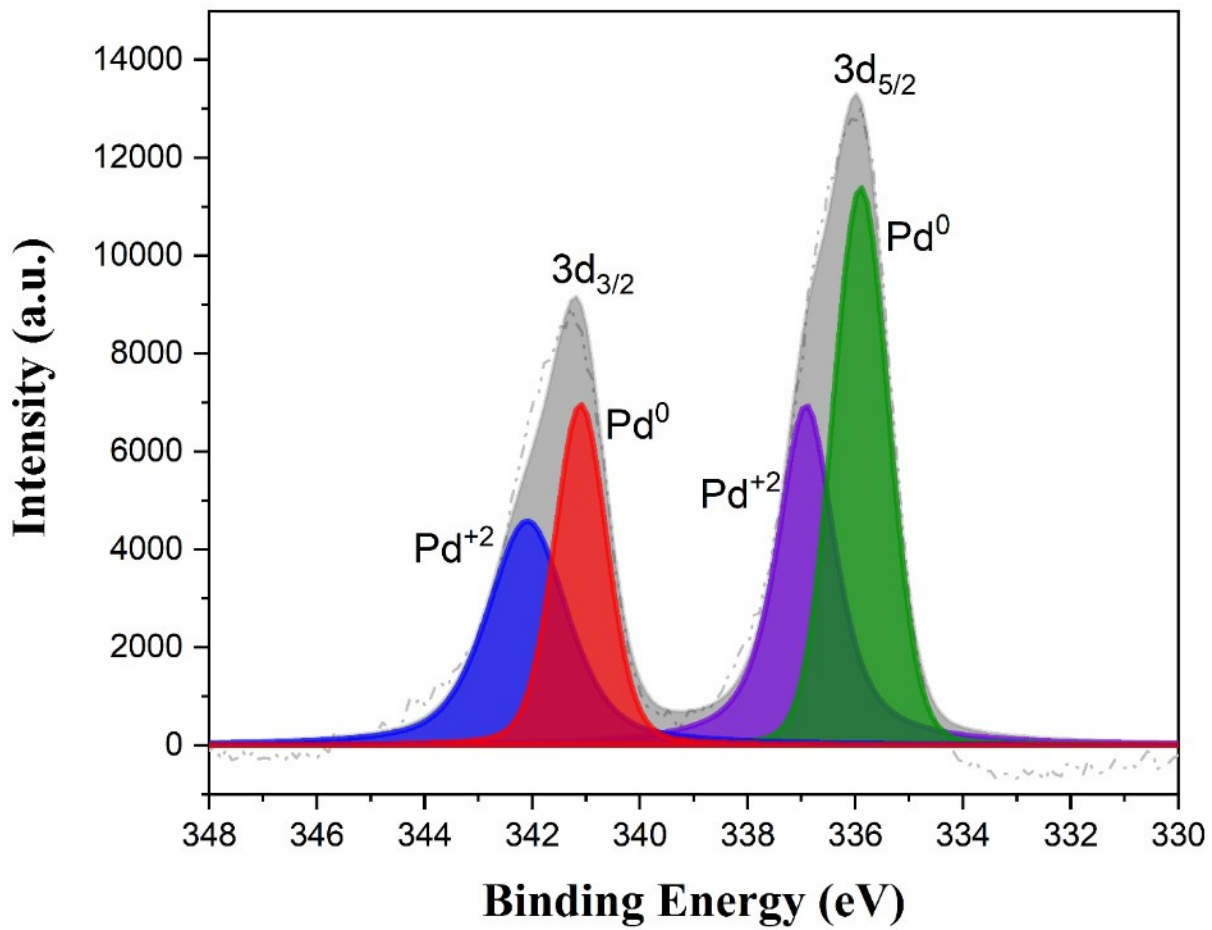


Fig. S8. XPS pattern of Pd-3d region of N3

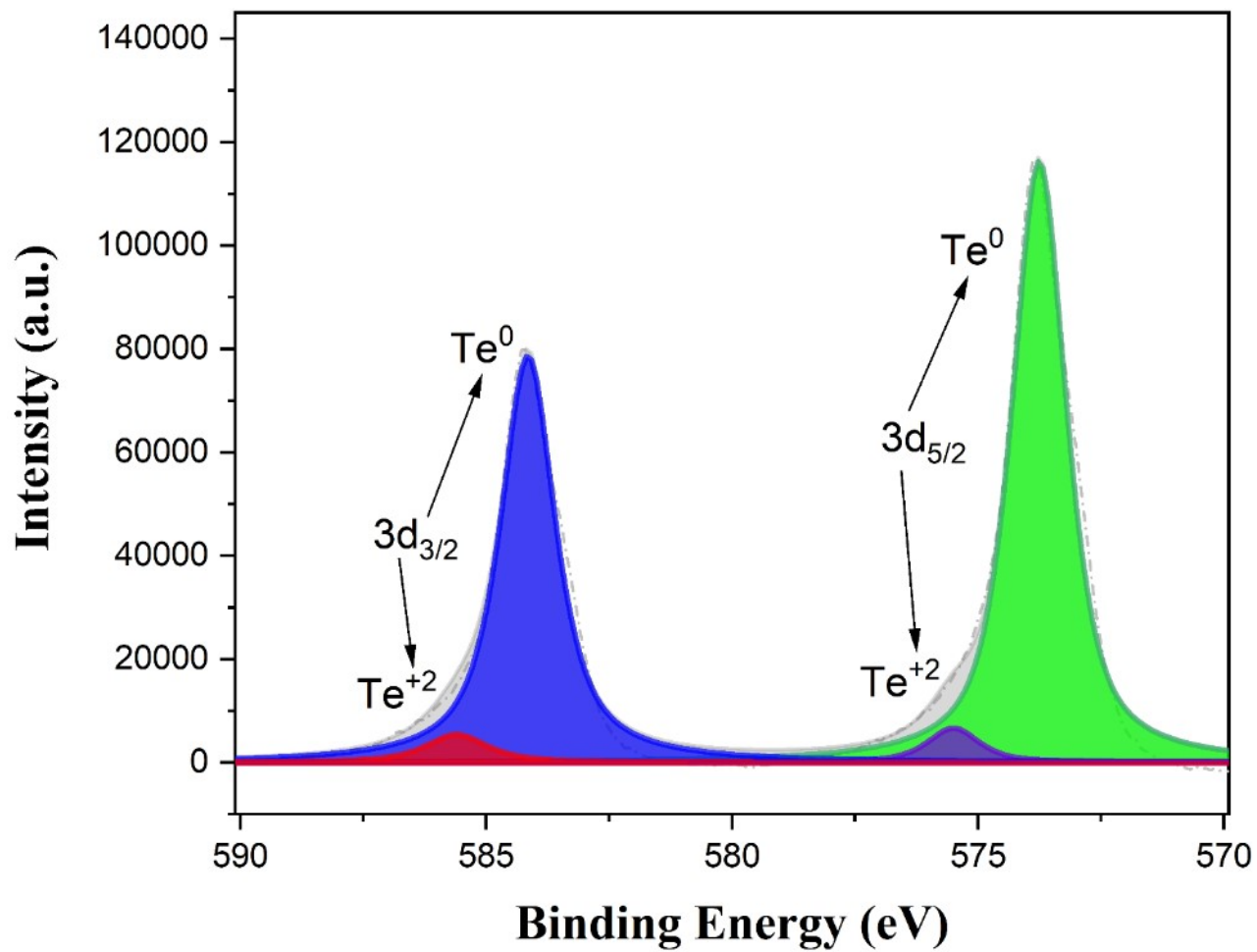


Fig. S9. XPS pattern of Te-3d region of N₂

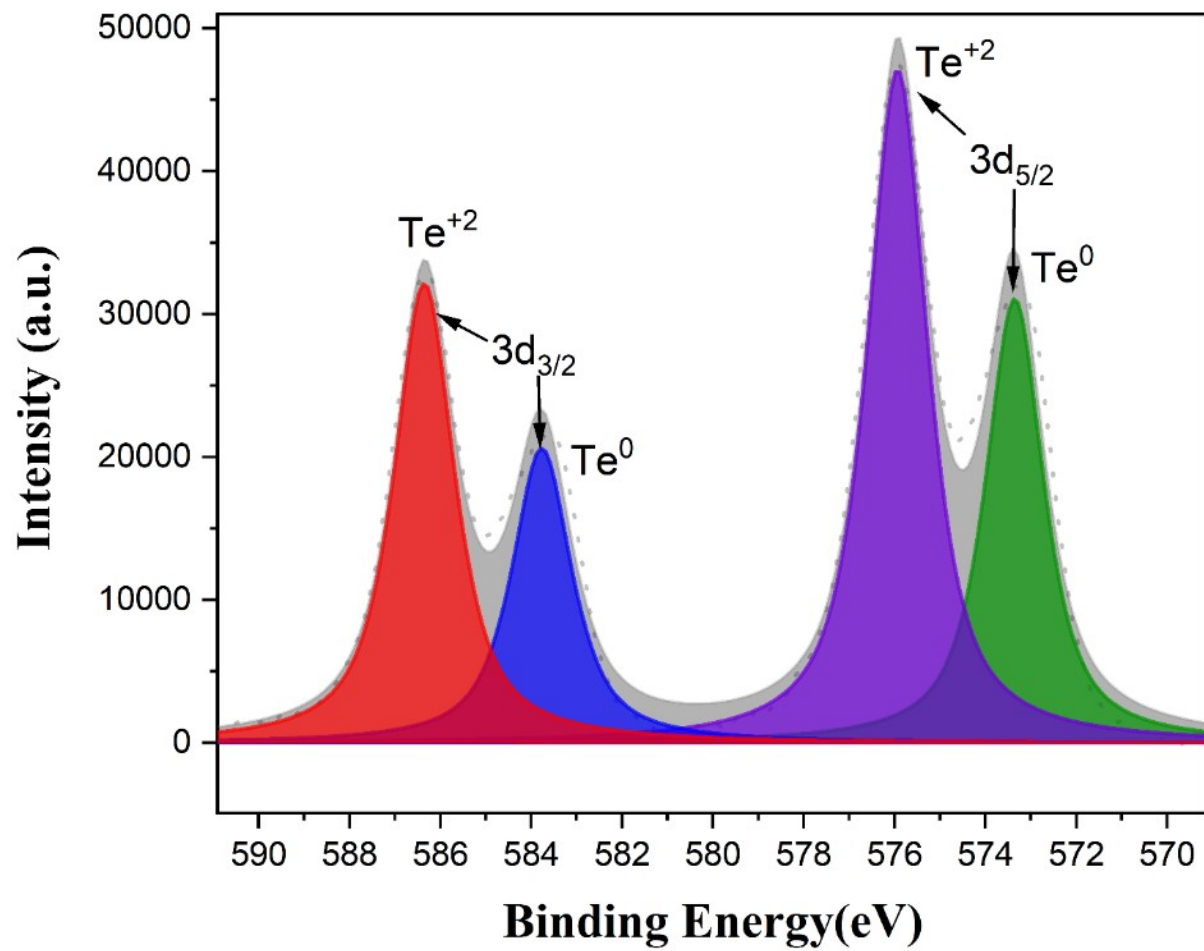


Fig. S10. XPS pattern of Te-3d region of N3

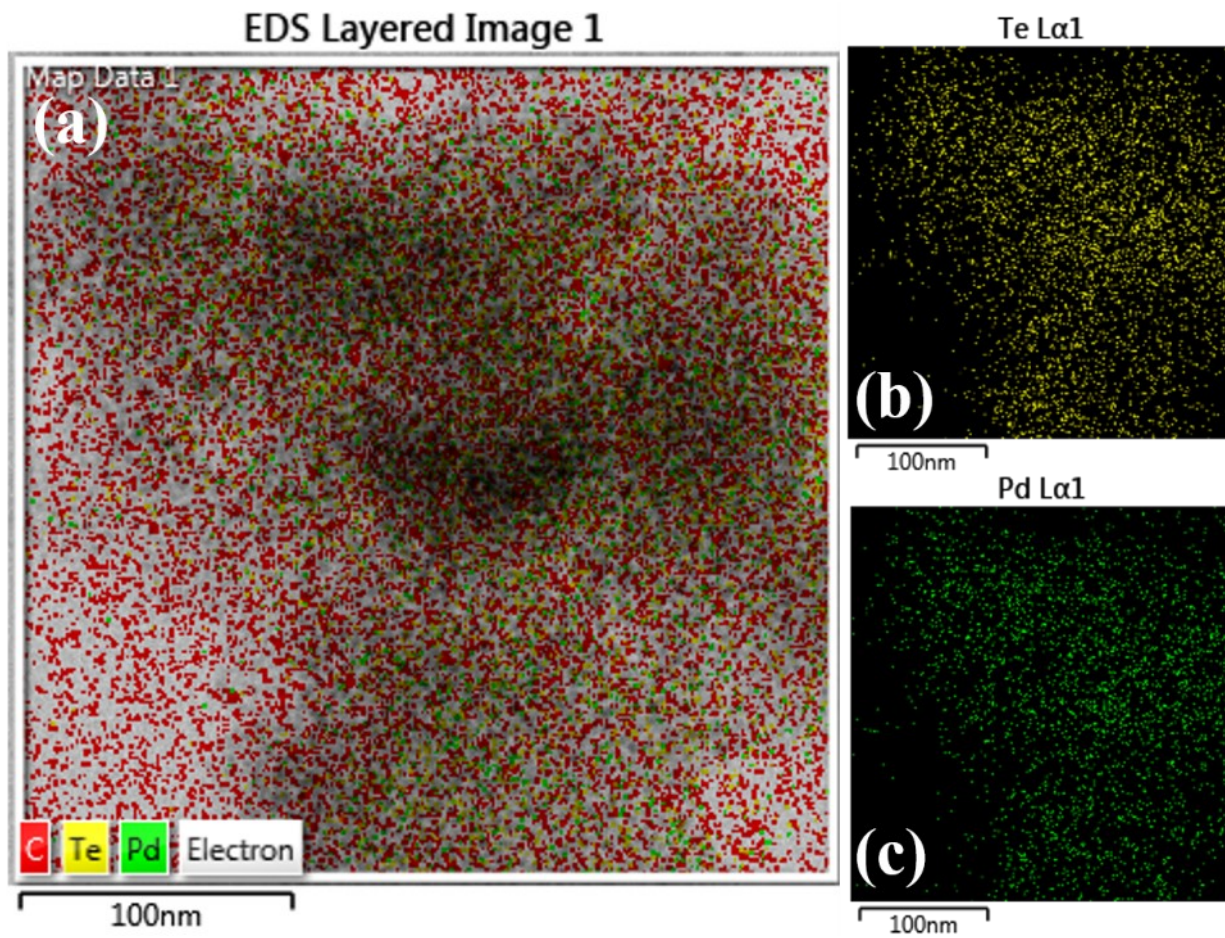


Fig. S11. Elemental mapping of N1. (a) Layered view (b) Tellurium (c) Palladium

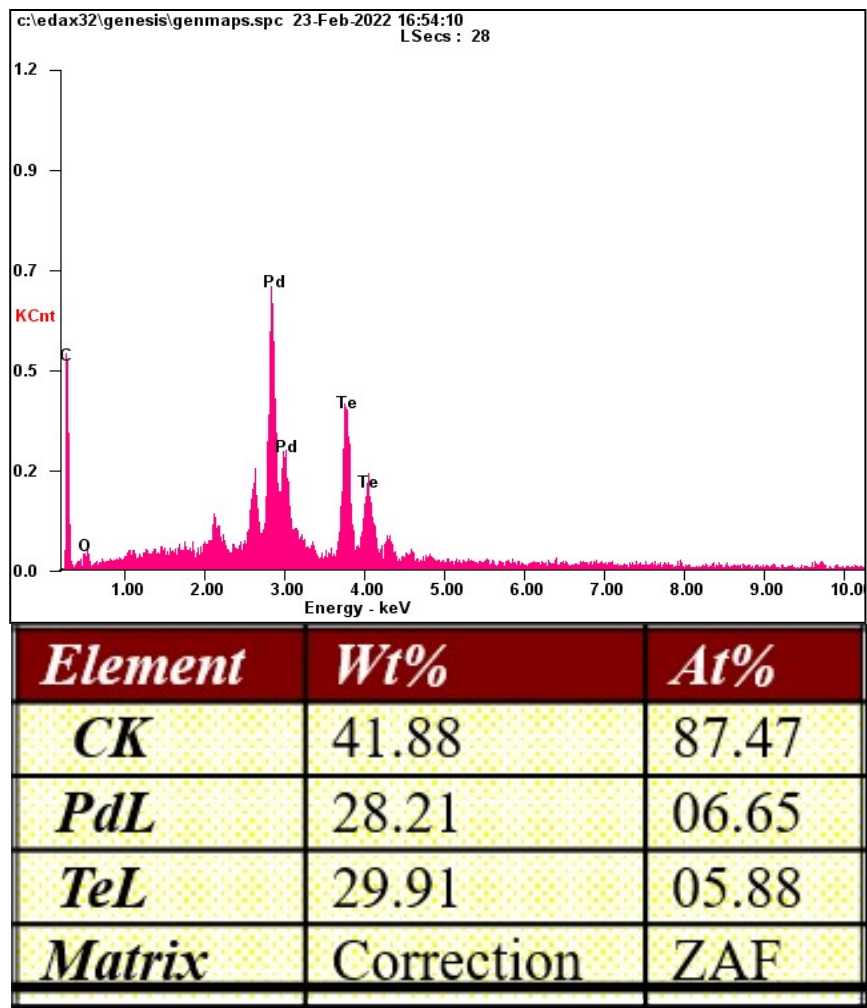


Fig. S12. EDS spectral data of N1

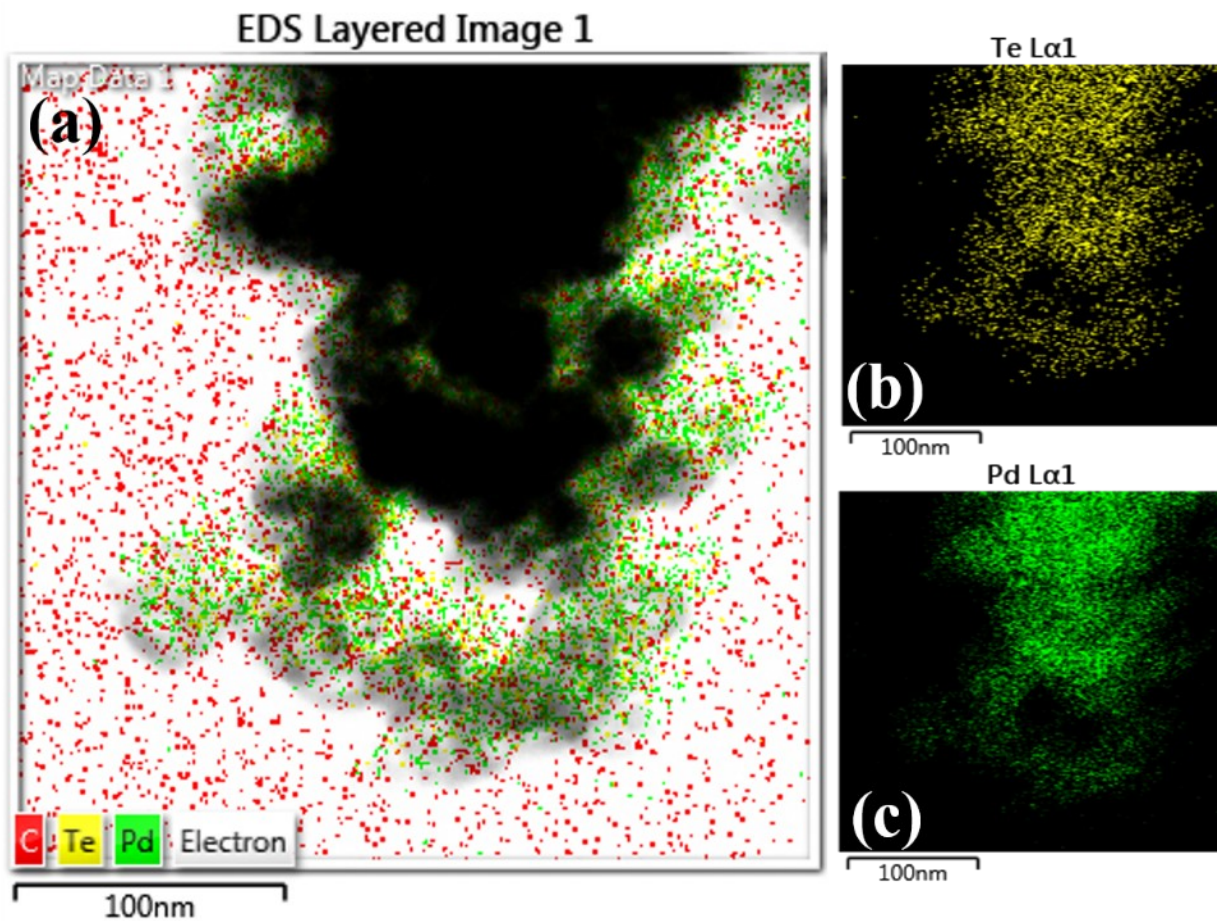


Fig. S13. Elemental mapping of N2. (a) Layered view (b) Tellurium (c) Palladium

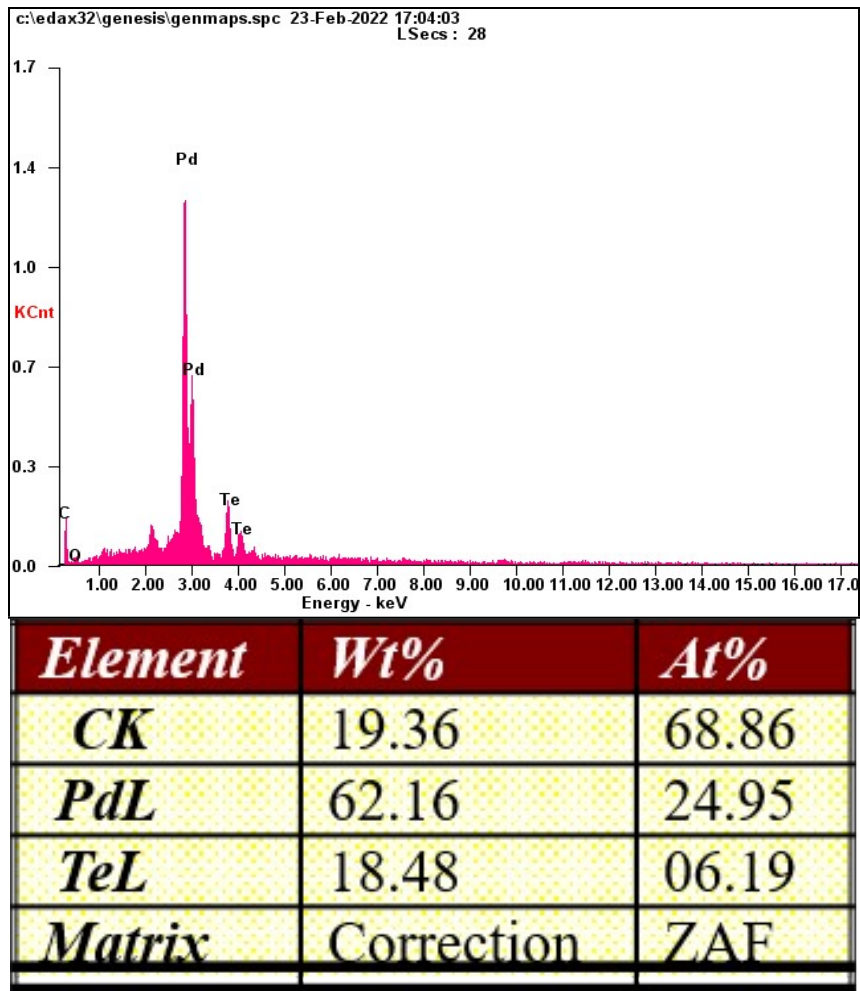


Fig. S14. EDS Spectral data of N2

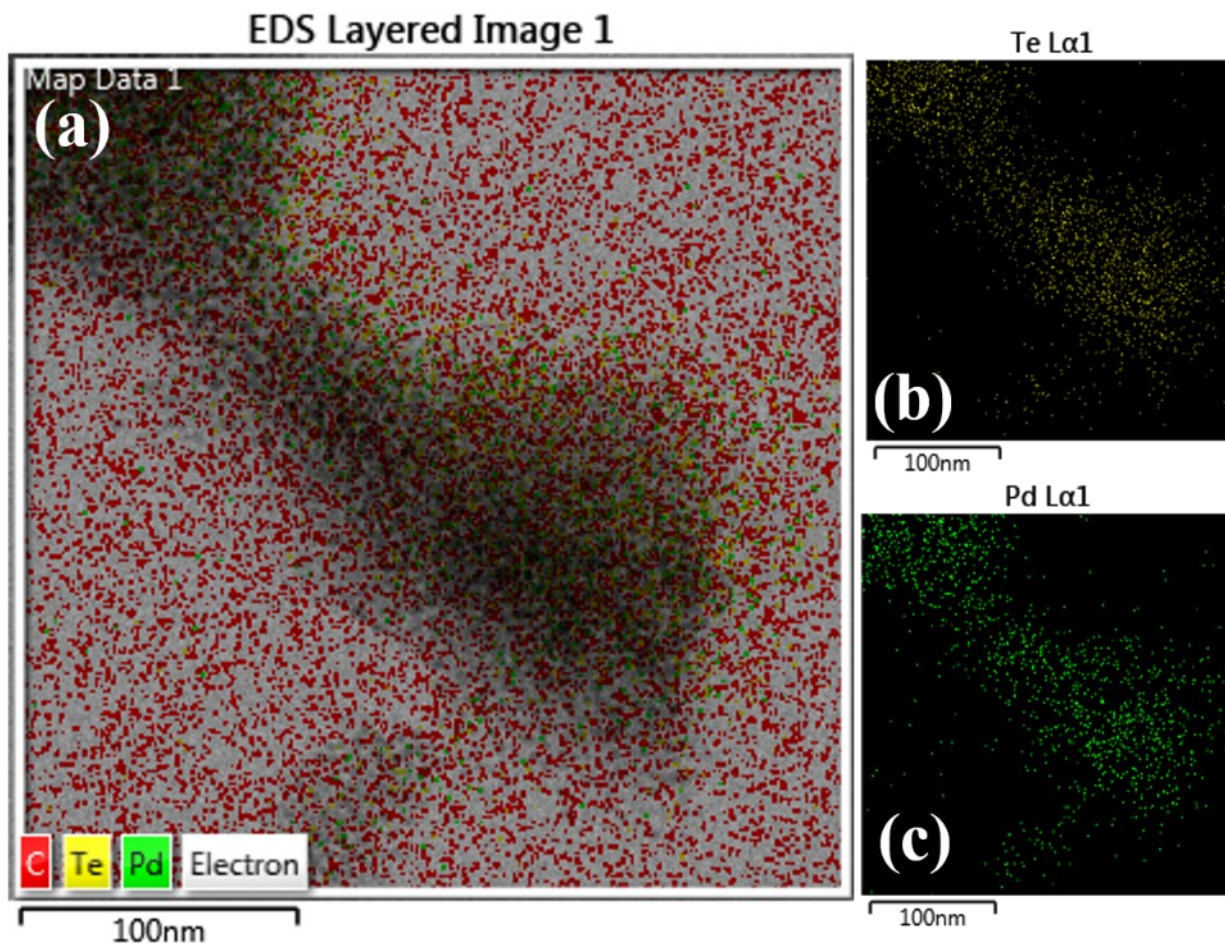


Fig. S15. Elemental mapping of N3. (a) Layered view (b) Tellurium (c) Palladium

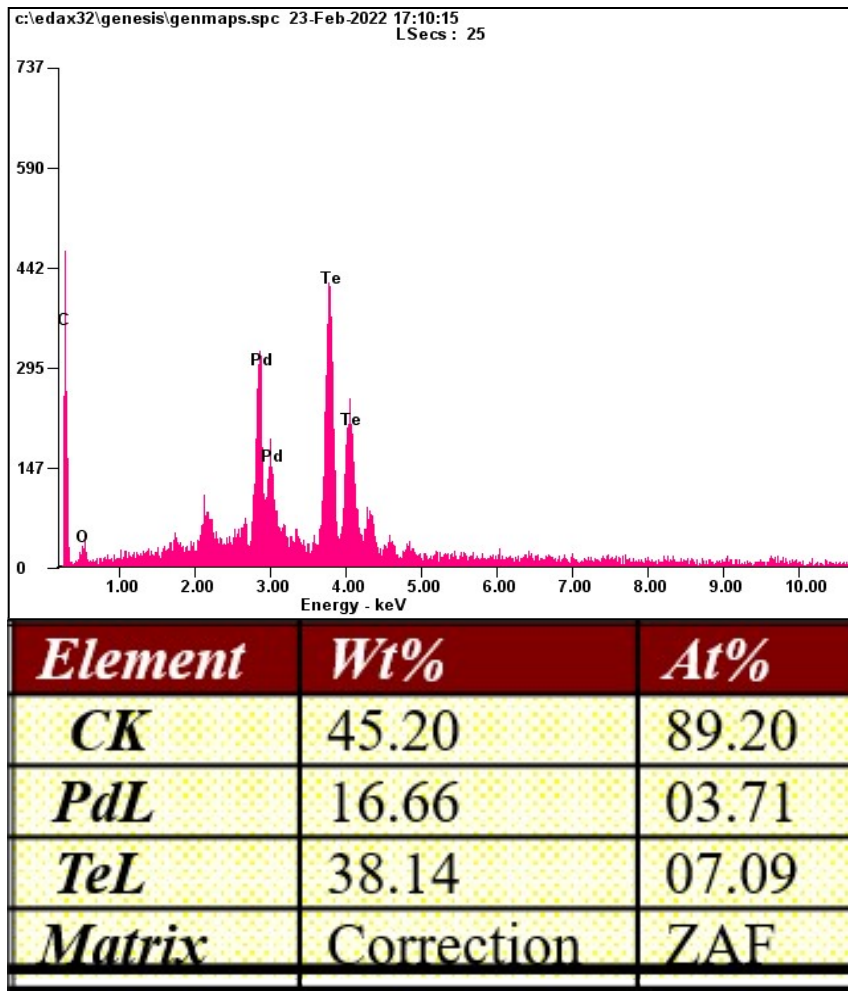


Fig. S16. EDS Spectral data of N3

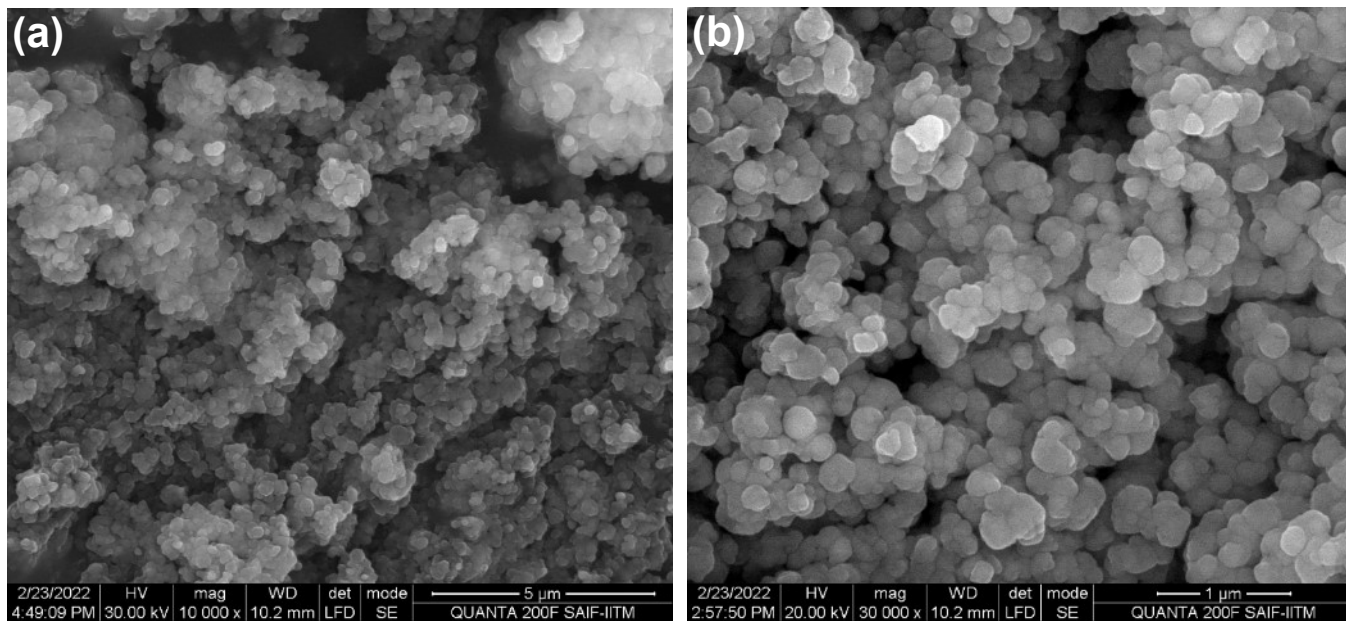


Fig. S17. SEM images of N1 at (a) 5 μ m and (b) 1 μ m scale

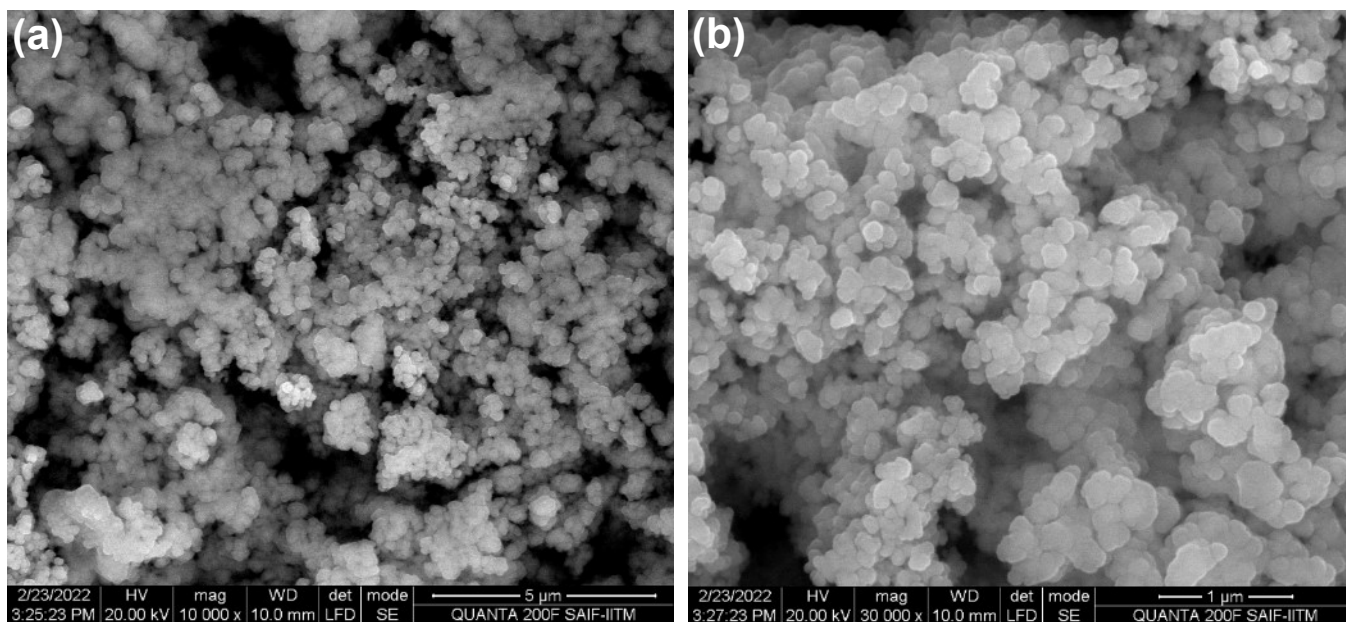


Fig. S18. SEM images of N2 at (a) 5 μ m and (b) 1 μ m scale

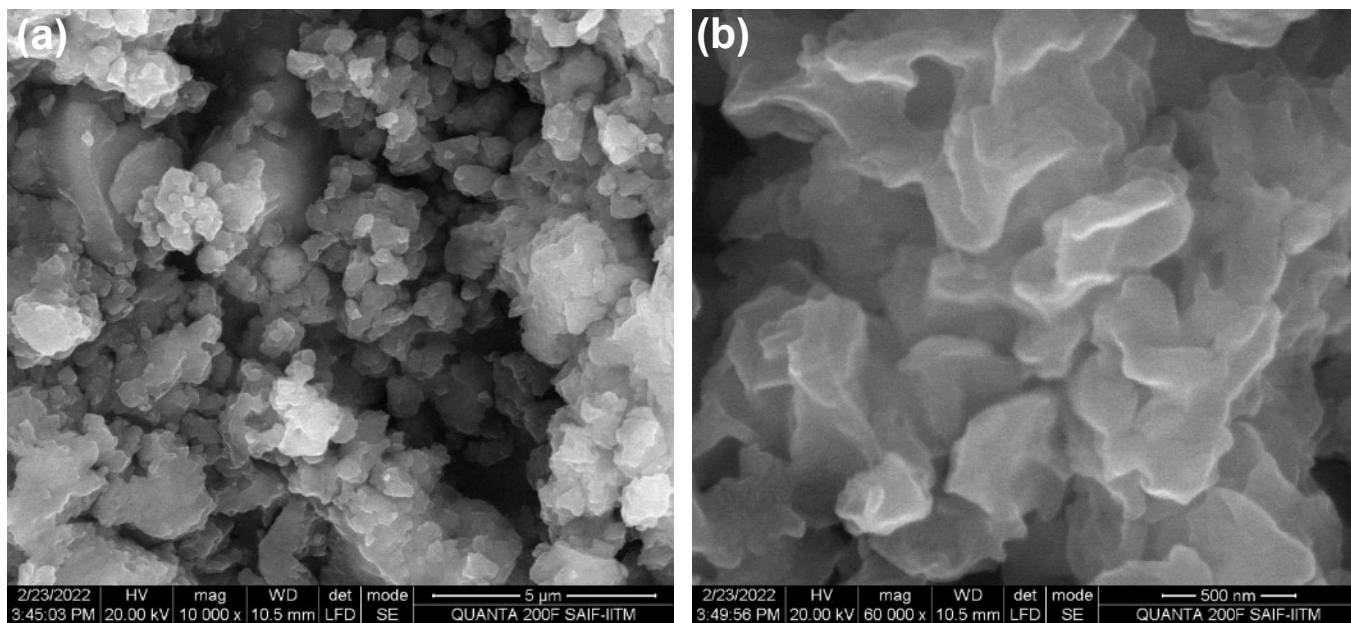


Fig. S19. SEM images of N3 at (a) 5 μm and (b) 0.5 μm scale

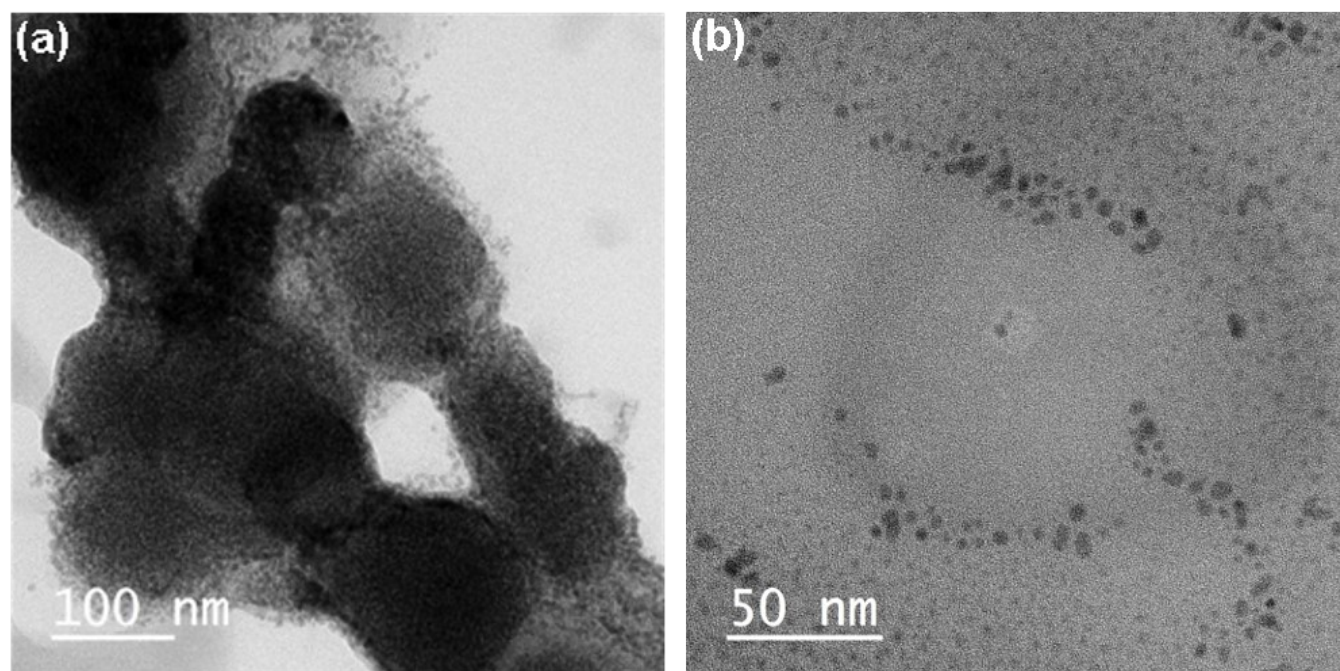


Fig. S20. HR-TEM images of N1 at (a) 100 nm and (b) 50 nm scale

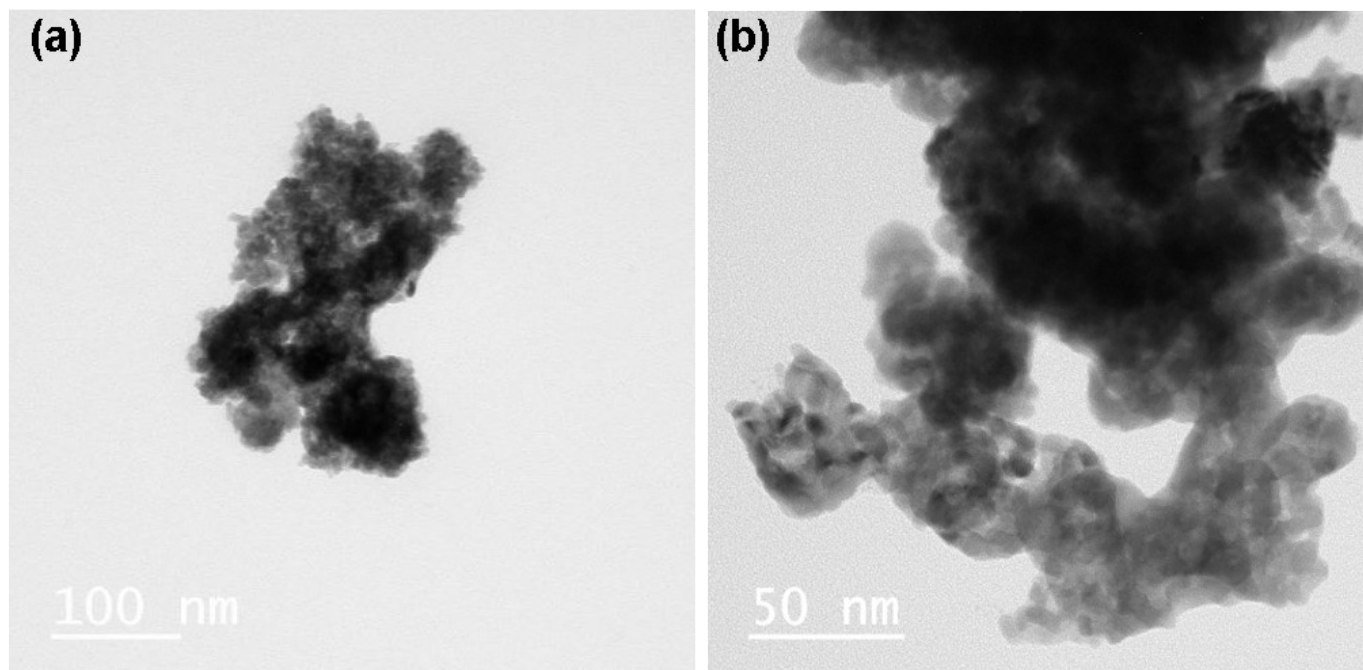


Fig. S21. HR-TEM images of N2 at (a) 100nm and (b) 50nm scale

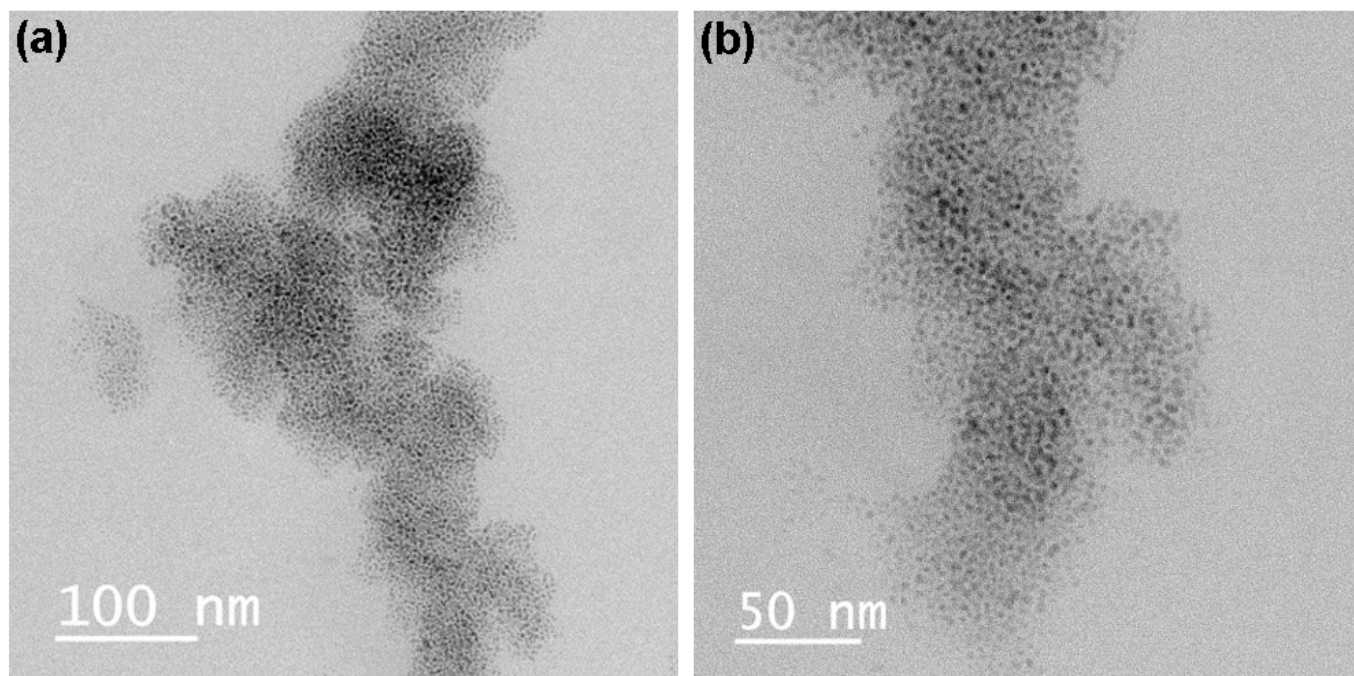
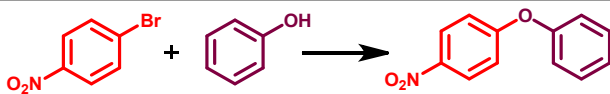


Fig. S22. HR-TEM images of N3 at (a) 100nm and (b) 50nm scale

Table S1. Optimization of the *O*-arylation reaction between phenol and 1-bromo-4-nitrobenzene

					
S. No	Solvent	Base	Catalyst Loading	Temp	% Conversion
1.	DMSO	K ₂ CO ₃	25mg	110°C	>99%
2.	DMF	K ₂ CO ₃	25mg	110°C	>99%
3.	Water	K ₂ CO ₃	25mg	110°C	Trace
4.	Toluene	K ₂ CO ₃	25mg	110°C	47%
5.	Ethanol	K ₂ CO ₃	25mg	110°C	50.5%
6.	DMSO	NaOH	25mg	110°C	79.3%
7.	DMSO	Na ₂ CO ₃	25mg	110°C	53.1%
8.	DMSO	Et ₃ N	25mg	110°C	50.7%
9.	DMSO	NaOAc	25mg	110°C	62.1%
10.	DMSO	K ₂ CO ₃	25mg	80°C	55.5%
11.	DMSO	K ₂ CO ₃	25mg	r.t.	Trace
12.	DMSO	K ₂ CO ₃	15mg	110°C	47.1%
13.	DMSO	K ₂ CO ₃	40mg	110°C	>99%
14. ^a	DMSO	K ₂ CO ₃	25mg	110°C	57.1%

Reaction Conditions: 1-Bromo-4-nitrobenzene(1.0 mmol); phenol(1.2 mmol); base(2.0 mmol); Solvent(5 mL); Reaction time :16h. ^aReaction time 6 hours

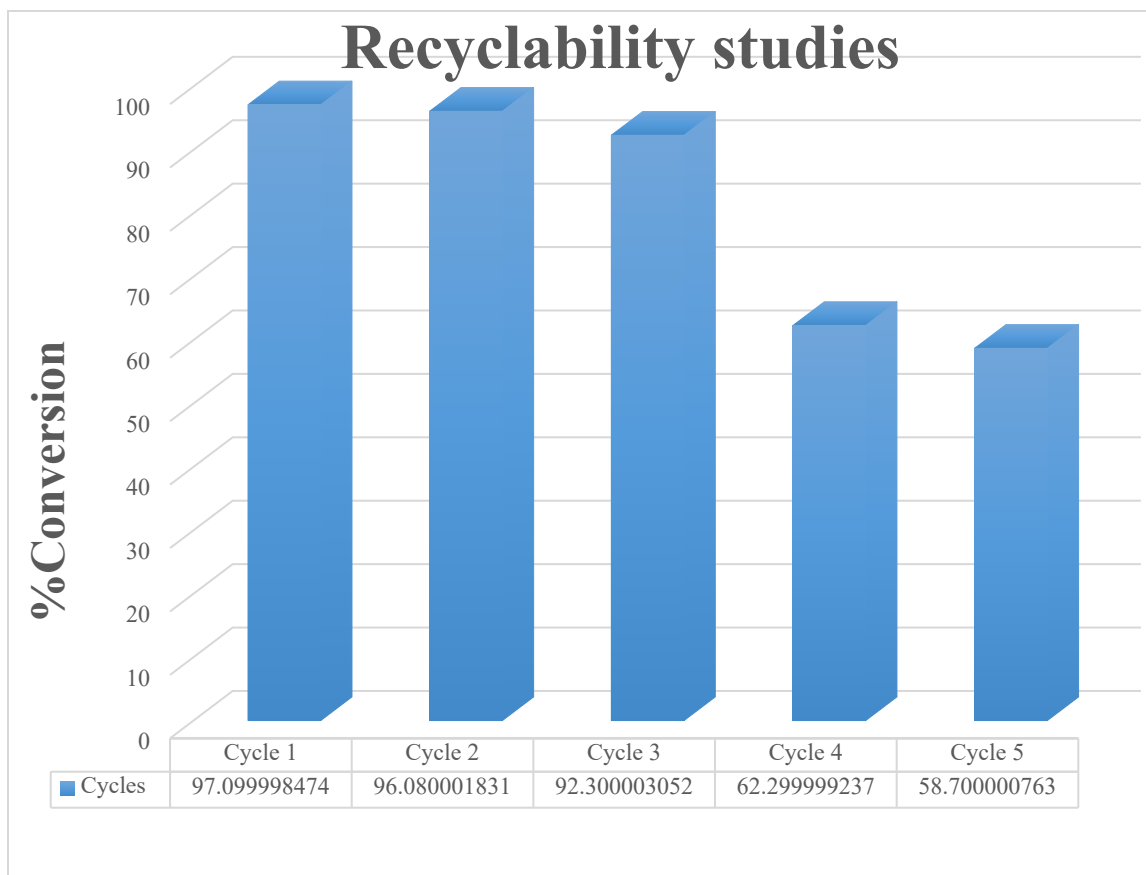


Fig S23. Results of recyclability studies of the **N2** in C–O coupling reaction under optimized reaction conditions for five reaction cycles