

# Recyclable Palladium Single-Atom Catalysts for the Room-Temperature, Light-Induced Ullmann Homocoupling of Aryl Halides

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## Highlights

- Pd single-atom catalyst enables efficient Ullmann coupling under UV light at ambient conditions.
- Base screening and solvent studies reveal critical factors influencing catalytic outcomes.
- DFT calculations elucidate electronic and geometric factors impacting catalytic efficiency.
- Pd single-atom catalyst exhibits superior stability and recyclability in comparison to nanoparticles.

## 1. Introduction

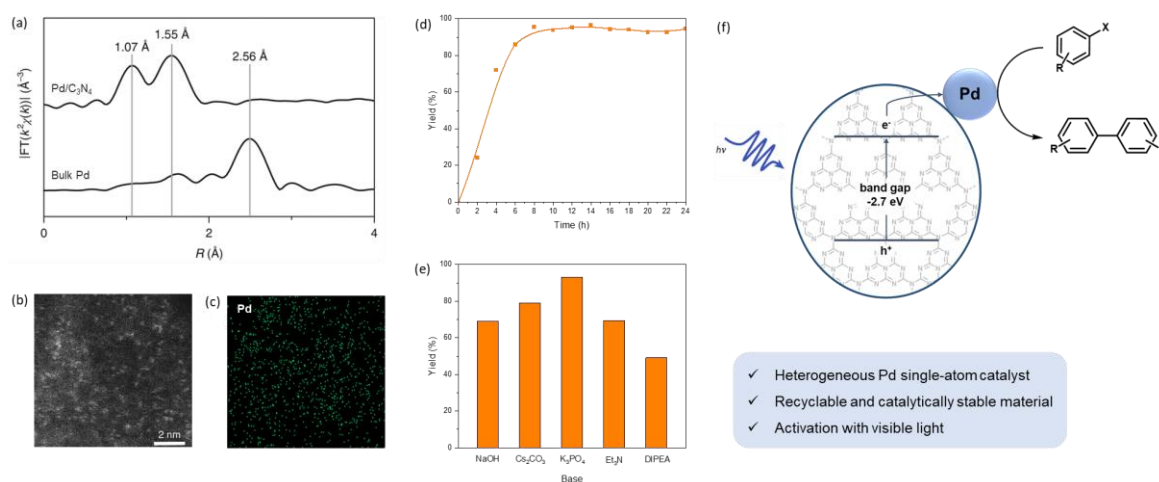
Transitioning from homogeneous to heterogeneous catalysis is gaining relevance today, as this can have a direct implication for the realization of the European Union's Green Deal objectives. In fact, heterogeneous catalysis offers facile catalyst separation and reuse, and less waste generation. The homocoupling of aryl halides is an example of a metal-based homogeneous process of great significance for the fast and high-throughput production of value-added chemicals, such as biaryl skeletons. However, the high reaction temperatures and the use of stoichiometric amount of homogeneous copper salts render this reaction impractical at scale. Great progress has been made in recent years for the development of palladium-catalyzed Ullmann reactions using thermal heterogeneous conditions.<sup>1,2</sup> Nonetheless, most of these catalytic methods require reductive conditions and suffer from inefficient utilization of the expensive Pd metal. Recently, photocatalytic strategies have become popular in catalysis, due to their advantages, including mild reaction conditions and the use of green solar energy. However, the combined exploitation of light and single-atom catalysts to drive the selectivity of Ullmann homocoupling reaction was never investigated to date. Herein, we fill this gap and present a new photocatalytic method that involve the use of palladium-based single-atom catalyst supported on mesoporous graphitic carbon nitride (Pd/mpgC<sub>3</sub>N<sub>4</sub>), for the direct Ullmann coupling of aryl halides at ambient conditions. The catalyst exhibits high activity and selectivity, and excellent stability over a wide functional group, making the protocol attractive for industry, and environmentally strategic.

## 2. Methods

To obtain the metal-based single-atom catalyst via copolymerization, cyanamide, and K<sub>2</sub>PdCl<sub>4</sub> were mixed and stirred at 40 °C. The resulting mixture was heated to 500 °C and maintained at this temperature for 4 h. The solids were separated by filtration, washed, and calcined. The composition and chemical status of the catalytic material were investigated with a plethora of characterization techniques (ICP, XRD, XPS, TEM, XAS, IR, NMR). For the catalytic tests, a 4 mL glass vial was charged with catalyst (2-5 mg), aryl halide (0.1-0.5 mmol), base (0.1-0.5 mmol), and solvent (2-8 mL) and was sealed with a silicon septum. The contents were stirred under UV light irradiation ( $\lambda = 457$  nm) for the desired time. After the reaction, the liquid phase was filtered using a syringe equipped with a PTFE filter and analyzed by high pressure liquid chromatography. DFT calculations were carried out using the VASP code.

## 3. Results and discussion

Following a comprehensive catalyst characterization that unveiled the complete isolation and uniform dispersion of Pd sites on the carbon nitride support, we embarked on our investigation, aiming to establish pivotal structure-function relationships that can drive out catalyst design. We began the investigation by monitoring the Ullmann homocoupling of iodobenzene as a model reaction. Control experiments highlighted the role of the catalyst, light, and base for the catalytic cycle. In particular, organic bases afforded moderate to low yields, while inorganic bases worked more effectively, and the reaction was completed within 8 h achieving quantitative yield in the presence of  $K_3PO_4$ . These findings were further substantiated by DFT calculations, which elucidated the electronic and geometric factors of the base responsible for the divergent catalytic outcomes. The effect of the solvent on the reaction was also tested and the results corroborated by DFT, understanding the role of its polarity and proticity. Amongst the different solvents, polar and protic solvents were found to be ideal to yield the desired product (99.9% conversion and 93.2% yield at 25°C, 8 h). DFT calculations revealed that the protic solvents facilitated crucial hydrogen bonding interactions, enhancing the reaction's overall efficiency and selectivity. The performance of the Pd single-atom catalyst was then compared to a nanoparticle-based Pd supported on mpgC<sub>3</sub>N<sub>4</sub> and the results revealed that Pd in the form of single-atoms afforded higher activity but was also the only catalyst that remained stable during recycling runs. Hence, the effectiveness of the material was attributed to the highly atomically dispersed Pd species. Our protocol was then extended to other halogenated aromatic compounds to verify the scope of the method, showing good catalytic performances of our materials. The catalyst finally underwent recyclability studies and post-catalysis characterization, proving the excellent catalyst reusability (and stability) for up to 8 consecutive cycles.



**Figure 1.** Normalized magnitudes of the  $k^2$ -weighted Fourier transform (FT) of the extended X-ray absorption fine structure spectra in radial distance (R) (a), AC-STEM image of the catalyst (b), EDX mapping of Pd (c), Yield vs. time (d), Base screening (e), schematic representation of the Ullmann homocoupling reaction on the heterogeneous catalyst (f).

#### 4. Conclusions

This work shows the high atom efficiency, excellent performance, and high reusability of our Pd single-atom catalyst for light-driven Ullmann-type homocoupling of aryl halides at ambient reaction conditions.

#### References

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#### Keywords

Photocatalysis; Single-atom catalyst; Ullmann coupling; Catalytic efficiency.