Silyl Ether Passivation of Silicon Quantum Dots Via Catalytic Dehydrocoupling Reactions

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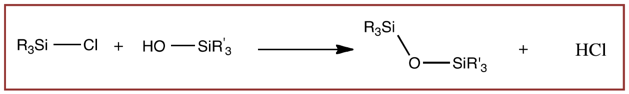
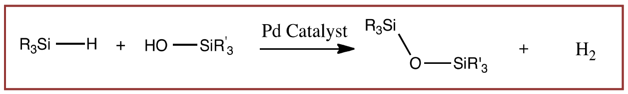
Toxicity in the State of the Art Method

Silicon quantum dots (SiQD) have been researched as potential materials for use in solar cells, photovoltaic devices, organic light emitting diodes, luminescent markers for biological imaging, and even ink-jet printable displays[1]. Passivation of the SiQDs with organic ligands can be used to protect the dots from oxidation, improve solubility, and stabilize luminescence by tuning the distance of the electronic band gap. Passivating the dots with silyl ethers is not a new process, but the state-of-the-art method requires chlorosilane precursors, resulting in the production of toxic and corrosive HCl gas[2].

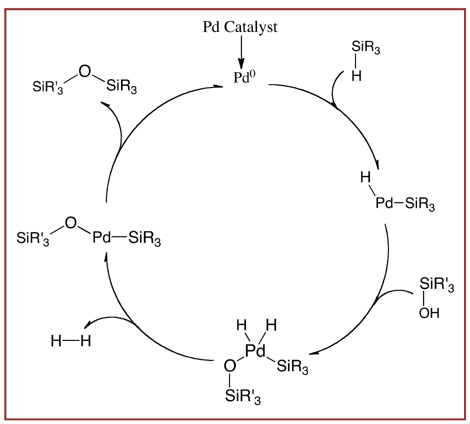


Our method utilizes a palladium catalyzed process for the *direct conversion* of a silyl hydride to silyl ether. This process eliminates the Si-Cl generation step and produces a milder by-product, hydrogen gas[3].



This project looks at the formation of Si-O-C bonds and the more hydrolytically stable Si-O-Si bonds using this method.

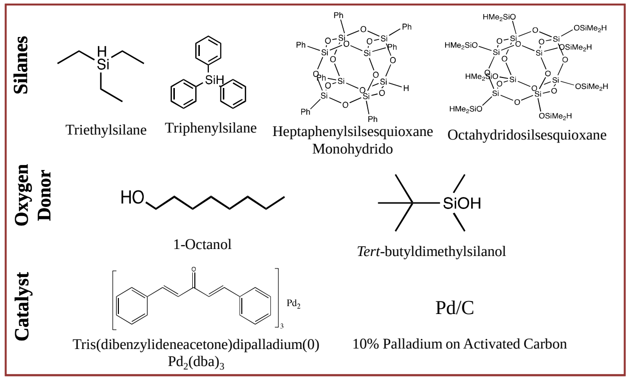
Palladium Catalyzed Reaction Cycle



The proposed catalytic cycle enters two rounds of oxidative addition followed by two subsequent rounds of reductive elimination[4,5].

Model Compound Reactions

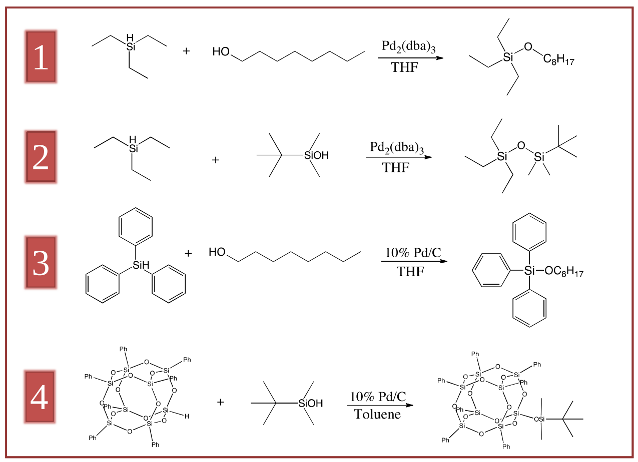
Reactants



Twelve reactions were completed with various combinations of the above compounds. Reactions were run in either tetrahydrofuran or toluene, and temperatures ranged from 55°C to 150°C depending on the size and reactivity of the starting compounds.

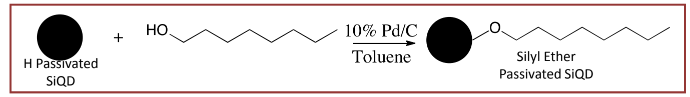
Products were confirmed using NMR, FT-IR, and GC-MS.

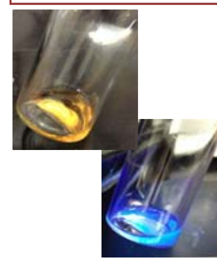
Effective Conditions

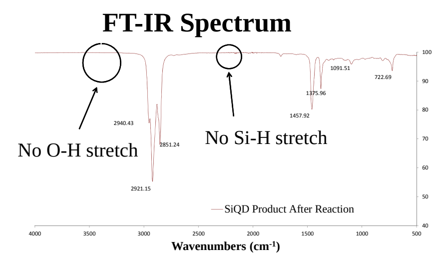


Quantum Dot Application

- Palladium on activated carbon was the most effective catalyst
  - $Pd_2(dba)_3$ coagulated as the reaction proceeded, reducing reaction rate
- Reflux at higher temperatures
  - Higher temperatures were effective for SSQ molecules
  - Toluene chosen as solvent for reflux at 110°C







After 24 hours, reaction mixture was golden yellow (characteristic of SiQDs) and emitted blue photoluminescence.

Conclusions and Future Work

- The work demonstrates that it is possible to synthesize Si-O-C and Si-O-Si linkages from Si-H and alcohols or silanols using mild chemistry, by-passing the use of corrosive and toxic chlorinating agents and chlorosilanes.
- Preliminary evidence indicates that this chemistry is effective in the passivation of SiQDs. This would be a great contribution to the scientific community.
  - The passivated dots are soluble and have strong blue photoluminescence.
  - FT-IR analysis shows the reaction of the Si-H group, the disappearance of the starting alcohol, and the presence of the alkyl chains and Si-O bonds.
- Future work will focus on additional SiQD reactions, including replication and control experiments, and monitoring of surface passivation stability.
- Synthesis of Si-O-Si passivated dots should also be explored, as these are more hydrolytically stable and have their own unique applications.

Acknowledgements

Thank you to Jacob Bell for preparing the silicon quantum dots used in this project. The funding for this project was provided by NSF awards DMR-0820518 and DMR-1063150.

References

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