Young Zhou

Catalytic Ability of TiO_2 Nanoparticles Functionalized on Ag-coated Fe_3O_4 Microspheres

September 1st, 2019 - ? 2021

PRISMS Chemistry Lab

I. Project Summary

In my research over the next two years, I plan to investigate how different synthetic pathways and variables, such as the material used for the coating of the nanoparticles, can lead to varying catalytic properties of the resulting TiO_2 nanoparticles.

Titanium dioxide nanoparticles have photocatalytic abilities (1) - it can absorb the energy from light in the UV range, specifically at 346 nm and 362 nm, to catalyze organic reactions. To improve the recyclability of the diamagnetic TiO_2 nanoparticles, the nanoparticles had been enchanted on Fe_3O_4@SiO_2 microspheres by Shen et al. (2) to grant TiO_2 magnetic properties, and a gold coating was used to enhance its catalytic ability by reducing the bandgap of TiO_2.

For the first part of my research, I plan to synthesize Fe_3O_4@SiO_2@TiO_2 microspheres according to the synthetic route of Shen et al. but with coating metals other than gold to investigate if a metal coating substitute, such as silver, can be successfully synthesized on the Fe_3O_4@SiO_2@TiO_2 microspheres and be used to replace gold for enhanced photocatalytic abilities and for the reduced cost of the TiO_2 microspheres. Specifically, SEM will be applied to determine the 3D structure of the microspheres, and dye absorption will be used to determine the catalytic activity of the microspheres.

Another part of my research will be the synthesis of urchin-like TiO_2 whose structure was first provided by Xiang et al. (3). Notably, the double-layered urchin-like TiO_2 microspheres showed elevated reactivity compared to spherical or empty urchin-like microspheres of the same size. I plan to test out an unpublished method of the synthesis of urchin-like TiO_2 microspheres with glucose and $TiCl_3$ in a hydrothermal cell and optimize it by manipulating the amount of each reagent in each trial and determining the catalytic properties of the products.

II. Table of Contents

III. Project Description

A. Project Goals & Significance

In this project, my primary goal is to synthesize and to examine the catalytic properties of Agl-coated ferromagnetic TiO_2 microspheres to determine which metal coating will grant the TiO_2 nanoparticles the lowest bandgap and the highest reactivity as a catalyst. Not only will this help improve the catalytic efficiency of TiO_2 microspheres in the future, but the cost of synthesizing TiO_2 spheres might also potentially be reduced due to the possible decreased cost of the new metal coating compared to gold.

An alternative goal of the research, if I have leftover time after the first is completed, is to test out and to publish the unpublished method of the synthesis of urchin-like TiO_2. The structure of the TiO_2 synthesized from the method will be analyzed with SEM, and its photocatalytic activities will be examined to optimize each variable in the synthetic method, such as the concentration of each reagent. If the procedures can successfully synthesize the double-layered urchin-like TiO_2 microspheres with high catalytic activity, future studies on such TiO_2 will potentially be eased due to the comparatively simpler synthesis via accessible reagents in the unpublished method.

B. Methodology

1. Synthesis of Fe_3O_4@SiO_2@Ag@TiO_2 Microspheres (from Refs 2, 4, 5)

$FeCl_3$ (1.3 g, 8 mmol), trisodium citrate (0.5 g, 1.7 mmol), and sodium acetate (2.0 g, 24.4 mmol) were dissolved in ethylene glycol (40 mL) with magnetic stirring. The solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave, heated at 200 C for 10 h, and then cooled to room temperature. The black products were washed three times in ethanol and ultrapure water, respectively. An aqueous dispersion of the above-mentioned magnetite particles

(35 mL, 0.02 g/mL) was added to a three-neck round-bottom flask charged with absolute ethanol (140 mL) and concentrated ammonia solution (2.5 mL, 28 wt %) under mechanical stirring for 15 min at room temperature. The volume of 2.0 mL TEOS was added dropwise in 1 min, and the reaction proceeded for 10 h under continuous mechanical stirring. The resultant core-shell Fe_3O_4@SiO_2 microsphere product was separated and collected with a magnet, followed by washing with ethanol 6 times. Finally, the product was dried at room temperature for further uses. (4)

To grow the Ag NPs on the microspheres, the surfaces of the nanostructures were functionalized with APTES which supplied amidocyanogen for capturing the noble metal NPs. Following this process, the particles were dispersed into an aqueous solution of $AgNO_3$ by mechanical stirring. Then, fresh ice-cold $NaBH_4$ solution was added. Owing to the presence of amidocyanogen, silver NPs adhered to the nanostructures once they formed. (5)

The MG microspheres were dispersed in H_2O and stirred with CMC overnight. The sample was then washed twice with ethanol. Then the aqueous solution of the sample was mixed with 0.06 mL H_2O, and 25 mL of absolute ethanol under continuous mechanical stirring for 30 min. 0.612 g TBOT previously dissolved in 5 mL of ethanol was introduced drop by drop, followed by refluxing at 85 C for 90 min. The products were washed with ethanol several times, and then dried in vacuum for 4 h, and this intermediate product was defined as MG/TiO2-amorphous. Finally, 0.2 g MG/TiO2-amorphous and 0.185 g NH_4F were mixed with 33 mL of ethanol and 17 mL H2O under mechanical stirring for 60 min. The mixture was hydrothermally treated at 180 C in a Teflon-lined stainless steel autoclave for 24 h. After the reaction, the final product Fe_3O_4/SiO_2/AgNPs/TiO_2 was collected using a magnet, washed 3–4 times with ultrapure water to remove any ionic impurities, and dried at 80 C in air. (2)

2. Photocatalytic Testing of Fe_3O_4/SiO_2/AgNPs/TiO_2 Spheres (from Ref 5)

Analytical-grade methyl blue (MB, molecular formula: C37H27N3- Na2O9S3) was served as the target organic pollutant for photocatalytic experiments. The photocatalytic test was performed at room temperature. Typically, 10 mg of the photocatalyst was added into 30 mL of MB aqueous solution (40 mg/L). The suspension was stirred under complete darkness condition at least for 2 h to achieve the equilibrium adsorption of MB. Then, the suspension was exposed to UV–vis light irradiation using a 20 W low-pressure mercury lamp, which had spectral energy distribution centered at 365 nm, 405 nm, 436 nm, 547 nm, and 578 nm. After a regular interval, 2 ml of suspension was taken from the reaction vessels. The catalyst was separated by centrifugation, and the concentration of MB was analyzed by UV–vis spectrophotometer (HITACHI U-4100). (5)

C. Approximate Goals & Milestones

Weeks 1-8: Finish the synthesis of Fe_3O_4@SiO_2@AgNPs microspheres

Weeks 9-15: Analyze the properties of the resulting microspheres

Weeks 16-20: Enchant TiO_2 nanoparticles to the microspheres

Weeks 21-25: Test the photocatalytic properties of the microspheres

Weeks 25+: Conclusion and starting the second topic (Urchin-like TiO_2)

IV. References

1. P. Anandgaonker, G. Kulkarni, S. Gaikwad, A. Rajbhoj, Synthesis of TiO2 nanoparticles by electrochemical method and their antibacterial application. *Arab. J. Chem.* (2015), DOI:10.1016/J.ARABJC.2014.12.015.1.
2. J. Shen, Y. Zhu, X. Yang, C. Li, Magnetic composite microspheres with exposed {001} faceted TiO 2 shells: A highly active and selective visible-light photocatalyst. *J. Mater. Chem.* **22**, 13341–13347 (2012).

3. L. Xiang, X. Zhao, J. Yin, B. Fan, Well-organized 3D urchin-like hierarchical TiO2 microspheres with high photocatalytic activity. *J. Mater. Sci.* **47**, 1436–1445 (2012).
4. Y. Zhu *et al.*, Multifunctional magnetic composite microspheres with in situ growth Au nanoparticles: A highly efficient catalyst system. *J. Phys. Chem. C.* **115**, 1614–1619 (2011).
5. L. Xiang, X. Zhao, C. Shang, J. Yin, Au or Ag nanoparticle-decorated 3D urchin-like TiO2 nanostructures: Synthesis, characterization, and enhanced photocatalytic activity. *J. Colloid Interface Sci.* **403**, 22–28 (2013).

V. Biographical Sketches

A. Honors Chemistry, AP Chemistry, Currently taking Organic and Inorganic/Analytical Chemistry

B. Summer Research at Fudan Univ. (Summer 2019), Research Assistant at Jiaotong Univ. (Winter 2018)

C. Dr. Chen: ECAR club mentor, PRISMS Chemistry Club mentor, Teacher of AP Chemistry, Organic Chemistry, and Inorganic Chemistry

VI. Facilities, Equipment and Other Resources

1. Autoclave for the synthesis of ferromagnetic microspheres
2. (PU) SEM for the visual analysis of the image of the microspheres synthesized
3. FTIR for the analysis of the emission spectrum of the microspheres

4. UV lamp to provide UV radiation in the photocatalytic testing
5. Centrifuge to separate the catalyst in the catalytic testing
6. UV-vis Photospectrometer to analyze the emission spectrum of the spheres

VII. Budget and Budget Justification

Item Description	Supplier	Unit Cost	Quantity	Estimated Cost
$FeCl_3$	Sigma-Aldrich	41.30	100g	41.30 USD
TEOS	Sigma-Aldrich	47.40	25mL	47.40 USD
APTES	Sigma-Aldrich	70.90	100mL	70.90 USD
$NaBH_4$	Sigma-Aldrich	31.80	25g	31.80 USD
TBOT	Sigma-Aldrich	40.70	100g	40.70 USD
				Total Cost: 232.10 USD

PS: Quartzy is not working for me, and I cannot check what reagents our lab has right now. I will delete the repeating items after my email is set up for quartzy.

VIII. Current / Pending Support

Currently N/A.