# Assessment of the Photocatalytic Performance of Silica-Bound Photocatalysts For Sulfide Oxidation

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## Introduction

Heterogeneous photocatalysis is an effective strategy to improve the synthesis of organic compounds, but their characterization has been a long-standing challenge.

This work has explored using silica particles as substrates for heterogeneous photocatalysts, which are potentially easier to characterize. Silica is particularly well-suited for this due to its chemical inertness, low cost, and high availability.

The oxidation of sulfide to sulfoxide has wide applications in the synthesis of commercial pharmaceutical drugs making it a model reaction to test photocatalyst-bound silica. The selectivity and changes in chemical environment in reactant and product structures allow for quantitative NMR analysis.

## Objective

This project investigates the effect of different surface loading of molecular photocatalysts on silica on their photocatalytic performance.

The central goal is to synthesize a series of photocatalyst-bound silica by systematically tuning and controlling the density of surface photocatalysts and experimentally determine their performance (reaction yield and selectivity) in the light-driven oxidation reaction of sulfide to sulfoxide.

In the long term, this research aims to improve the synthesis of complex organic compounds, increase recyclability and reuse of photocatalysts, and develop reliable analytical techniques to characterize heterogeneous photocatalysts.

## Materials and Chemicals

- Silica Gel 300 µm -700 µm diameter, Pyridine - Sigma Aldrich, Methanol - Sigma Aldrich, Ethanol - Thermo Scientific, 99.54%, Dimethyl Sulfoxide (DMSO) - EMO, 99.8%, Dimethylformaldehyde (DMF) - Sigma Aldrich, Acetone - Fisher Chemical, 99.9%, Dibenzyl sulfide - Sigma Aldrich, Dibenzyl sulfoxide - Sigma Aldrich, Perylenetetracarboxylic dianhydride (PTCDA) - Sigma Aldrich, (3-Aminopropyl) triethoxysilane (APTES) - Sigma Aldrich, >99.0%, Chloroform ( $CHCl_3$ ) - Sigma Aldrich, Deuterated Chloroform ( $CDCl_3$ ) - Sigma Aldrich

## Instruments

- Centrifuge X Pro Series - Thermo Scientific
- 400 MHz Nuclear Magnetic Resonance Spectroscopy
- Photoreactor 450nm - HepatoChem
- Thin Layer Chromatography

## Methods and Results

### Step 1: Covalent Attachment of APTES to Silica Gel

- Weigh out 200 mg of silica gel
- Make 5%, 10%, 20%, 40%, 60% solutions of APTES with Pyridine and DMSO
- Centrifuge for 10 minutes at 14,000 rpm
- Decant the supernatant
- Wash and centrifuge with DMF (2x), MeOH (2x) Acetone (3x)
- Decant and dry in oven at 95°F for 30 min, then air dry overnight
- Characterized with ninhydrin test and IR spectroscopy

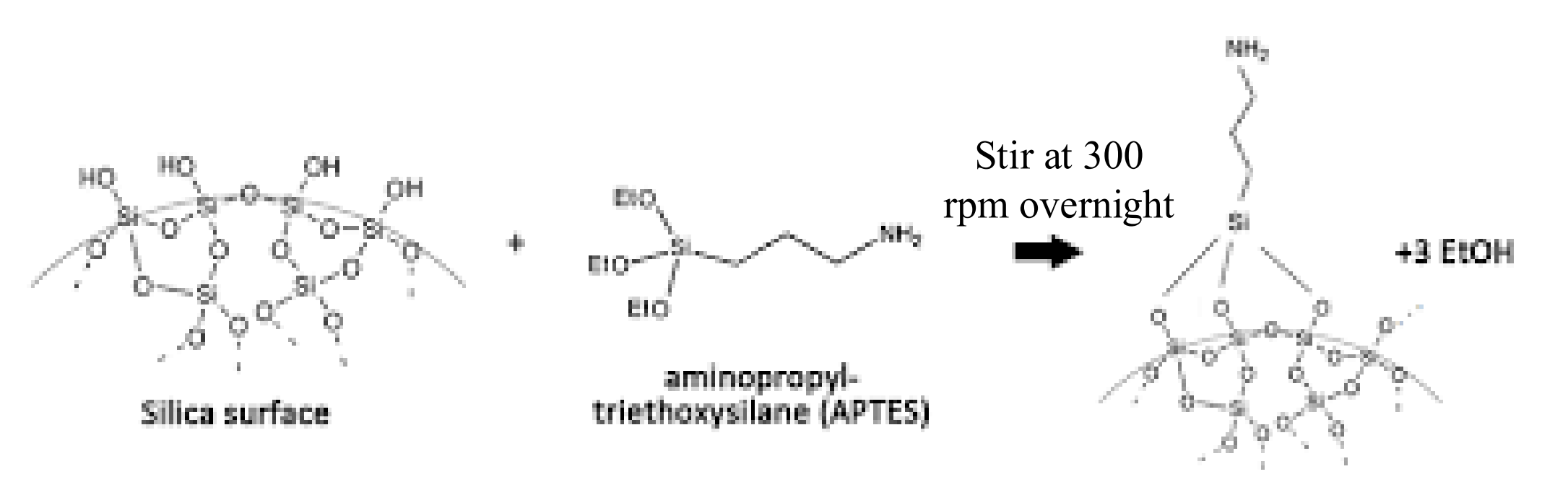

**Figure 1:** Covalent Attachment of APTES to Silica Gel

**Figure 2:** Results of Ninhydrin test showing a deeper color correlates to more APTES present on silica

### Step 2: Covalent Attachment of PTCDA to APTES-Silica Gel

- Fill each vial with 10mL DMSO and 45 mg of PTCDA
- After overnight reaction, centrifuge for 10 minutes at 140,00 rpm and decant supernatant
- Centrifuge and washed with DMF (2x), MeOH (2x) Acetone (3x)
- Decant and air dry

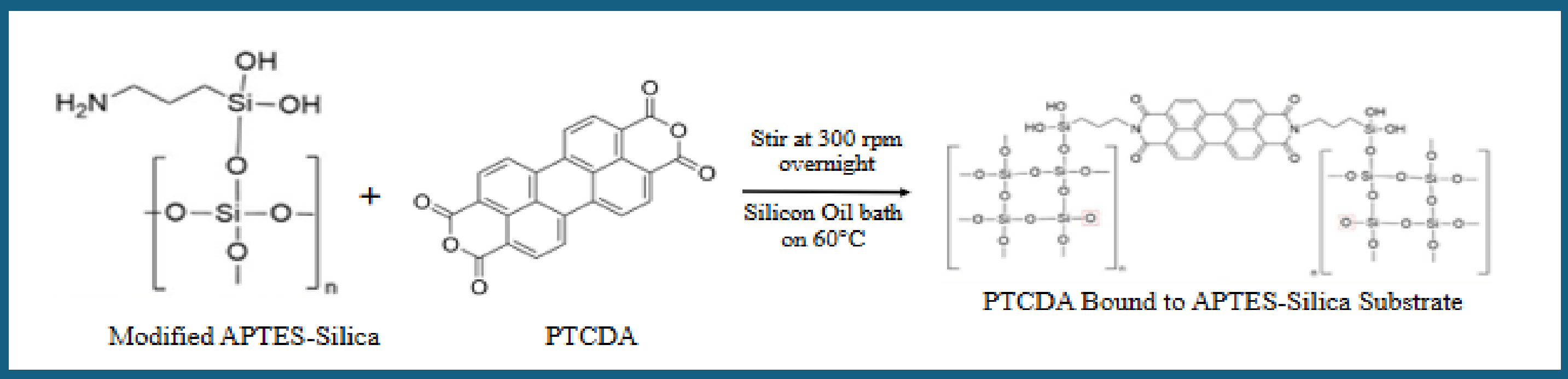

**Figure 3:** Covalent Attachment of PTCDA to Modified Silica Gel

### Step 3: Oxidation of Benzyl Sulfide to Benzyl Sulfoxide using the PTCDA Silica

- In 8 mL vial, add 100 mg dibenzyl sulfide, 20 mg of the 60% PC-silica, and 5 mL $CHCl_3$
- Take a 100 µL aliquot every 1.5 hours under 450 nm light
- Dilute aliquot with 900 µL of $CDCl_3$ to perform NMR spectroscopy

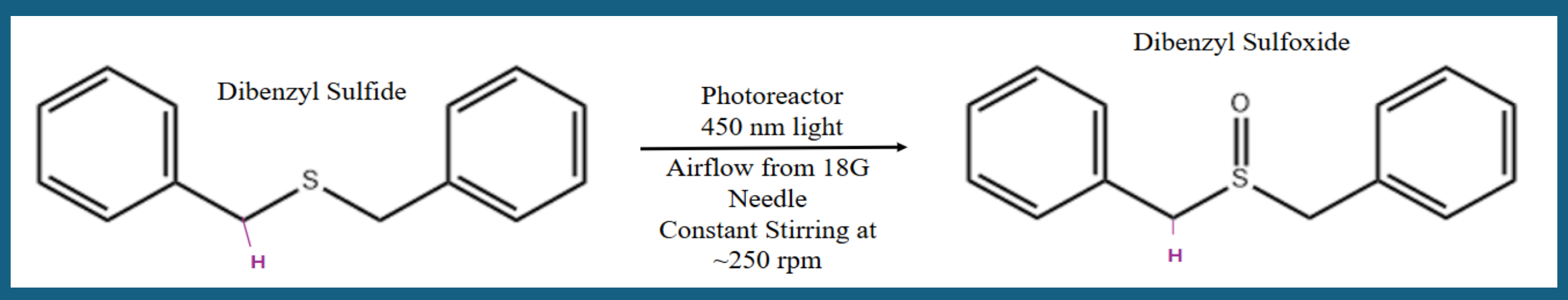

**Figure 4:** Oxidation Reaction of Sulfide to Sulfoxide. The reaction scheme above shows the change in the C-H bond environments as the reaction progresses from sulfide to sulfoxide. These NMR handles are detected and used for quantification of each component. This is shown visually in the Stacked NMR, Figure 6.

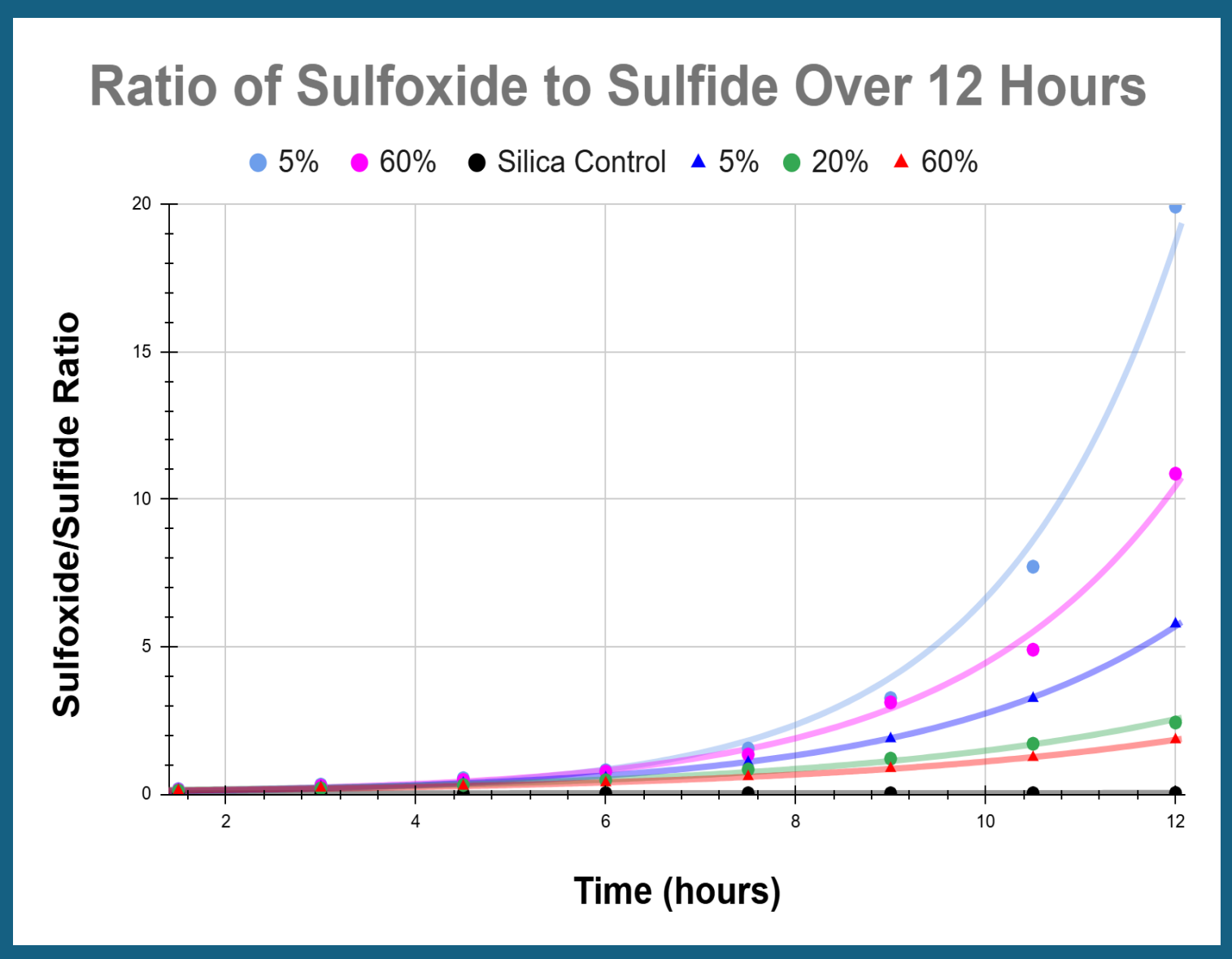

**Figure 5:** Graph indicates the exponential increase in the [Sulfoxide]/[Sulfide] ratio in each aliquot (90 minutes apart) over 12 hours total.

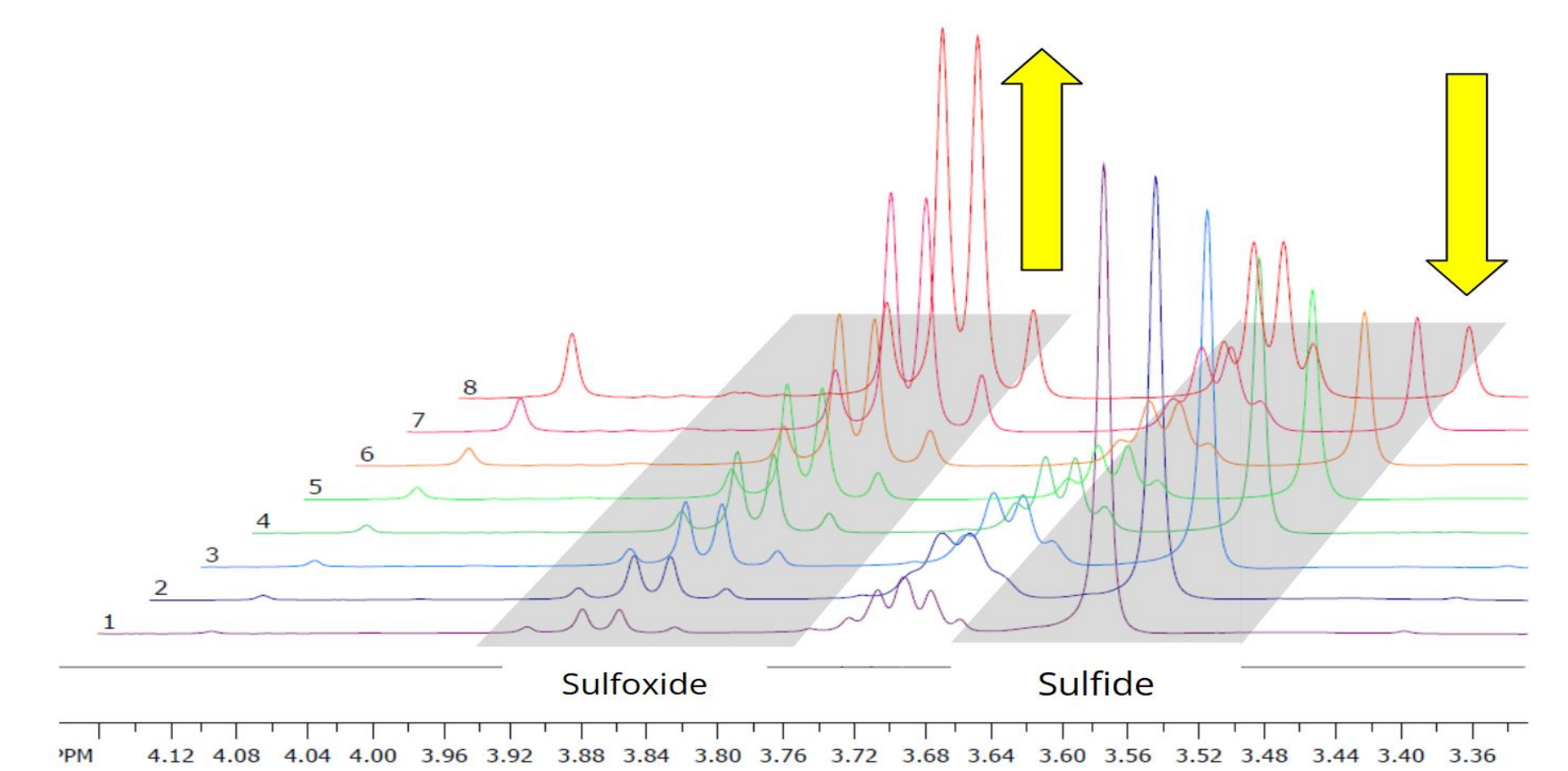

**Figure 6:** Stacked NMR Graph displaying Sulfoxide increases as Sulfide decreases with each aliquot over 12 hours of time ($CDCl_3$ solvent, 32 scans, 400 MHz NMR, limits of integrals stay the same for each sample).

## Summary and Conclusions

- Ninhydrin test confirmed amino groups on the surface of silica and red coloration indicated photocatalyst attachment
- Photocatalyst samples with higher concentrations of APTES were visibly darker suggesting higher loading
- NMR analysis and control tests showed that both photocatalyst-attached silica and light were required to drive sulfide oxidation under light
- Ratio of [Sulfoxide]/[Sulfide] present in each aliquot was higher for photocatalyst samples with lower loading
- Significant variation in reaction rates was observed between batches plausibly due to the influence of vial position and the cleanliness of reflecting mirrors in the photoreactor on the intensity of the incident light

## Future Work

- Assessing the effect of control parameters – changes in light intensity due to vial position and reflecting mirrors
- Testing the effect of recycling the photocatalyst on their performance in sulfide oxidation over multiple cycles
- Using a reaction standard (benzyl benzoate) in NMR analysis for determining absolute reactant and product concentrations as a function of reaction time
- Improving the protocols for synthesizing photocatalyst-bound silica

## References

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