Catalyst-Free “Click Chemistry” of Zinc Oxide Surfaces

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“Click chemistry” describes reactions that can modify the surface functionality of a material simply and quickly by joining small molecules together. In this research, a five step process was developed involving the surface modification of zinc oxide surfaces with propiolic acid and “clicking” with azidobenzene or 1-azido-4-fluorobenzene without the use of a catalyst. This process successfully modified the surface as determined by water contact angle, AFM imaging, absorption spectra, and PM IRRAS measurements.

Click Chemistry

Zinc oxide (ZnO) is an attractive material for inorganic-organic hybrid devices due to its low cost and its natural abundance. One application of these devices is organic/inorganic photovoltaics.[1]

The material’s electrical and structural properties can be modified by functionalizing the surface.[1]

However, finding chemicals that can attach to the ZnO surface that also provide the desired surface functionalization can be challenging.

The azide/alkyne “click” reaction modifies the surface in a modular fashion; the same alkyne attached to the surface can be changed by adding any azide.[2]

The general azide/alkyne click reaction is

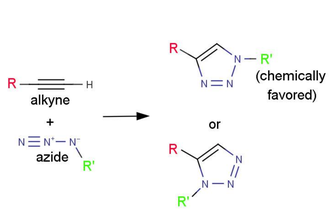


Figure 1: General azide/alkyne click reaction.

This versatile reaction had not been explored for planar ZnO films before this research.

Modifying ZnO Surfaces

The azide/alkyne reaction was applied to ZnO films in two main steps:

First, attach the alkyne:
Propiolic acid (PA), a carboxylic acid that easily attaches to ZnO.[3]

This step is seen in Figure 2.

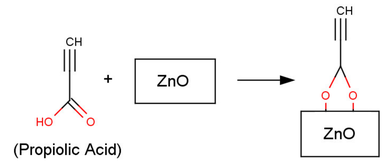


Figure 2: Attaching PA to ZnO surface

Second, attach the azide:
While any azide would attach to the PA, azidobenzene (AZB) and 1-azido-4-fluorobenzene (AFB) were used in this experimental reaction due their commercial availability, and their easily identifiable characteristics.

This step is seen in Figure 3.

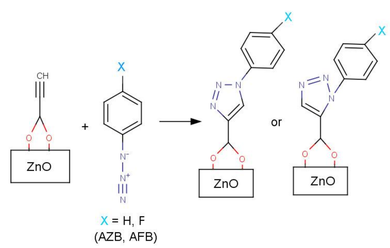


Figure 3: Clicking AZB or AFB to PA-modified ZnO surface

References

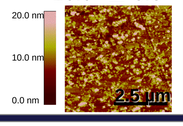
[1] C.G. Allen, *et al.*, Langmuir. **24**, 13393-13398 (2008).
[2] W.H. Binder and R. Sachsenhofer, Macromol. Rapid Commun. **29**, 952-981 (2008).
[3] M. Sato, *et al.*, Appl. Surf. Science. **258**, 786-790

The Process

Create ZnO surfaces

Sol-gel method used to deposit thin ZnO films on glass substrates

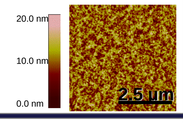
Water contact angle (CA): 16.0º ± 0.6º



Attach PA to surface

Soak ZnO samples in 0.1 mM propiolic acid in hexane for 3 minutes

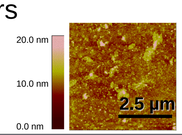
CA: 31º ± 1º



Soak in hexane

Soak in hexane stirred at 200 RPM for 12 hours to remove physisorbed molecules

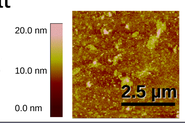
CA: 46º ± 2º



Attach azide

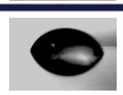
Soak in 0.1 mM AZB or AFB in methyl tert-butyl ether (MTBE) stirred at 200 RPM for 24 hours heated at 45° C

CA (AZB): 61º ± 1º

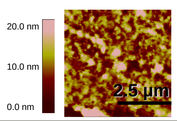


Soak in MTBE

Soak in MTBE stirred at 200 RPM for 4 hours to remove physisorbed molecules



CA (AZB): 68º ± 1º



Successful Modification

The water contact angle measurements (black and white photos on the left) indicate the wettability of the sample’s surface. Because every step of the process had a unique water contact angle, there is evidence that the surface was modified.

The atomic force microscope (AFM) images (orange photos on the left) give an indication that surface roughness changed throughout the process.

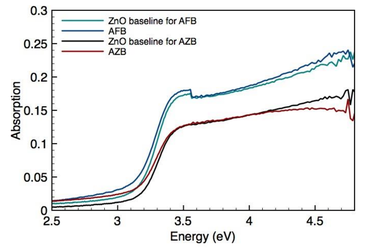


Figure 4 shows the absorption spectra of ZnO samples before and after surface modification. Because the spectra did not change significantly, only the sample’s surface was modified - the rest of the film remained unchanged.

Figure 4: Absorption spectra of ZnO before and after surface treatments.

Figures 5 and 6 show the PM IRRAS measurements of the AZB and AFB modified surfaces, respectively, along with the PA attachment scan.

The PA scans show the carbon-carbon triple bond peak and the characteristic carboxylic CO_2^- stretch region, indicating successful PA attachment.

The AZB and AFB scans show the strong benzene ring C-H peaks and aromatic C-C stretch bands, indicating the presence of the benzene ring. The C-N peak indicates that the carbon and nitrogen ring formed between the PA and the click chemical is also present.

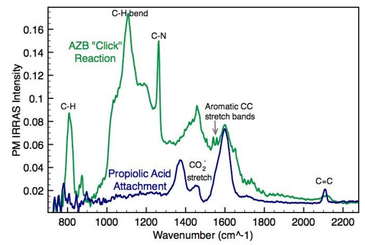


Figure 5: PM IRRAS scans of ZnO after PA attachment and the AZB “click” reaction. Both curves are normalized by ZnO background.

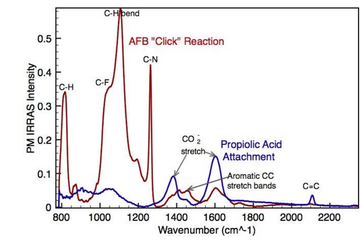


Figure 6: PM IRRAS scans of ZnO after PA attachment and the AFB “click” reaction. Both curves are normalized by ZnO background.

From these measurements, it is evident that the click reaction on the ZnO surface was successful.

Acknowledgements

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