

# Modification of coal surface with alkyl layers

Gentiana Hasani<sup>1</sup>

Fetah Podvorica<sup>1,2,4</sup>

Dardan Hetemi<sup>3,4</sup>

Avni Berisha<sup>1,4</sup>

<sup>1</sup>Chemistry Department of Natural Sciences and Mathematics Faculty, University of Prishtina, rr. "Nëna Tereze" nr. 5, 10000 Prishtina, Republic of Kosovo

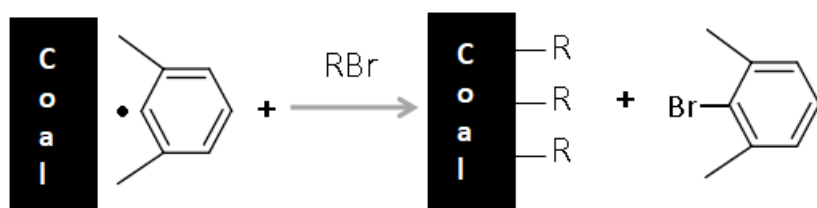
<sup>2</sup>Academy of Sciences and Arts of Kosova, Rr. "Agim Ramadani" nr 305, 10000 Prishtina, Republic of Kosovo

<sup>3</sup>Pharmacy Department of Medical Faculty, University of Prishtina, rr. "Nëna Tereze" nr. 5, 10000 Prishtina, Republic of Kosovo

<sup>4</sup>NanoAlb-Unit of Albanian Nanoscience and Nanotechnology, 1000 Tirana, Albania

[gentiana.hasani@uni-pr.edu](mailto:gentiana.hasani@uni-pr.edu)

Coal surface is chemically modified with alkyl moieties when it is immersed in the aqueous acid solution of alkyl bromide, in the presence of 2,6-dimethylbenzediazonium salt, (2,6-DMBD). 2,6-DMBD is synthesized in situ from 2,6-dimethylaniline when it reacted with the equivalent amount of sodium nitrite. Alkyl bromide serve as a source of alkyl radicals and they are generated when aryl radicals obtained during the chemical reduction of 2,6-DMBD remove the bromine atom of corresponding alkyl bromide. [1] This crossover reaction of aryl radicals is enabled due to the particular behaviour of 2,6-DMBD radicals, which because of steric hindrance don't react with the coal surface at the difference of other aryl radicals, Scheme 1. [2] This new approach enabled the modification of GC, Au and polymer surface with alkyl layers when aryl radicals were produced during the electrochemical reduction of 2,6-DMBD. [3,4] We have modified coal with hexyl carboxylic groups derived from 6-bromohexanoic acid and after rinsing in ethanol and acetone under sonication during 10 min, the sample is characterized with ATR IR and XPS techniques. ATR IR spectrum of modified coal presents a strong pic at 1715  $\text{cm}^{-1}$  attributed to the absorption of C=O groups while XPS high resolution spectrum of C1s showed the presence of the pic at around 289 eV which is characteristic for the presence of COOH groups. This results confirm the attachment of hexylcarboxylic acid groups onto coal surface by diverting the reactivity of aryl radicals derived from 2,6-DMBD in the presence of 6-bromohexyl carboxylic acid.



**Scheme 1:** Grafting of coal surface with alkyl layers derived from alkyl bromide through C-Br activation with a sterically hindered aryl radical obtained by reduction of the 2,6-dimethylbenzen diazonium salt.

## References

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[3] Electrografting of Alkyl Films at Low Driving Force by Diverting the Reactivity of Aryl Radicals Derived from Diazonium Salts. D. Hetemi, F. Kanoufi, C. Combellas, J. Pinson and F. I. Podvorica. *Langmuir*, 2014, 30, 13907-13913.

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