doi:10.1017/S1431927611009391
Microsc. Microanal. 17 (Suppl 2), 2011

Synthesis and Characterization of Chlorine and Bromine Doped TiO_2 Nanoparticles for Photocatalytic Methanol Production

A. McGuiness,* J. Baltrusaitis,* and R.A. Nessler*

* Central Microscopy Research Facility, University of Iowa, Iowa City, IA 52242

Methanol (CH_3OH) production from natural gas remains an important challenge in obtaining more readily transportable and storable fuel [1]. Methanol is the initial product of methane oxidation and is liquid at room temperature thus allowing for a facile distribution using existing petroleum pipeline or tanker infrastructure [2]. Synthesis gas, a mixture of CO and H_2, production has for decades been the most effective way to convert methane into the energy feedstock, H_2, which lacks convenient and inexpensive transportability properties. Syngas could later be used in high pressure/high temperature conversion reaction into CH_3OH. Several previous studies have shown that methane dissolved in water at moderate temperatures of >100 ^oC in the presence of semiconductor catalyst and solar light can be converted to methanol and hydrogen. TiO_2, a robust photocatalyst has been mostly used for this purpose. Here we synthesized and characterized chlorine and bromine doped TiO_2 with a goal to increase the efficiency of methane conversion to methanol via aqueous photocatalysis.

TiO_2 particles were synthesized using $TiCl_4$ and HBr as precursors [3]. Stainless steel autoclave with Teflon liner containing mixed solutions of 30 mL ethanol and 5 mL HBr were sealed and heated by convection oven at 100^{o}C for 1 day. The products were filtrated, washed with ethanol and residual Cl^- was tested with silver nitrate. Samples were dried at 60^{o}C before characterization.

TEM was performed using JEOL 2100F microscope equipped with Thermo Noran EDS detector operating at 200 kV. Samples were deposited on 400 mesh lacey carbon TEM grids from ethanol suspension. Cliff Lorimer k-factors were used for EDS elemental composition.

TiO_2 particles synthesized from $TiCl_4$ with and without HBr shown in Figure 1 are less than 10 nm in diameter. In general, nanoparticles are very efficient catalysts due to their large surface area; thus, synthetic method used in this work was successful in obtaining required particle size. SAED patterns shown in Figure 1 insets confirmed polycrystalline nature of TiO_2 nanoparticles. Elemental composition of synthesized particles was confirmed using EDS. Synthesized with and without HBr, EDS elemental composition was 61.8, 1.5 and 36.7 atomic percents for O, Cl and Ti, respectively, with Br concentration below detection limit. Presence of Br was later confirmed using other methods (XPS)

Synthesis and characterization of well defined polycrystalline Cl and Br doped TiO_2 nanoparticles was accomplished in this work. These particles will be used in photocatalysis experiments of methane to methanol conversion at low temperatures in aqueous solutions [4].

References
[1] C. E. Taylor and R. P. Noceti, *Catalysis Today*, 55 (2000) 259.
[2] C. E. Taylor, *Catalysis Today*, 84 (2003) 9.
[3] H. Luo et al., *Chemistry of Materials*, 16 (2004) 846.
[4] This research was partially supported by NSF grant AGS-0927944. Central Microscopy Research facility at University of Iowa is acknowledged for providing instrumental resources.

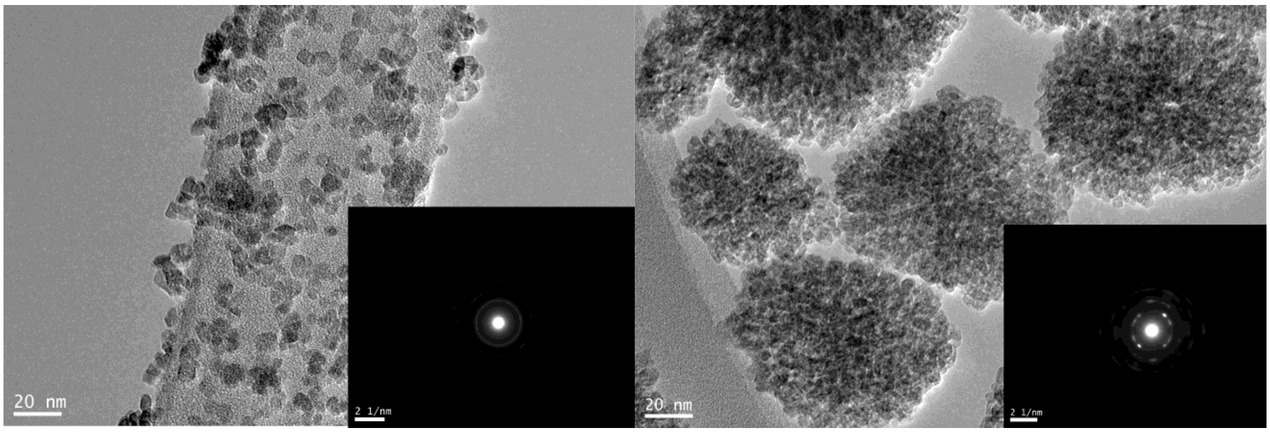

FIG. 1. TEM images of TiO_2 particles synthesized from $TiCl_4$ without (left) and with (right) HBr. SAED patterns are shown in insets.

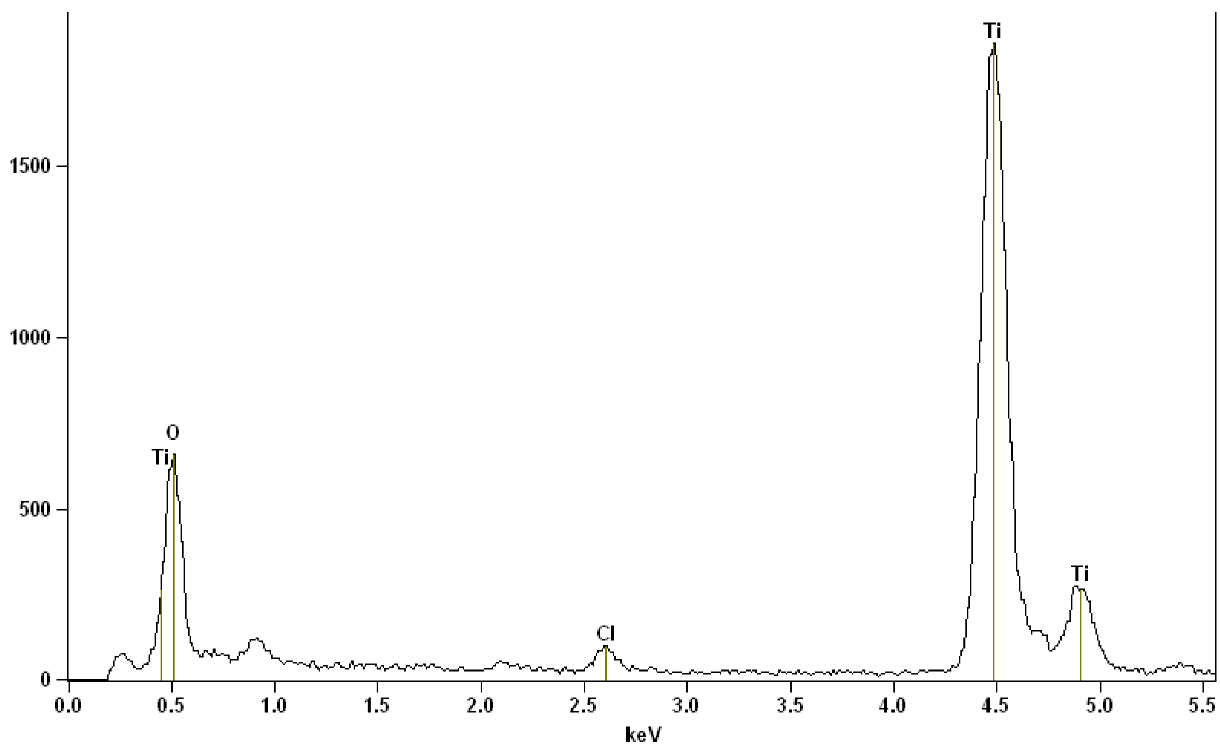

FIG. 2. EDS spectrum of TiO_2 particles synthesized from $TiCl_4$ synthesized without HBr.