STRONTIUM TITANATE PHOTOCATALYSTS: PREPARATION, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY

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Abstract
In this study strontium titanate photocatalysts were prepared *via* a hydrothermal method. The effect of various synthesis parameters (synthesis time, pH) on the properties of the samples obtained was investigated. The photocatalysts were characterized by X-ray diffractometry, scanning electron microscopy and transmission electron microscopy. The photocatalytic activity of the samples was evaluated by the photocatalytic reduction of carbon dioxide. A direct correlation was observed between the efficiency and strontium carbonate content of the photocatalysts.

Introduction
Due to the utilization of fossil fuels, carbon dioxide (CO_2) is constantly being emitted into the atmosphere. CO_2 is a well-known greenhouse gas that can trap heat, leading to global warming. Consequently, developing techniques that can reduce the concentration of CO_2 in the atmosphere is of utmost importance. Strontium titanate ($SrTiO_3$) is a promising candidate to address this issue. This material has beneficial properties such as long lifetime of electron–hole pairs, high chemical/thermal stability, and high catalytic activity [1]. To carry out photocatalytic reduction reactions, the energy of photoexcited electrons (and conduction band) must be higher than the redox potential of the reduction reaction of interest [2]. $SrTiO_3$ is considered to be a semiconductor with a wide band gap, and such materials are the most suitable for CO_2 photoreduction [3]. The reason for this is that they provide sufficiently negative and positive redox potentials concerning their conduction and valence bands, respectively. Taking these factors into account, in this work $SrTiO_3$ photocatalysts were prepared and their applicability for CO_2 photoreduction was investigated. Emphasis was put on examining the casual relationship between the synthesis parameters and efficiency.

Experimental
For the preparation of $SrTiO_3$ photocatalysts, multiple synthesis procedures were applied. Based on the publication of Ramos et al., 5 M NaOH (80 mL), 2 M urea (10 mL) and 3 M $Sr(NO_3)_2$ solutions were prepared [4]. After magnetic stirring for 10 min, these solutions were poured into a Teflon-lined stainless-steel autoclave, to which 2 g of P25 titanium dioxide was added. The synthesis mixtures were heat treated at 180 °C for 24 h ($SrTiO_3$_I), 48 h ($SrTiO_3$_II) or 72 h ($SrTiO_3$_III). Once they cooled down to room temperature a 5 M hydrochloric acid (HCl) solution was used to set the pH to 7.

Based on the publication of Jiang et al., 0.625 M $Sr(NO_3)_2$ solutions were prepared, which were added to 6 M ($SrTiO_3$_IV) 12 M ($SrTiO_3$_V) and 18 M ($SrTiO_3$_VI) potassium hydroxide solutions each containing 5 mmol of P25 titanium dioxide [5]. The synthesis mixtures were transferred into Teflon-lined stainless-steel autoclaves and heat treated at 180 °C for 12 h. Subsequently, the materials obtained were washed with Milli-Q water and ethanol four times. To reduce carbonate content, $SrTiO_3$_VI was additionally subjected to HCl treatment (0.01 M) for 2 h ($SrTiO_3$_VII).

X-ray diffraction (XRD) measurements were carried out with a Rigaku Miniflex II diffractometer to determine the crystalline composition of the samples using the following parameters: $\lambda_{Cu\ K\alpha}$ = 0.15406 nm, 30 mA and 40 kV. Scanning electron microscopy (SEM) measurements were performed with a Hitachi S-4700 Type II microscope applying 10 kV acceleration voltage. Transmission electron microscopy (TEM) measurements were also carried out, with a FEI Tecnai G2 20 X-Twin microscope, to investigate the morphology of $SrTiO_3$ photocatalysts.

The photocatalytic activity of the samples was evaluated by the photocatalytic reduction of CO_2. Analyses of the gases were performed with an Agilent 4890D gas chromatograph (GC). For the measurements a 2-m-long 0.25-inch-wide column containing Porapak QS was used, which enabled the complete separation and determination of the reactants and products.

Results and discussion

The XRD patterns of the photocatalysts are shown in **Fig. 1**. The patterns could be attributed to the cubic phase of the $SrTiO_3$ perovskite structure (JCPDS 00-035_0734). It was ascertained that the synthesis conditions (i.e., synthesis time and pH) did not have a significant influence on the crystalline structure of the samples. However, the application of HCl treatment for $SrTiO_3$_VII resulted in the remarkable reduction of carbonate ($SrCO_3$) content. As the amount of carbonate is an uncontrollable result of the synthesis it was beneficial to remove it in order to get a more clear view about the real activity of these materials.

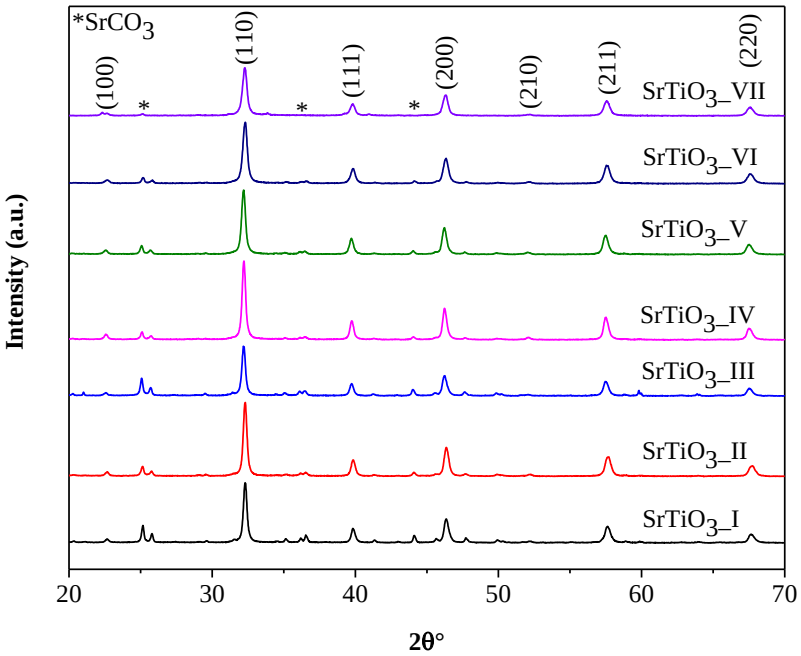

Figure 1. XRD patterns of $SrTiO_3$ photocatalysts.

Since all photocatalysts showed similar morphology, a SEM and TEM micrograph representative of them are shown in **Fig. 2**. It was ascertained that samples of perfect 3D cubic

morphology were obtained with an average size of 65 nm (calculated based on the TEM micrographs).

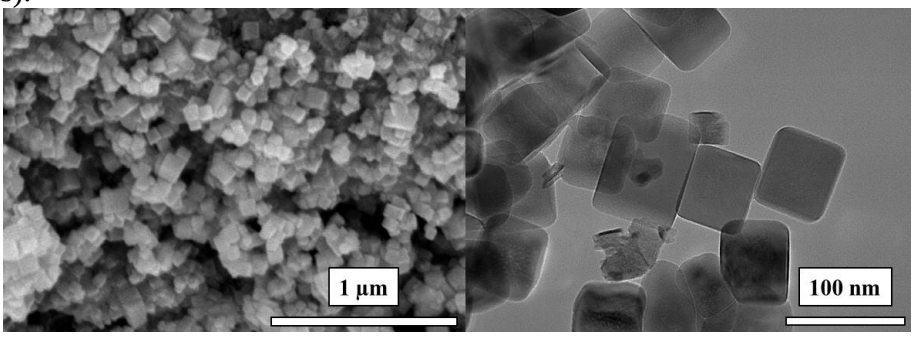

Figure 2. A typical SEM (left) and TEM (right) micrograph of the $SrTiO_3$ photocatalysts.

The results of photocatalytic evaluation obtained by GC measurements are shown in **Fig. 3**. It was observed that the samples with the lowest carbonate content (that is, $SrTiO_3$_VI and $SrTiO_3$_VII) had the best photoreduction activity. Comparing the samples synthesized with ($SrTiO_3$_VII) and without ($SrTiO_3$_VI) additional HCl treatment, it was ascertained that including it was beneficial for the photocatalytic activity. This result is in good agreement with the results obtained by XRD measurements.

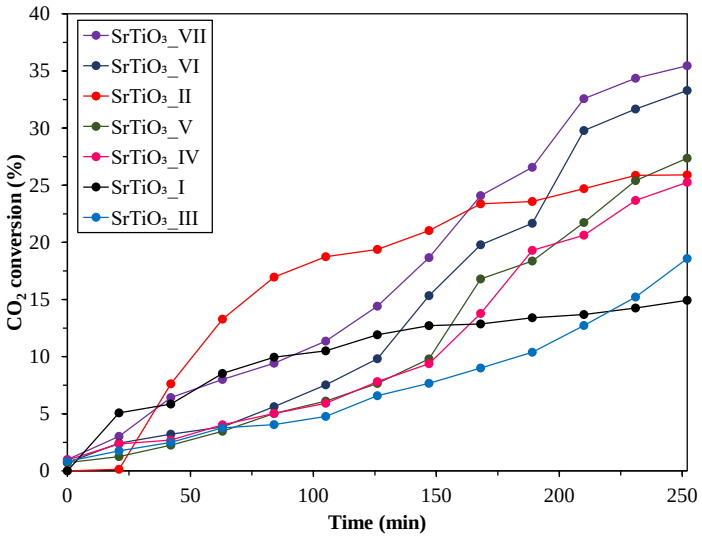

Figure 3. Photocatalytic reduction of CO_2 *via* as-prepared $SrTiO_3$ photocatalysts.

Conclusions

The applicability of $SrTiO_3$ was successful in the reduction of CO_2, resulting dominantly CO. The removal of $SrCO_3$ proved to be beneficial as the best sample was carbonate free, which was achieved with the addition of HCl. The morphology of the particles was cubic, with 50 nm as the particle size. No doping or other kind of structural modifiers were detected in the investigated samples.

Acknowledgements

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References

[1] B.L. Phoon, C.W. Lai, J.C. Juan, P.-L. Show, G.-T. Pan, Int. J. Hydrog. Energy 44 (28) (2019) 14316-14340.
[2] P. Kanhere, Z. Chen, Molecules 19 (12) (2014) 19995-20022.
[3] W.-N. Wang, J. Soulis, Y.J. Yang, P. Biswas, Aerosol and Air Quality Research 14 (2) (2014) 533-549.
[4] J.E. Ramos-Sanchez, R. Camposeco, S.-W. Lee, V. Rodríguez-González, Catal. Today 341 (2020) 112-119.
[5] D. Jiang, X. Sun, X. Wu, L. Shi, F. Du, Materials Research Express 7 (1) (2020) 015047.