Production of nanostructures, especially 3D branched architectures with controlled morphology and size, has been the focus of research in the recent years. One of such materials that can be grown in complex branched morphologies is rutile (TiO$_2$). While being applicable in variety of applications, rutile is known to be prone to twinning, which can be exploited as a basic structural element for growing branched structures. Branched structures of rutile-type TiO$_2$ are obtained in an acidic medium with the use of metalorganic Ti-precursor. Several nucleation mechanisms have been proposed in the literature, however the true nature of branching is yet to be explained. Several synthesis routes have been tested to study twinning of rutile. Following the synthesis pathway suggested by Tomita et al. (2006), 1st generation of twinning was obtained. Briefly, titanium powder was dissolved in H$_2$O and NH$_3$, to produce titanium oxyhydroxide. This was followed by a ligand exchange reaction with glycolic acid, to form Ti-glycolato complex, which was hydrothermally treated at 200 °C for 1-24 hours to obtain nanocrystalline rutile. 2nd generation of twins was obtained by a subsequent hydrothermal treatment of already existing twins by the addition of Ti-butoxide in strongly acidic medium. Another approach, following Zhou et al. (2011), yielded 2nd generation of twins in a single synthesis step. Two generations of twinning were obtained through hydrothermal synthesis in acidic medium. As precursor, Ti-butoxide was used and dissolved in 7-10M HCl aqueous solution. The syntheses were conducted at different temperatures and processing times. Morphology and composition of the products were characterized by SEM and TEM. The first route yielded clusters of twinned rutile crystals (Fig. 1). Electron diffraction study of twin relations indicated that the products are composed of (101) and (301) twins, with the characteristic angles of 114° and 55°, respectively. The second synthesis route led to formation of complex-branched structures, with abundant twinning and other types of intergrowths (Fig. 2a). Unlike in the first synthesis route, the rutile crystals here are composed of numerous parallel rutile fibers lined along the crystallographic c-axis (Fig. 2b and 2c). In crystals that are oriented along the c-axis inherent porosity can be observed, which might be a consequence of imperfect fiber alignment. Further, the presence of anatase phase, as suggested by several authors, could not be confirmed, nevertheless some unidentified reflections that could correspond to this TiO$_2$ phase are observed in electron diffraction patterns (Fig. 2d). Pores and imperfect alignment of the fibers indicate the possible mechanism of rutile formation and branching.

Fig. 1: (a) {101} and {301} twins of rutile obtained from Ti-glycolato complex, (b) TEM image of (301) twin. Fig. 2: (a) Rutiles synthesized from Ti-butoxide. (b) Fibrous rutiles coinciding in twin-type orientations. (c) Close-up of rutile roughly aligned fibers. (d) Single rutile fiber in [001] projection. Diffraction rings mainly correspond to rutile.