ELECTRONIC SUPPLEMENTARY INFORMATION for

Facile and scalable synthesis of Ti_5Si_3 nanoparticles in molten salts for metal-matrix nanocomposites

Marc Estruga,[a] Steven N. Girard,[a] Qi Ding,[a] Lianyi Chen,[b] Xiaochun Li[b] and Song Jin*[a]

[a]Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin, 53706 USA.
[b]Department of Mechanical Engineering, University of Wisconsin-Madison, 1513 University Avenue, Madison, Wisconsin, 53706 USA.
E-mail: jin@chem.wisc.edu; Fax: +1-608-262-0453; Tel: +1-608-262-1562.

Materials and Methods

Materials and Reagents

Aeroxide® P25 titanium dioxide nanoparticles (TiO_2, ≥99.5 %, CAS# 13463-67-7, Evonik Degussa Gmbh, 21 nm particle size), microsized TiO_2 particles (≥99 %, CAS# 13463-67-7, Sigma Aldrich, <40 µm particle size), silicon dioxide nanoparticles (SiO_2, ≥99.8 %, CAS# 7631-86-9, Sigma Aldrich, 12 nm particle size), microsized SiO_2 particles (>99 %, CAS# 7631-86-9, Sargent Welch, 325-mesh), lithium chloride (LiCl, ≥98 %, CAS# 7447-41-8, Sigma Aldrich), potassium chloride (KCl, ≥99 %, CAS# 7447-40-7, Sigma Aldrich), sodium chloride (NaCl, ≥99 %, CAS# 7647-14-5, Sigma Aldrich) magnesium powder (Mg, ≥99.5 %, CAS# 7439-95-4, Sigma Aldrich, 325-mesh), aluminum powder (Al, ≥99.7 %, CAS# 7429-90-5, Sigma Aldrich, granular, <1 mm) and hydrochloric acid (HCl, 37 % in H_2O, CAS# 7647-01-0) were used as received.

Ti_5Si_3 Nanoparticle Synthesis

The Ti_5Si_3 NP synthesis was initially developed in a tube furnace system under a dynamic Ar flow, where ~ 100 mg of product could be obtained. In order to satisfy the higher demand of Ti_5Si_3 NPs, the synthesis was successfully scaled up by a factor of 10 using a home-built stainless steel autoclave, so that ~ 1 g of NPs could be obtained in a single reaction. No difference in terms of phase purity and NP size distribution could be observed when comparing the products from the two synthetic approaches.

For a typical autoclave synthesis, Mg powder (2.000 g, 82.3 mmol) was manually ground in a mortar together with TiO_2 NPs (1.640 g, 20.5 mmol), SiO_2 (0.740 g, 12.3 mmol) and pre-dried LiCl/KCl eutectic mixture (15.640 g, 45/55 wt. %) for 15 min until a fine greyish powder was obtained. These amounts correspond to a 20:5:3 Mg:TiO_2:SiO_2 molar ratio, and a Mg concentration of 10 wt. % in the salt melt. Subsequently, the mixture was transferred to the stainless steel autoclave inside an Ar-filled glovebox and the container was tightly sealed, brought out of the glovebox, and heated to 700 ˚C for 2 h in a box furnace. After reaction, the autoclave was allowed to cool down to room temperature naturally and opened, and then the salts were washed with water and the MgO by-product was dissolved using a 2 M HCl solution. The remaining solid was collected by centrifugation and further washed with water until the supernatant solution reached neutral pH. After drying overnight at 60 ˚C, the Ti_5Si_3 NP product was recovered as a fine black powder (0.967 g, ~73 % yield).

In order to elucidate the silicide formation mechanism, several synthesis experiments were performed following the same procedure but modifying parameters such as the SiO_2 and TiO_2 particle size and the concentration of reagents in the salt melt (see main text for further details). In the case of the Ti_5Si_3 NPs prepared using Si NPs, a 12.5:5:3 Mg:TiO_2:Si molar ratio was used.

Preparation of the Al-Ti_5Si_3 Nanocomposite Powder

For the nanocomposite powder experiments, 0.250 g of the as-prepared Ti_5Si_3 NPs were grinded together with Al powder (0.5 g) and eutectic NaCl/KCl mixture (61.8 g, 44/56 wt. %), and then heated up to 700 ˚C in an alumina crucible under Ar flow. Once the salt melt reached constant temperature, an ultrasonic system [composed of a niobium C103 alloy waveguide (1.27 cm in diameter, 9.2 cm in length) coupled with a 20 KHz 600 W ultrasonic transducer (Misonix Inc., Newtown, CT, USA)] was turned on. Peak to peak amplitude was adjusted to 50 μm and the probe was submerged 0.5 cm deep into the liquid. The melt was ultrasonic processed for 30 min at 700 ˚C, and then left to cool down naturally to room temperature before washing away the NaCl/KCl with water. The obtained powder after centrifugation (consisting of Al-Ti_5Si_3 droplets) was cold rolled in a Sn foil and subjected to ion milling (Fischione 1010) to expose the cross sections of the Al microparticles.

Characterization

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance Powder diffractometer using Cu $K_{\alpha 1}$ radiation. Scanning electron micrographs (SEM) were acquired using a LEO Supra 55 VP field emission microscope operating at 3 kV and Energy-dispersive X-ray spectroscopy (EDXS) mapping was performed in a LEO 1530 SEM. Ti_5Si_3 NP suspension in ethanol was drop-casted onto transmission electron microscopy (TEM) grids (Ted Pella, lacey carbon type-A on 300 mesh Cu grids, #01890-F). TEM was carried out using a FEI Titan Aberration-corrected (S)TEM electron microscope operating at 200 kV.

Supplementary Figures

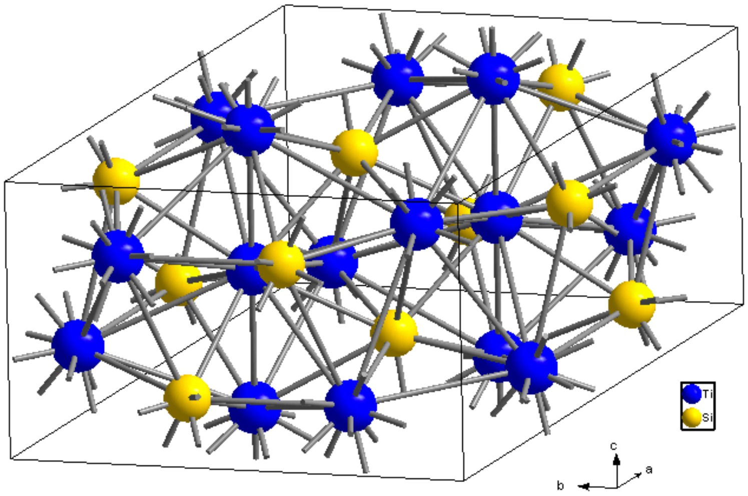


Fig. S1. Crystal structure of the Ti_5Si_3 phase (plotted using Diamond software).

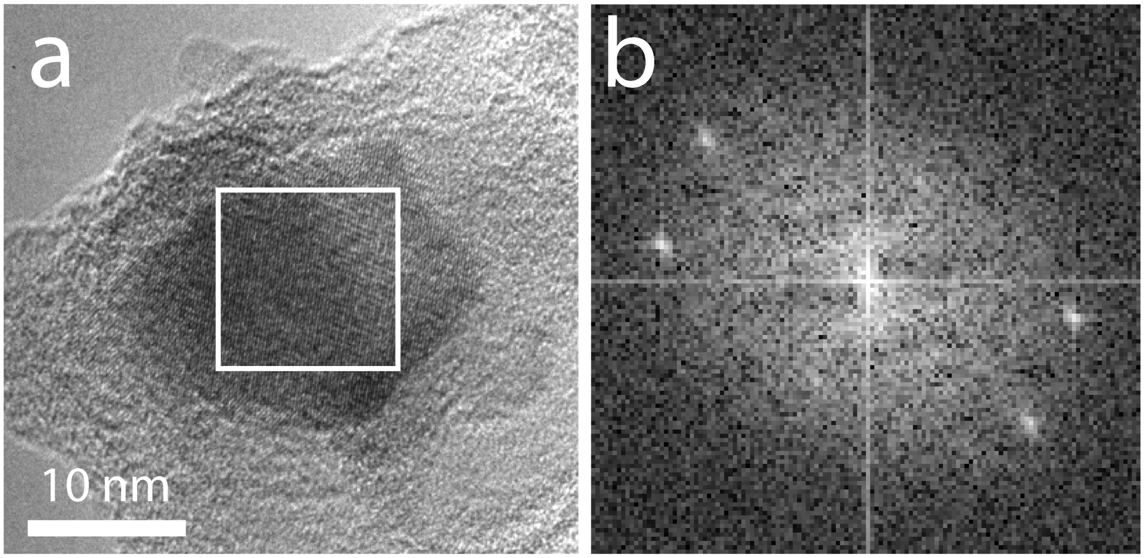


Fig. S2. HRTEM (a) and the corresponding FFT (b) of a single Ti_5Si_3 NP, showing the clearly resolved lattice fringes corresponding to the (211) plane of Ti_5Si_3 phase (0.22 nm).

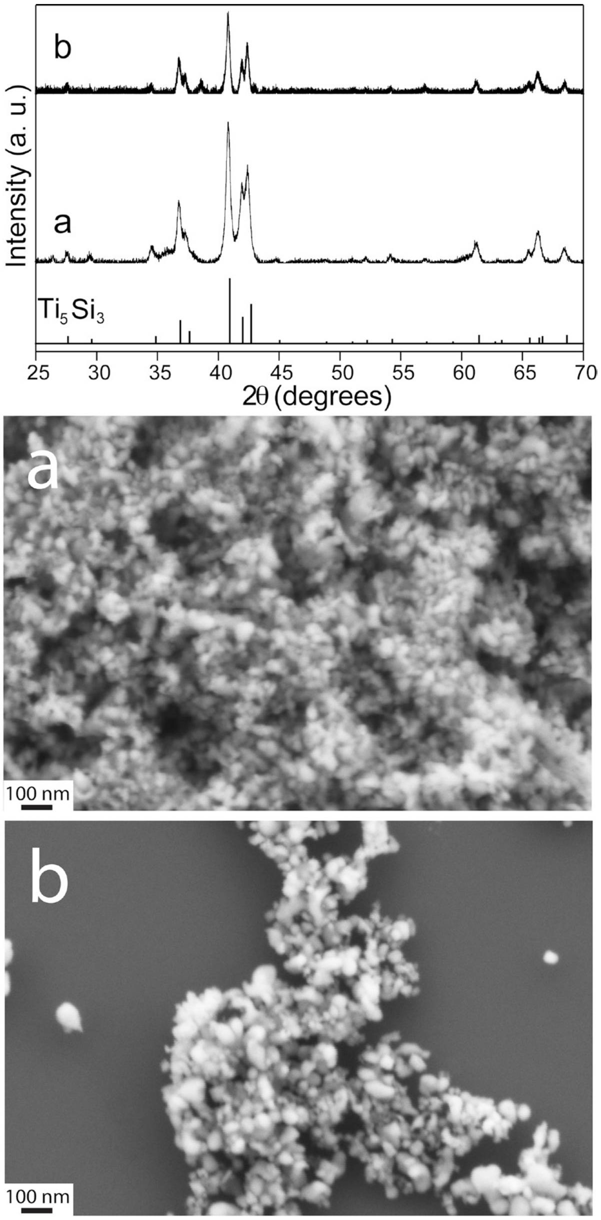


Fig. S3. PXRD and SEM micrographs of the Ti_5Si_3 NPs synthesized at different Mg concentration: 10 wt. % (a); and 18 wt. % (b).

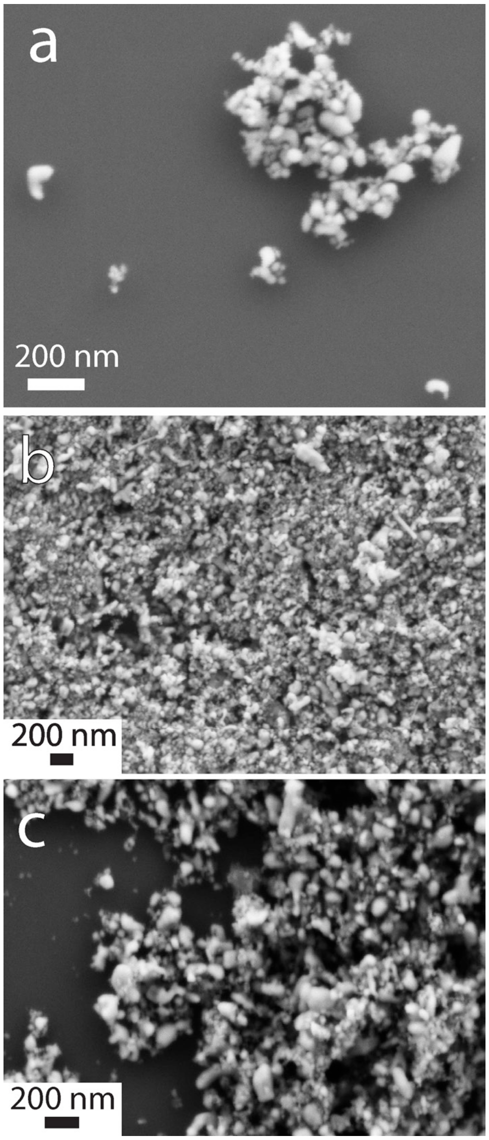


Fig. S4. SEM micrographs of the Ti_5Si_3 NPs obtained using different SiO_2 and Si sources: 12 nm SiO_2 NPs (a), ~40 µm SiO_2 microparticles (b), and ~ 100 nm Si NPs (c). The phase identity is confirmed by the PXRD patterns shown in Fig. 3 in the main text.

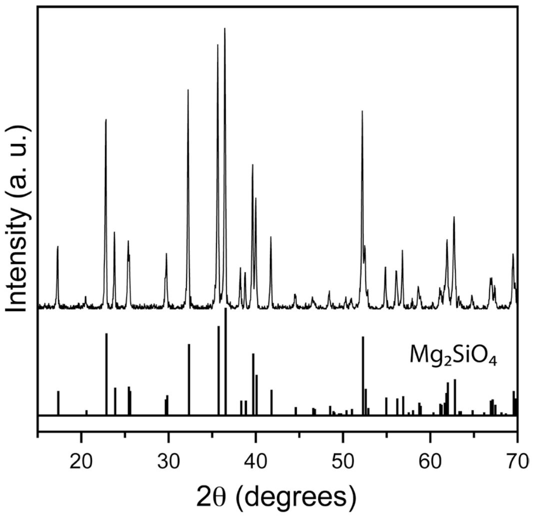
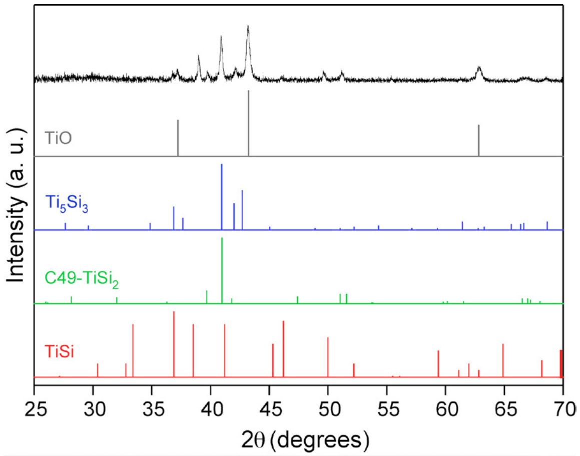


Fig. S5. PXRD pattern of the Mg_2SiO_4 powder obtained by reacting MgO with SiO_2 in LiCl/KCl salt melt in comparison with the standard diffraction pattern of Mg_2SiO_4 (PDF #34-0189).



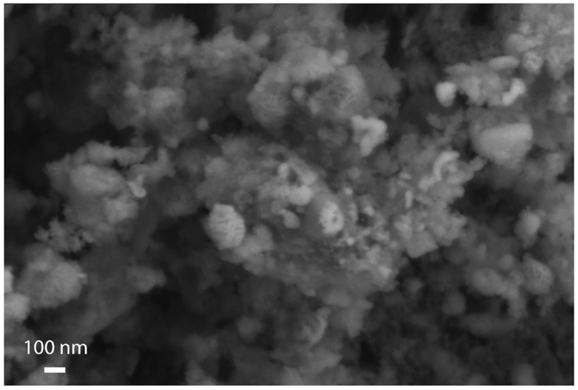


Fig. S6. PXRD and SEM micrographs of the mixed phase product obtained using large TiO_2 microparticles.

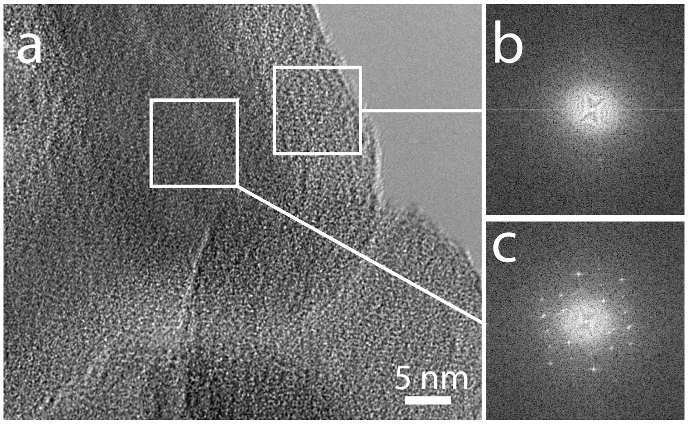


Fig. S7. HRTEM (a) and FFT micrographs (b and c) of a single Ti_5Si_3 NP, showing the amorphous nature of the shell and the crystallinity of the core.

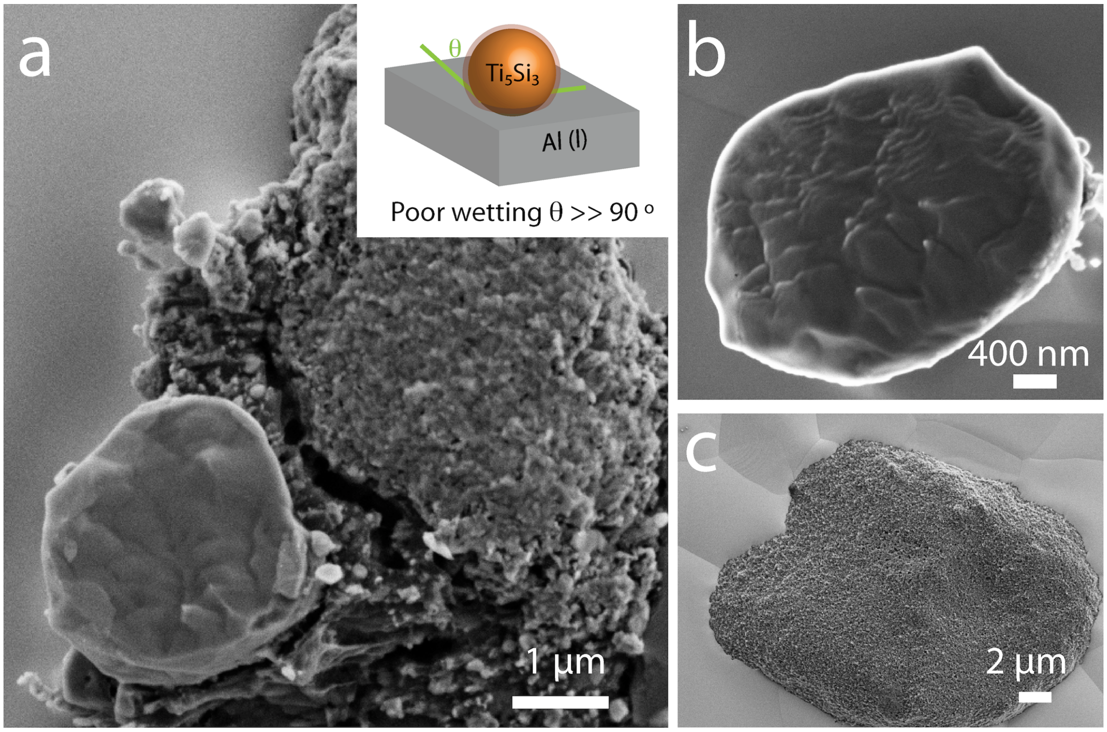


Fig. S8. SEM (and schematics, inset) of the poorly mixed Al and Ti_5Si_3 powders obtained using the Ti_5Si_3 NPs that have an amorphous layer on their surface.

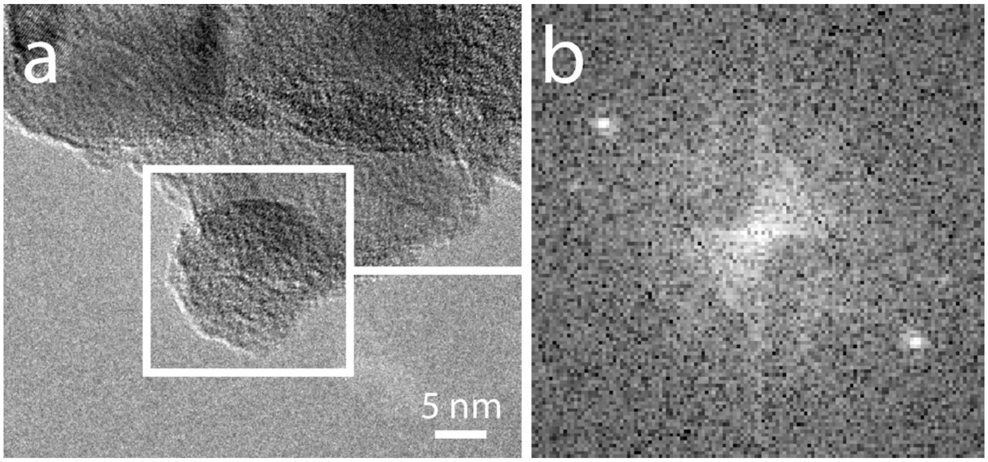


Fig. S9. HRTEM (a) and the corresponding FFT (b) of a crystalline surface-clean Ti_5Si_3 NP obtained after washing the MgO byproduct with 0.1 M HCl.