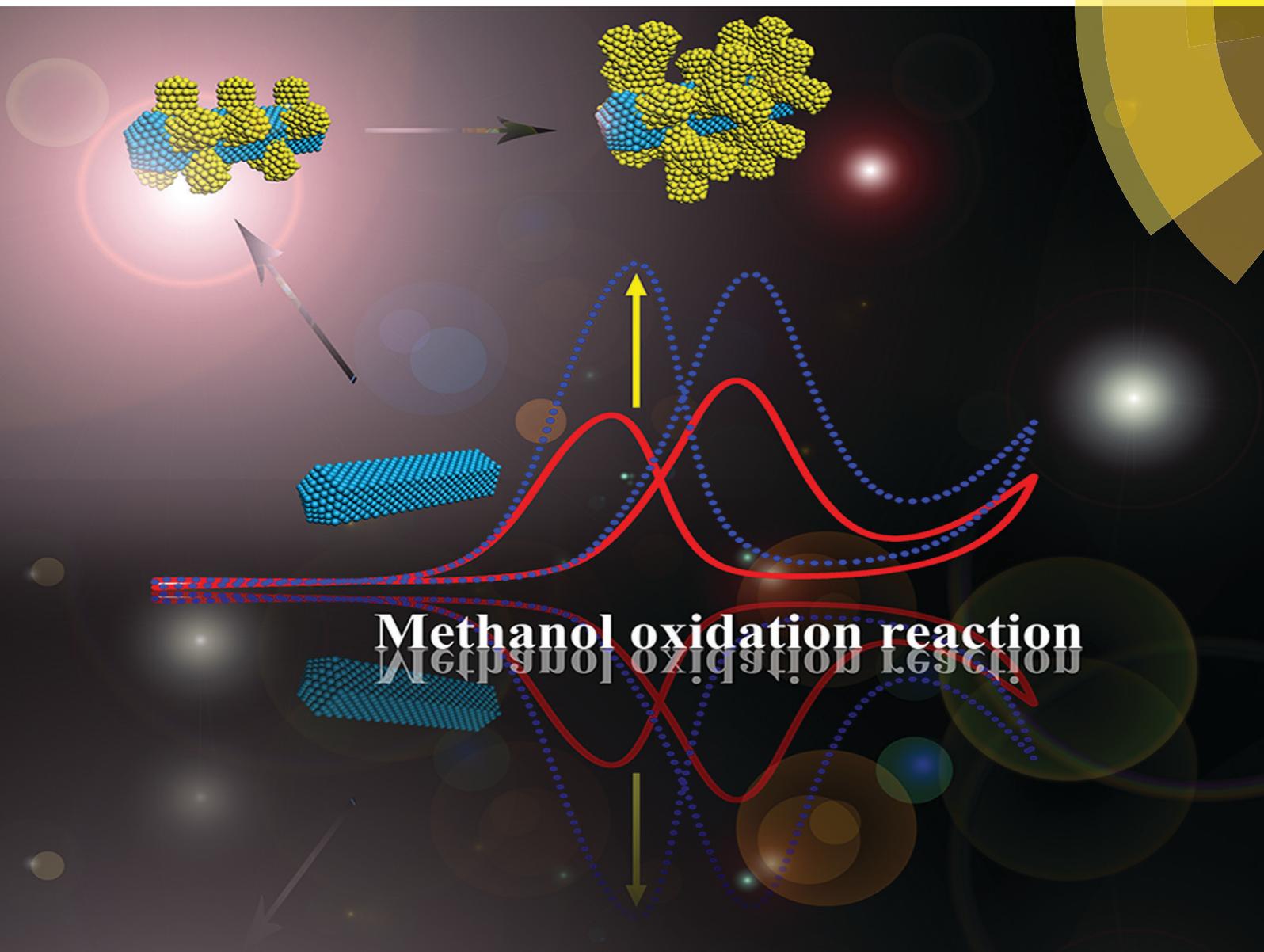


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**COMMUNICATION**

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## Twinning boundary-elongated hierarchical Pt dendrites with an axially twinned nanorod core for excellent catalytic activity†

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Twinning boundary-elongated hierarchical Pt nanostructures with excellent electrocatalytic activity were prepared by using axially twinned Pt<sub>3</sub>Ni nanorods as the platform for epitaxial transfer of a twinned crystal structure. The high electrocatalytic activity of the hierarchical nanostructures results from the synergistic effects of lattice mismatch between the Pt<sub>3</sub>Ni core and the Pt shell and the elongated twinning boundary.

### Introduction

The catalytic activity of a nanoparticle is greatly affected by the proportion of highly energetic structural features<sup>1–8</sup> in the entire nanostructure as well as by its surface area.<sup>9</sup> Accordingly, the preparation of facet-controlled nanoparticles with exposed high energy facets, steps, and kinks<sup>1–8</sup> and core-shell nanoparticles with lattice mismatch between the core and the shell has been extensively pursued to render high surface energy to a nanoparticle.<sup>10–13</sup> Recently, we have found that the presence of a twinning boundary on the nanoparticle surface greatly enhances the catalytic activity.<sup>14,15</sup> The highly energetic nature of a twinning boundary, however, usually leads to the formation of nanostructures with minimized exposure of the twinning coastline, although an extended coastline of a twinning boundary might be greatly beneficial to the catalytic activity.<sup>14,16</sup> On the other hand, the highly energetic twinning boundary of an axially twinned nanorod could serve as a preferred nucleation site for the growth of nanocrystals because the growth of new nanocrystals on it

would provide the desired surface energy minimization to the original twinning boundary.<sup>17–19</sup> The epitaxial growth of a nanocrystal on the twinning boundary would transfer the twinning properties to the newly grown nanostructures, leading to the elongation of an energetic twinning boundary on the surface of the resulting nanostructures. Furthermore, by growing new crystallites with a different composition on the existing twinning boundary, it would be feasible to create a highly energetic surface due to the presence of lattice mismatch between the original twinned nanostructure and newly grown nanocrystallites. Such a twinning boundary coastline-elongated nanostructure is expected to possess high catalytic activity due to i) a high surface area, ii) a highly active extended twinning boundary at the surface, and iii) surface energy elevating lattice mismatch between the core and the shell. Herein, we report the proof-of-concept experiment for the formation of twinning boundary maximized Pt<sub>3</sub>Ni@Pt heterohierarchical nanostructures by growing Pt nanodendrites on axially twinned nanorods of Pt<sub>3</sub>Ni as well as their excellent catalytic activities towards methanol oxidation reaction.

### Results and discussion

The transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images of hierarchical heteronanostructures are shown in Fig. 1. Thin Pt<sub>3</sub>Ni nanorods with diameters of 2–3 nm were prepared by using a procedure modifying the synthesis conditions for five-fold Pt nanorods (see the ESI† for synthesis details). The Pt<sub>3</sub>Ni nanorods are axially twinned as clearly seen in Fig. 1b. However, it is difficult to discern the exact twinning nature such as the five-fold twinning of related Pt nanorods due to the difficulty in vertical alignment of the thin nanorods. The energy dispersive X-ray spectroscopy study demonstrates an elemental composition of 3/1 (Pt/Ni) for the Pt<sub>3</sub>Ni nanorods (ESI,† Fig. S2). Small Pt nanocrystals could be grown on the twinning boundary of axially twinned Pt<sub>3</sub>Ni nanorods (Fig. 1a and b) *via* ethylene glycol-assisted thermal decomposition of Pt(acac)<sub>2</sub> at low temperatures. In a

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