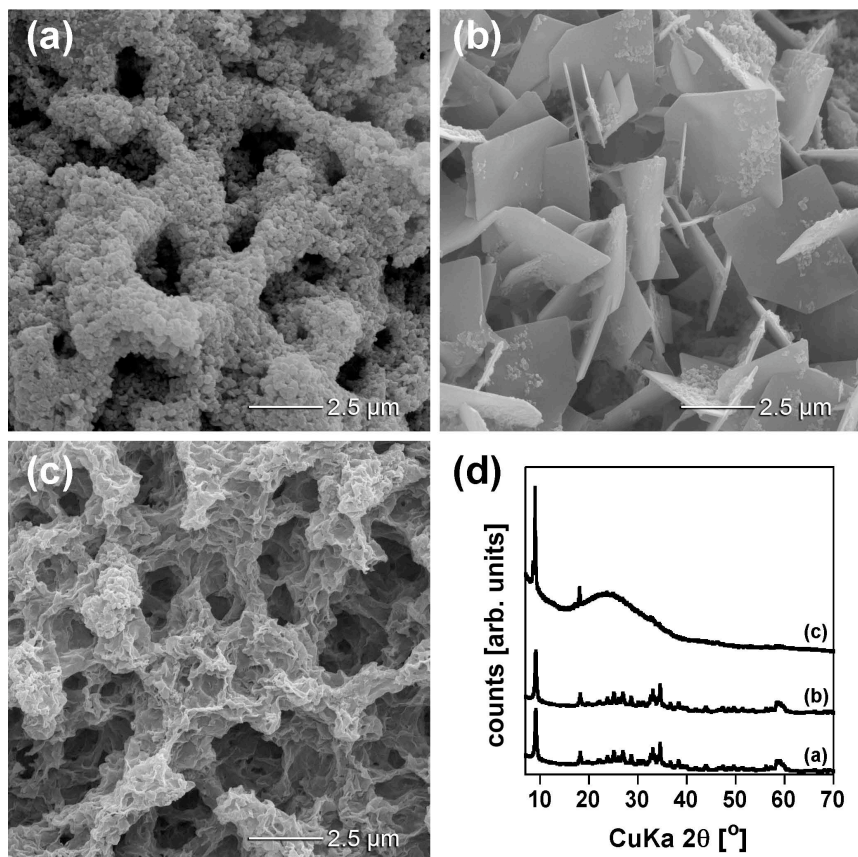**Supporting Information**

Details of the study of the unsupported thin films that formed around the substrates:

Figure S1. Scanning Electron Microscopy (SEM) images of thin films grown from an aqueous 0.1 M $Zn(NO_3)_2$ solution by vapor-diffusion catalysis over the course of 6 h at the water-air interface surrounding different exogenous substrates: (a) $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ at the air-water interface surrounding an amorphous glass substrate, (b) $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ at the air-water interface surrounding an FTO coated glass substrate, (c) $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ at the air-water interface surrounding a substrate of epitaxially grown ZnO, and (d) XRD pattern of the respective $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and ZnO films.

The low intensity of the XRD pattern (Figure S1 d) for the unsupported thin film grown

around the exogenous ZnO substrate is a result of the extremely thin film, rather than a

result of any difference in film properties. SEM images show that films nucleated around FTO substrates (Figure S1 b) contain well-defined thin plates growing into the reaction solution. They protrude from a connecting backplane at the air-water interface. In contrast, unsupported films that have been grown in reaction vessels with an amorphous glass substrate present (Figure S1 a) display an ordered, agglomerated network of fused nanocrystals (< 500 nm in diameter). A similarly porous network of fused material with no individual nanoparticles visible is observed for films grown in proximity to ZnO substrates (Figure S1 c). Films grown around ITO coated glass (not shown) display the same morphology and degree of crystallinity as the material nucleated in the region surrounding FTO coated glass (Figure S1 b).

All of the observed unsupported films are inhomogeneous in thickness but appear highly crystalline. The difference in morphology and structure of the unsupported films shown in Figure S1 compared to the previously reported template-free $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$[9] films most likely results from the disruption of the air-liquid interface by the substrate.

Experimental Details

All starting materials were commercially available and used without further purification. A dilute solution of NH_4OH (0.6 %) and a separate solution of aqueous 0.1 M $Zn(NO_3)_2$ were placed in the same enclosed chamber.[9] For growth of thin films on different substrates (glass, ITO coated glass and ZnO) the substrates were floated on the surface of the $Zn(NO_3)_2$ precursor solution. The film on FTO coated glass was grown by fixing the substrate with tape on the uncoated side, the oxide coated side facing downward, and adjusting the amount of precursor solution until the meniscus touched the substrate

surface. The synthesis of zinc hydroxide and oxide thin films, respectively, occurred at room temperature and ambient pressure over the course of 6 h.

After formation, the unsupported films were transferred onto a doubly distilled water surface to remove traces of starting material solution, using a Langmuir-Blodgett technique; the films grown on substrates were cleaned of $Zn(NO_3)_2$ solution by dipping the substrate with the film in doubly distilled water. All films were dried at room temperature under air overnight.

Scanning electron microscopy (SEM) was performed on dried samples using a Tescan Vega 5130 SEM. Powder X-ray diffraction (XRD) was performed using a Bruker D8 diffractometer with monochromatic Cu Kα radiation (λ=1.540 Å). For measurements on ZnO substrates a program was used in which the detectors of the diffractometer were offset by 14˚ so the dominant peak from the underlying substrate does not show up in the spectrum. All detected signals for samples containing ZnO substrates are due to the film grown by the vapor-diffusion method not to the substrate. For all other substrates peaks from the underlying substrates were visible; main peaks that can be indexed to the grown Zn-containing films on top of the substrates are clearly marked in Figure 1. The crystalline correlation length for the material grown on the epitaxial ZnO substrate was calculated with the Scherrer formula using the FWHM of the 100 and 002 reflections. The film thicknesses were determined using a DekTak[3] Surface Profilometer.