

**“Hybrid Materials of Polyaniline and Acidic Hexaniobate Nanoscrolls:
High polaron formation and improved thermal properties”**

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Supporting Information

Preparation of dispersion of emeraldine salt polyaniline (PANI-ES)

The dispersion of PANI-ES in water/*N,N*-dimethylacetamide (pH 2.5) was prepared following procedure from literature.¹⁻² Dedoped polyaniline (PANI-EB) powder (200 mg) was slowly added to 10 mL of *N,N*-dimethylacetamide (DMA) under stirring. The solution was stirred for 12 hours at room temperature and the insoluble particles were removed by filtration. The concentration of PANI-EB/DMA solution was determined by UV-VIS absorption spectroscopy considering the absorption coefficient at 630 nm per mole of the constitutional tetramer unit of PANI-EB ($\epsilon_{630} = 2.2 \times 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$).³ The PANI-EB/DMA solution was diluted by addition of DMA to result in a solution of concentration $4.2 \times 10^{-2} \text{ mol L}^{-1}$. One milliliter of this solution (dark blue color) was added to 9 mL of HCl solution (pH 3). The resulting dispersion (dark green color) was carefully acidified to pH 2.5 by addition of dilute HCl solution, and then

filtered. The acidifying of the dispersion was carried slowly to prevent the precipitation of polyaniline in medium of pH below 2.0. The estimated concentration of PANI-ES dispersion (pH 2.5) is *ca.* $4.2 \times 10^{-3} \text{ mol L}^{-1}$.

Exfoliation of $\text{H}_2\text{K}_2\text{Nb}_6\text{O}_{17}$ with tetra(*n*-butyl)ammonium hydroxide (TBAOH)

The exfoliation of acidic hexaniobate was carried out by following procedure described by Shiguihara *et al.*⁴⁻⁵ 500 mg of $\text{H}_2\text{K}_2\text{Nb}_6\text{O}_{17}$ (*ca.* 1.1×10^{-3} mol of H^+ -hexaniobate) were suspended in 250 mL of tetra(*n*-butyl)ammonium hydroxide solution (TBAOH). The concentration of TBAOH solution was $3.2 \times 10^{-3} \text{ mol L}^{-1}$, resulting in a suspension of molar ratio TBA^+/H^+ -hexaniobate of 0.75 (8.3×10^{-4} mol of TBA^+ / 1.1×10^{-3} mol of H^+ -hexaniobate). The suspension was stirred for 7 days at room temperature, and then kept without stirring for 1 day. Finally, the colloidal dispersion of exfoliated hexaniobate was carefully separated from the deposited solid by using a Pasteur pipette.

Additional results

Table S1. Values of EPR signal normalized by weight of PANI and EPR linewidth.

Sample	% wt of PANI ^a	weight of sample/ mg	weight of PANI in sample/ mg	EPR Signal (DI) ^b	DI normalized by weight of PANI (DI/m)/ mg ⁻¹	$\Delta H_{pp}/ G$
PANI-ES	84	5.3	4.5	250	56	9.3
PNb(pH2.5)	35	4.7	1.6	90.6	55	3.6
PNb(pH0.1)	32	4.5	1.4	41.6	29	4.7

^a Values determined by TGA analysis. ^b Values of double integration (DI) of the EPR signals.

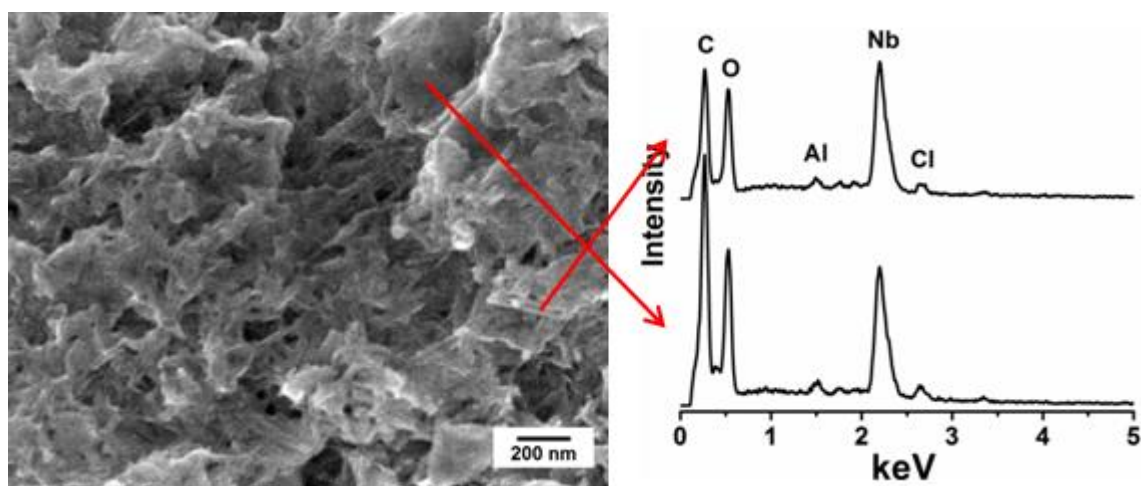


Figure S1. SEM image and EDX spectrum of hybrid material PNb(pH0.1).

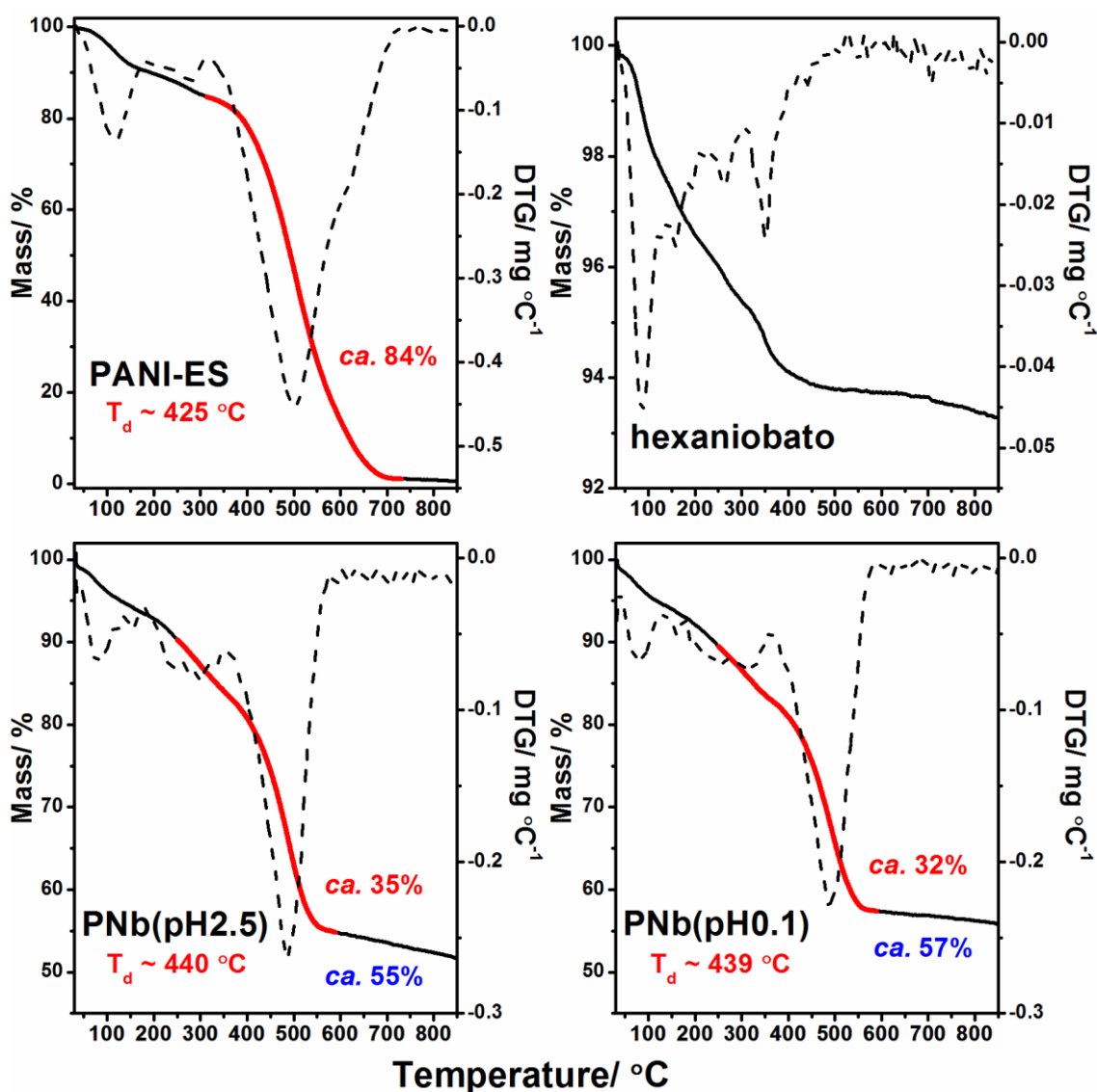


Figure S2. TGA (—) and DTG (---) curves of PANI-ES, hybrid materials PNB(pH2.5) and PNB(pH0.1), and hexaniobate. The polymer and hexaniobate contents are shown in red and blue, respectively. The temperature ranges considered for determination of the polymer contents are highlighted in red. T_d is the on-set temperature of irreversible decomposition of the PANI chains.

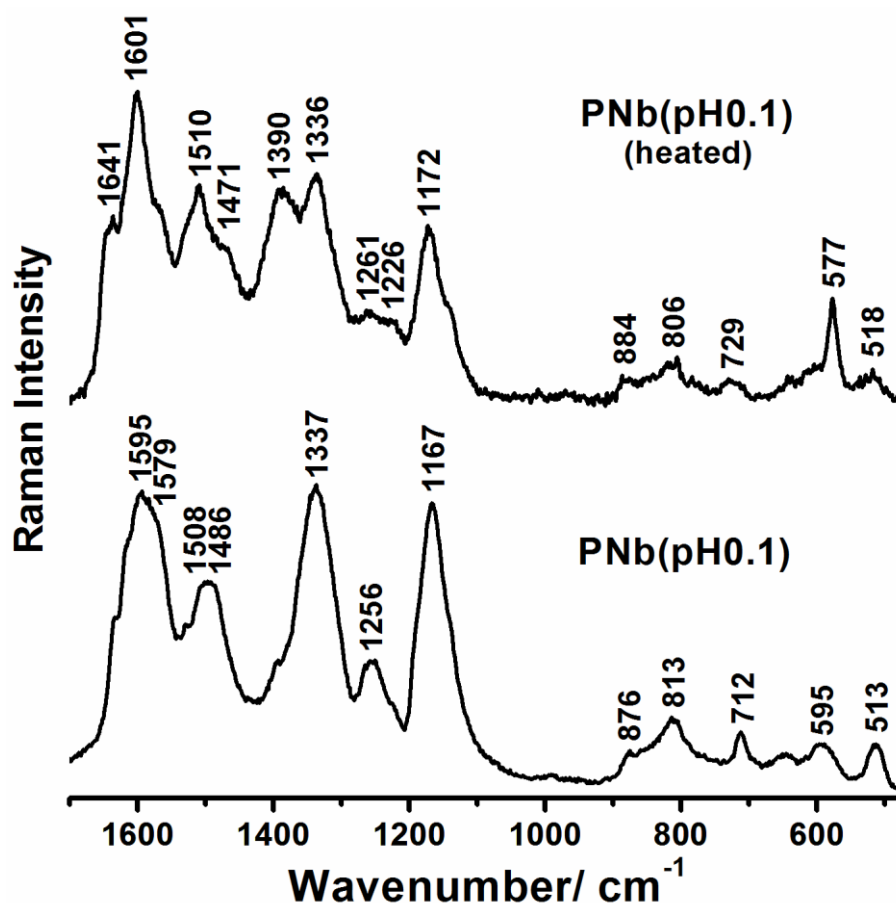


Figure S3. Resonance Raman spectrum ($\lambda_0 = 632.8$ nm) of hybrid material PNb(pH0.1) before and after heating treatment (150 °C during 90 min).

References

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