

Scanning ion selective electrode technique as a sensitive method for probing buffer activity of polyelectrolyte layers

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The polyelectrolyte multilayer films formed by the layer-by-layer (LBL) technique are attractive materials with large scale potential applications in the fields of surface modification, sensors, separation membrane for gases as well as supporting layers in biomaterials [1]. The morphology and chemical properties of polyelectrolytes alter significantly depending on such parameters as molecular weight, charge density, pH, temperature, and others [1, 2]. Despite the extensive research efforts for governing of the LBL formation and modification under any external stimuli, certain aspects still remain unclear. In our study we focused on measuring the buffering capacity of pH-sensitive poly(ethyleneimine) (PEI) – poly(sodium-4 styrenesulfonate) (PSS) assembly. Nanostructured TiO₂ films were used as a light-sensitive substrate, producing a local change in the pH when UV-stimulated photocatalytic reactions take place on the semiconductor surface [3]. In order to monitor local pH changes near the surface, we applied scanning ion selective technique (SIET). This technique provides measuring the concentration of specific ions (here, H⁺ ions) at a nearly constant microdistance. SIET maps were recorded sequentially in 0.05 M Na₂SO₄ solution 100 μm above the TiO₂ surface before, during and after UV irradiation. In the dark, the pH is not changed appreciably over the bare titania surface and is about 5.8. After applying the local UV illumination of the surface the pH decreases significantly over the light spot. Local acidification of solution up to pH 3.8 occurs in the center of the irradiated zone. The pH decreases more rapidly after starting the illumination, reaches a limiting value for the period of 3-4 min and then relaxes to the initial value during appr. 40 min, indicating that the UV-triggered acidification process is reversible. PEI-PSS layers were deposited on the TiO₂ surface for studying the buffer activity of polyelectrolytes. During irradiation of polymer-covered titania films, the pH decreased from initial 7.0 to final 4.5. In comparison with bare TiO₂, the region of local pH change is significant wider and spreads outside the irradiated zone, which can be related to protons accumulation and spreading in the LBL layer owing to their binding to amine groups of PEI. Furthermore, the pH relaxation near the LBL-coated TiO₂ surface slows down after light switching off.

In conclusion, we have demonstrated successful application of SIET technique for mapping of H⁺ ions activity over the bare and LBL-covered nanostructured TiO₂ films under the local UV irradiation. Generation of protons during photocatalytic reactions on the TiO₂ surface leads to a local acidification in the irradiation zone. Spreading of H⁺ ions and slower pH relaxation near the TiO₂ surface modified by PEI-PSS layers in comparison with the bare TiO₂ have proved the high buffer activity of polyelectrolyte layers.

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