A minimally invasive approach represented by endoscopic surgery has become widely used in various clinical departments, including digestive surgery, thoracic surgery, and urology, as one of the operations that can decrease the burden on patients. To perform more elaborate procedures, the need for highly functional coatings to enhance operability and operation efficiency of the equipment even as the visibility through the endoscope lens has clearly been apparent. In the present study, therefore, we designed multi-functional surfaces with anti-thrombogenicity, anti-reflection, and anti-fogging by controlling nano-ordered hierarchical structures via layer-by-layer self-assembly.\(^1,\)\(^2,\)\(^3\) The coatings were composed of polyelectrolyte multilayers prepared from blends of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) that were deposited in alternate layers with blends of poly(allylamine hydrochloride) (PAH), PVA, and PAA. Although the mixing cationic (PAH) and anionic (PAA) solutions generally cause polyelectrolyte-polyelectrolyte complexes (PECs) to form through electrostatic interactions, we found that PAH and PAA hardly formed PECs when PVA was present in the solution containing PAA. Consequently, PAA behaved differently in cationic and anionic solution, resulting in hierarchical texture. The structures possessed antireflective properties with graded refractive index and a transmittance of more than 95%. Further critical properties of the coatings were the resistance to protein adsorption, as measured from the peak area of fibrinogen, and the anti-fogging performance derived from the free hydroxyl groups and hydrophilicity with strong hydrogen bonds of PVA, respectively. The results of this study would be valuable for the development of innovative biomedical and analytical devices through a simple and environmentally friendly approach.