The topic of probing waveform design has received considerable attention due to its numerous applications in active sensing. Apart from having the desirable property of constant magnitude, it is also anticipated that the designed sequence possesses low sidelobe autocorrelation and/or specified spectral shape. In this paper, the alternating direction method of multipliers (ADMM), which is a powerful variant of the augmented Lagrangian scheme for dealing with separable objective functions, is applied for synthesizing the probing sequences. To achieve impulse-like autocorrelation, we formulate the design problem as minimizing a nonlinear least-squares cost function in the frequency domain subject to the constraint that all sequence elements are of unit modulus. Via introducing auxiliary variables, we are able to separate the objective into linear and quadratic functions where the unimodular constraint is only imposed on the former, which results in an ADMM-style iterative procedure. In particular, fast implementation for the most computationally demanding step is investigated and local convergence of the ADMM method is proved. To deal with the spectral shape requirement, we borrow the concept in frequency-selective filter design where passband and stopband magnitudes are bounded to formulate the corresponding optimization problem. In this ADMM algorithm development, unit-step functions are utilized to transform the multivariable optimization into a quadratic polynomial problem with a single variable. The effectiveness of the proposed approach is demonstrated via computer simulations.