A novel composite of graphene sheets/Congo red-molecular imprinted polymers (GSCR-MIPs) was synthesized through free radical polymerization (FRP) and applied as a molecular recognition element to construct dopamine (DA) electrochemical sensor. The template molecules (DA) were firstly absorbed at the GSCR surface due to their excellent affinity, and subsequently, selective copolymerization of methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) was further achieved at the GSCR surface. Potential scanning was presented to extract DA molecules from the imprinted polymers film, and as a result, DA could be rapidly and completely removed by this way. With regard to the traditional MIPs, the GSCR-MIPs not only possessed a faster desorption and adsorption dynamics, but also exhibited a higher selectivity and binding capacity toward DA molecule. As a consequence, an electrochemical sensor for highly sensitive and selective detection of DA was successfully constructed as demonstration based on the synthesized GSCR-MIPs nanocomposites. Under experimental conditions, selective detection of DA in a linear concentration range of \(1.0 \times 10^{-7} - 7.8 \times 10^{-4} \text{M}\) was obtained, which revealed a lower limit of detection and wider linear response compared to some previously reported DA electrochemical MIPs sensors. The new DA electrochemical sensor based on GSCR-MIPs composites also exhibited excellent repeatability, which expressed as relative standard deviation (RSD) was about 2.50\% for 30 repeated analyses of 20\mu M DA.