Electronic supplementary information (ESI):

**Fig. S1.** The SEM image of the RGO.
Fig. S2. CV studies of SS-β-CD–Pd@RGO/GCE as a function of scan rate (50–400 mV s⁻¹) using 2.0 mM $[\text{Fe(CN)}_6]^{3-/4-}$ redox couple (1:1) with 0.1 M KCl as supporting electrolyte (A); Magnitude of current response vs. scan rate (B); Value of redox potential vs. scan rate (C).
Fig. S3 (A) CVs obtained for 20 μM baicalin at SS-β-CD–Pd@RGO/GCE in 0.1 M PBS (pH 3.0) at various scan rates: 50, 100, 150, 200, 250, 300, 350, and 400 mV s⁻¹; (B) Magnitude of redox peak currents vs. scan rate; (C) Value of redox peak potentials vs. scan rate.
Fig. S4 (A) CVs obtained for 10 μM luteolin at SS-β-CD–Pd@RGO/GCE in 0.1 M PBS (pH 3.0) at various scan rates: 50, 100, 150, 200, 250, 300, 350, and 400 mV s$^{-1}$; (B) Magnitude of redox peak currents vs. scan rate; (C) Value of redox peak potentials vs. scan rate.
Optimization of experimental conditions

The effect of pH value on the determination of baicalin and luteolin at SS-β-CD–Pd@RGO/GCE over the range of pH 3.0–7.0 was investigated by DPVs. As shown in Figs. S5 and S6, the anodic peak currents of baicalin and luteolin at SS-β-CD–Pd@RGO/GCE decreased gradually with the increasing pH value in the range of pH 3.0–7.0. Considering that the too low pH is not favorable for the detection, pH 3.0 was selected as the optimal solution pH for the simultaneous determination of baicalin and luteolin. The peak potentials and pH showed linear relationships with the regression equations, $E_P (V) = -0.067 \text{ pH} + 0.54$ for baicalin and $E_P (V) = -0.061 \text{ pH} + 0.59$ for luteolin (Fig. S7). The observed shifts of 67 mV for baicalin and 61 mV for luteolin per pH unit were approximately close to the theoretical value of 57.6 mV per pH unit, indicating that the electron transfer was accompanied by an equal number of protons in the electrode reaction. The corresponding mechanisms of electron generation for baicalin and luteolin were provided in Scheme S1.

The accumulation step is a simple and effective strategy to enhance sensitivity; thus, the effects of accumulation time and potential on the SS-β-CD–Pd@RGO/GCE sensor were investigated. The oxidation peak currents of 20 μM of baicalin and 10 μM of luteolin were compared at different accumulation times. Fig. S8 shows that oxidation peak currents gradually increase with increasing accumulation times of up to 200 s and then level off thereafter, which indicates that accumulation of baicalin and luteolin on the SS-β-CD–Pd@RGO/GCE can rapidly reach saturation. The impact of accumulation potential on the baicalin and luteolin oxidation peak currents was also investigated. Fig. S9 shows that the highest oxidation peak current is achieved at −0.2 V. Thus the accumulation step was performed at −0.2 V for 200 s.
Fig. S5. Effect of detection medium pH on the oxidation peak currents of 20 μM of baicalin at SS-β-CD–Pd@RGO/GCE in 0.1 M pH 3.0 PBS.

Fig. S6. Effect of detection medium pH on the oxidation peak currents of 10 μM of luteolin at SS-β-CD–Pd@RGO/GCE in 0.1 M pH 3.0 PBS.
**Fig. S7.** Variation of the peak potentials of baicalin and luteolin vs. pH of the detection medium.

**Scheme S1.** The corresponding mechanisms of electron generation for baicalin (a) and luteolin (b).
**Fig. S8.** Effect of accumulation time on the oxidation peak currents of 20.0 μM baicalin and 10.0 μM luteolin at SS-β-CD–Pd@RGO/GCE in 0.1 M pH 3.0 PBS by DPV. Pulse width: 0.05 s; amplitude: 0.05 V.

**Fig. S9.** Effect of accumulation potential on the oxidation peak currents of 20.0 μM baicalin and 10.0 μM luteolin at SS-β-CD–Pd@RGO/GCE in 0.1 M pH 3.0 PBS by DPV. Pulse width: 0.05 s; amplitude: 0.05 V.
Fig. S10. The oxidation currents of 20 μM baicalin and 10.0 μM luteolin in the absence (control) and presence of various interferents: 200 μM of glucose, 200 μM of oxalic acid, 200 μM of citric acid, 200 μM of urea, and 200 μM of AA.