Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary information

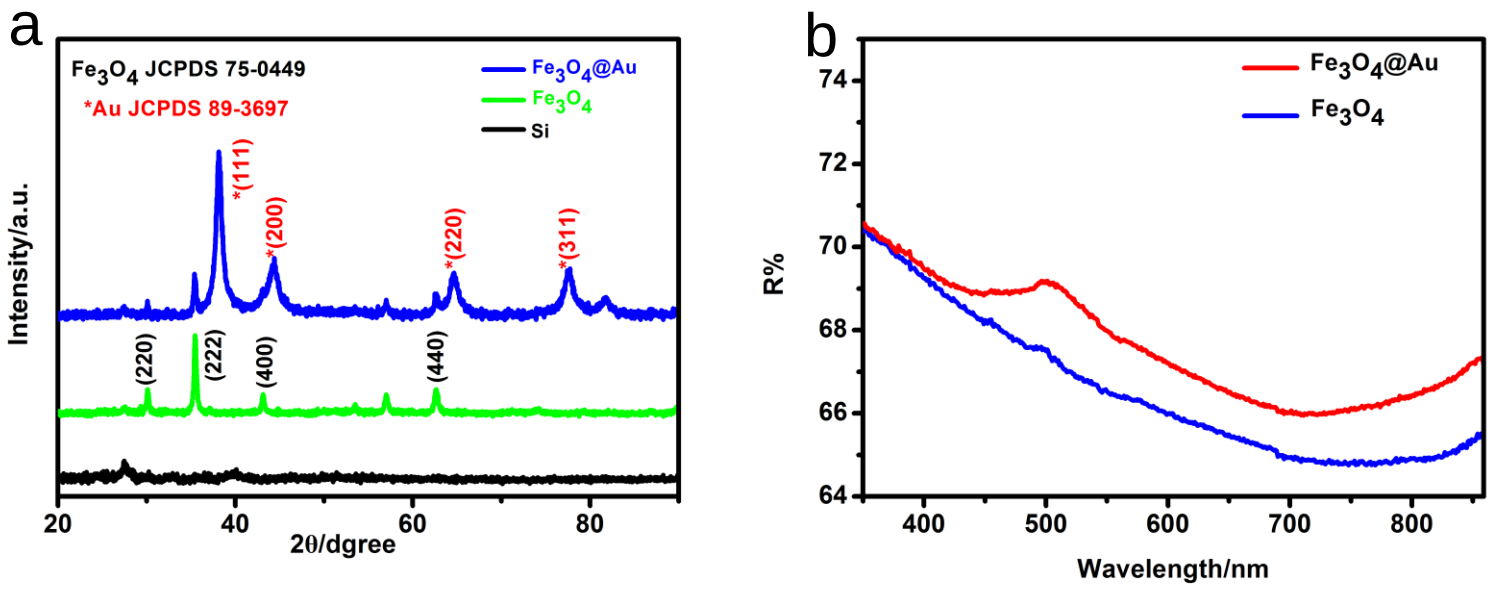


Figure S1. a) XRD patterns of prepared Fe_3O_4 NPs (green curve), Fe_3O_4@Au NCs (blue curve) and the silicon substrate (black curve, control substrate for XRD) . b) Reflection spectra of the Fe_3O_4 NPs and Fe_3O_4@Au NCs in aqueous solutions.

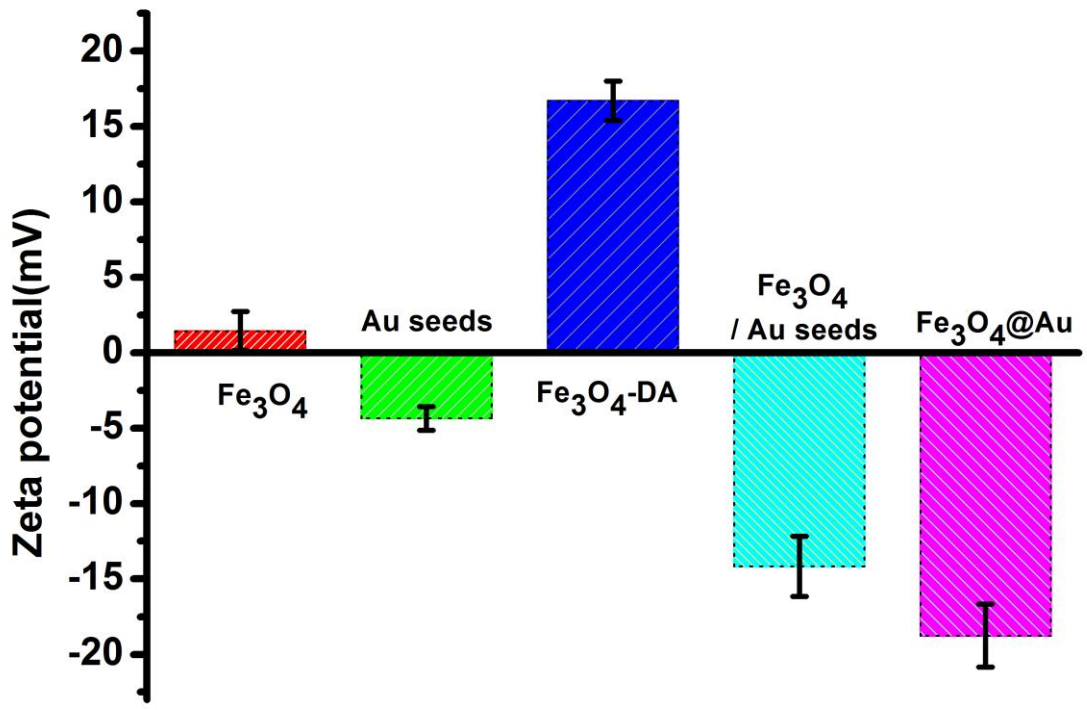


Figure S2. Measurements of Zeta potential of intermediate and final products during the synthesis, error bar : standard deviation (n=3).

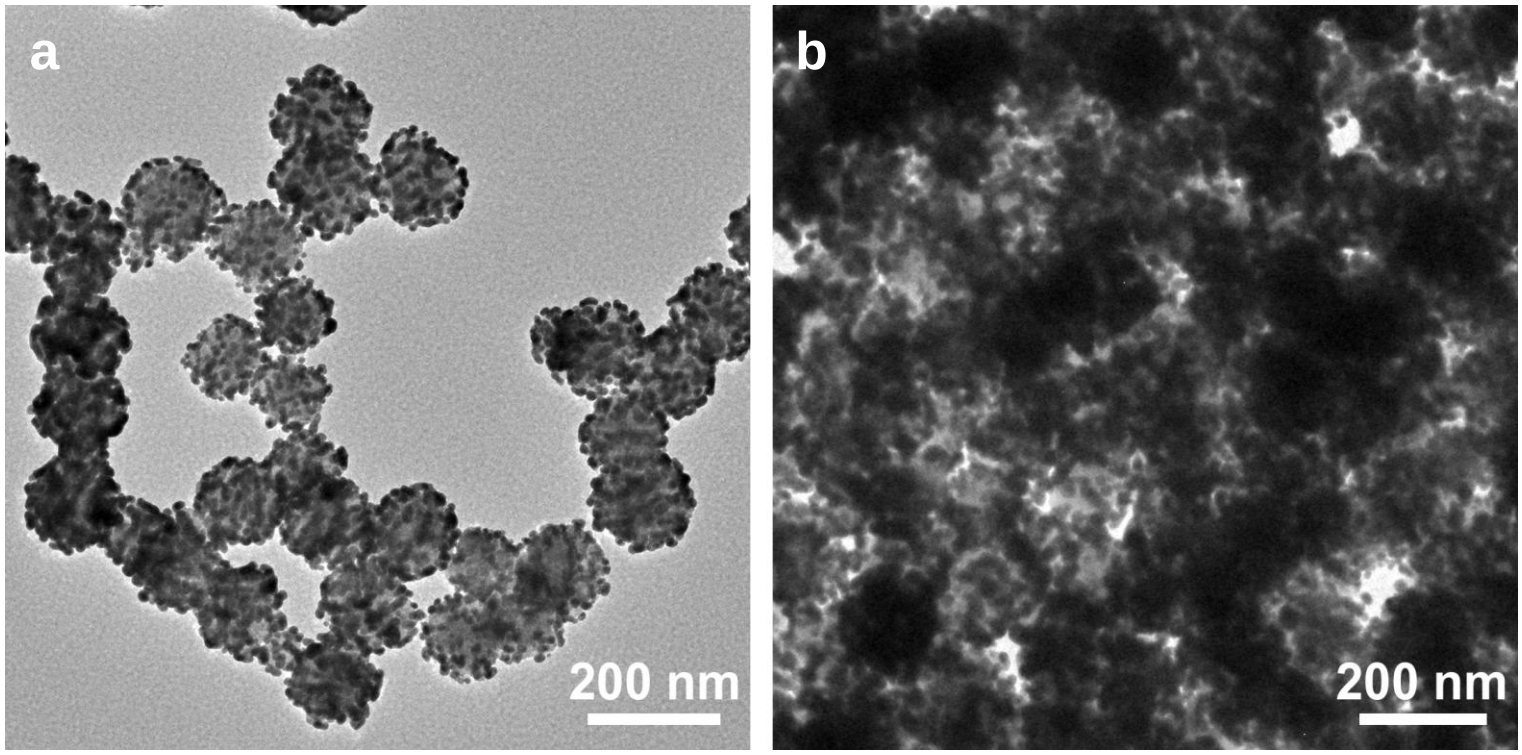


Figure S3. TEM images of Fe_3O_4@Au NCs without a) or with b) the external magnetic field.

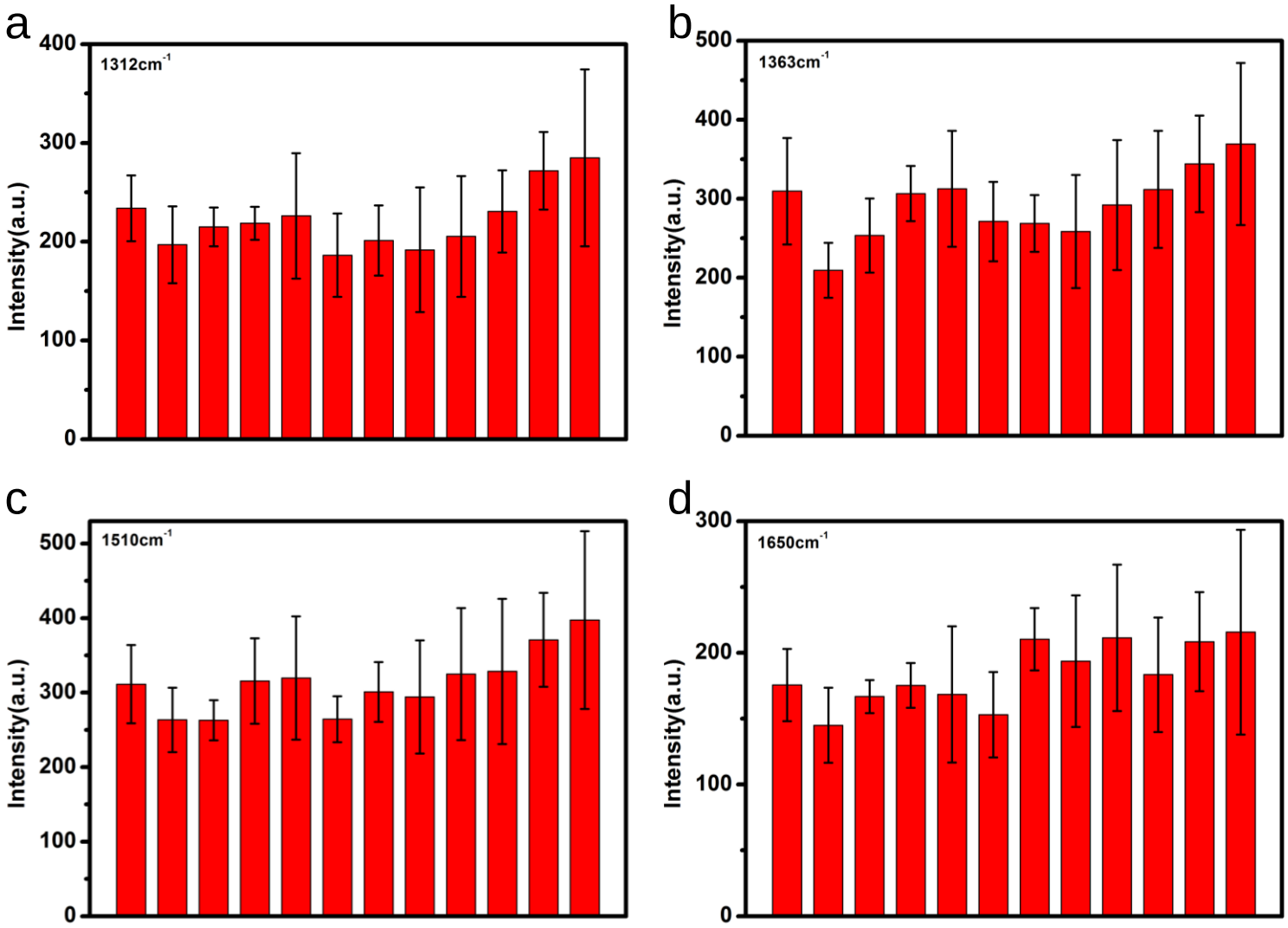
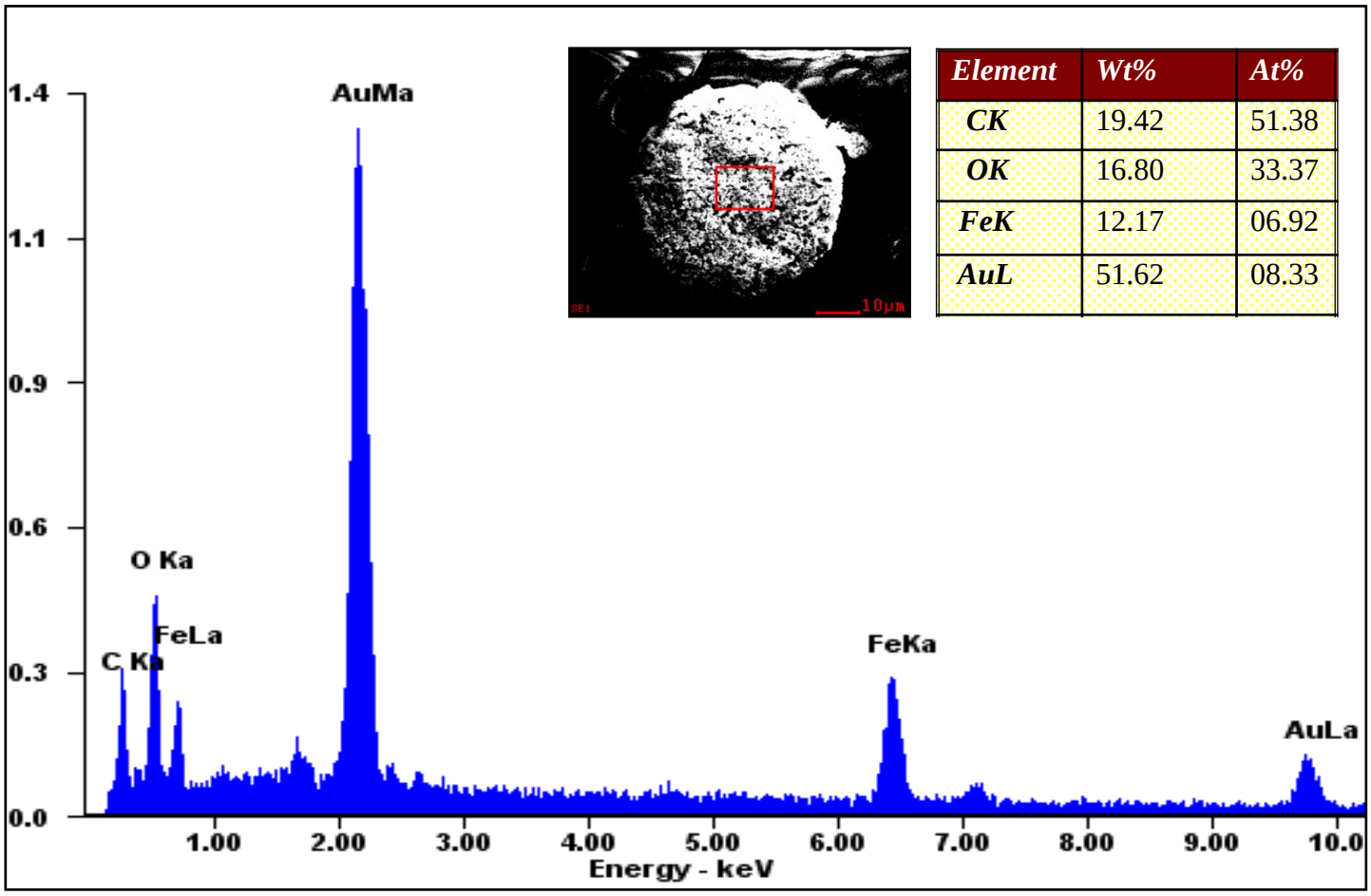


Figure S4. Reproducibility of the SERS signals using the silicon-based substrates from different batches, including 12 separate substrate samples, error bar: standard deviation showing well-to-well variations (n=5), R6G (1×10^{-6}M).



Element	*Wt%*	*At%*
CK	19.42	51.38
OK	16.80	33.37
FeK	12.17	06.92
AuL	51.62	08.33

Figure S5. The EDS analysis of Fe_3O_4@Au NCs on the PAM hydrogel-based substrates, with the insets showing the transfer and the aggregation morphology of Fe_3O_4@Au NCs on a single PAM hydrogel micropillar (left), the composition and ratios of the main elements of the PAM hydrogel-based substates (right).

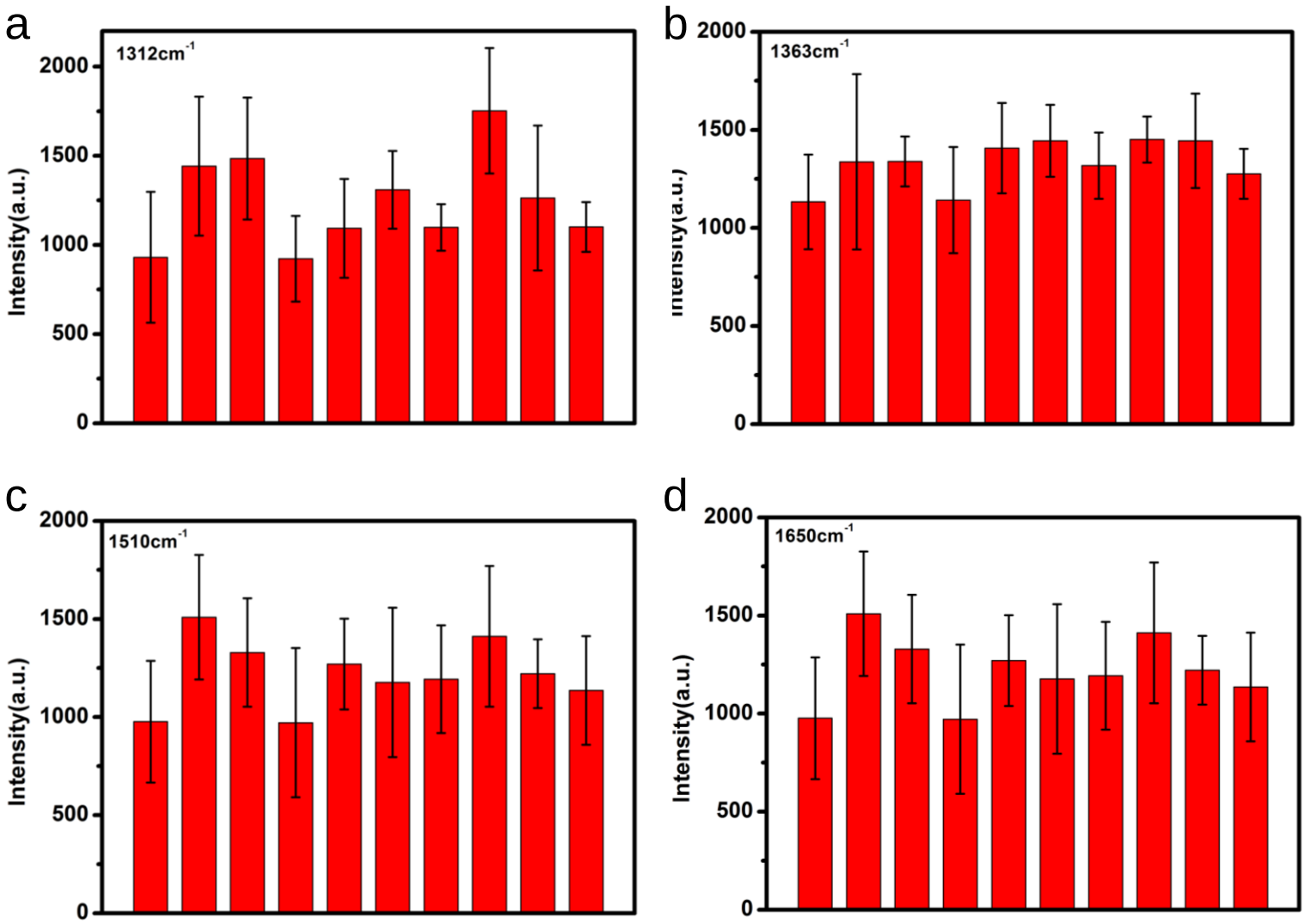


Figure S6. Reproducibility of the SERS signals using the PAM hydrogel-based substrates from different batches, including 10 separate substrate samples, error bar: standard deviation showing well-to-well variations (n=5), R6G (1×10^{-5} M).

Table 1. Enhancement factors (EF) of different substrates for R6G.

	1312 cm^{-1}	1363 cm^{-1}	1510 cm^{-1}	1650 cm^{-1}
Silicon-based substrate	7.45×10^6	7.12×10^6	4.95×10^6	3.46×10^6
Hydrogel-based substrate	1.87×10^6	1.03×10^6	1.03×10^6	0.59×10^6
Control[1]	1.59×10^4	1.63×10^4	1.28×10^4	1.03×10^4
Control[2]	2.52×10^4	3.25×10^4	2.61×10^4	1.77×10^4
Control[3]	1.66×10^4	2.54×10^4	2.38×10^4	1.43×10^4
Control[4]	1.57×10^5	1.52×10^5	1.42×10^5	1.32×10^5

Table 2. Relative standard deviation (RSD) of different substrates for R6G.

	1312 cm^{-1}	1363 cm^{-1}	1510 cm^{-1}	1650 cm^{-1}
Silicon-based substrate	13.7%	14.7%	13.2%	13.0%
Hydrogel-based substrate	16.6%	14.8%	16.8%	19.2%
Control[1]	82.3%	74.9%	79.3%	87.3%
Control[2]	51.4%	46.5%	34.9%	43.4%
Control[3]	59.7%	61.9%	64.2%	61.2%
Control[4]	68.9%	68.2%	67.7%	66.9%

Note:
control[1]: Fe_3O_4@Au NCs deposited into the micro-wells without a magnet.
control[2]: Fe_3O_4@Au NCs deposited on the smooth wafer with a magnet.
control[3]: Fe_3O_4@Au NCs deposited on the smooth wafer without a magnet.
control[4]: A monolayer of Fe_3O_4@Au NCs deposited on the smooth wafer without a magnet.(Reference: Y.J. Li, W.J. Huang, S.G. Sun, *Angew. Chem. Int. Ed.*, 2006, 45, 2537-2539.)

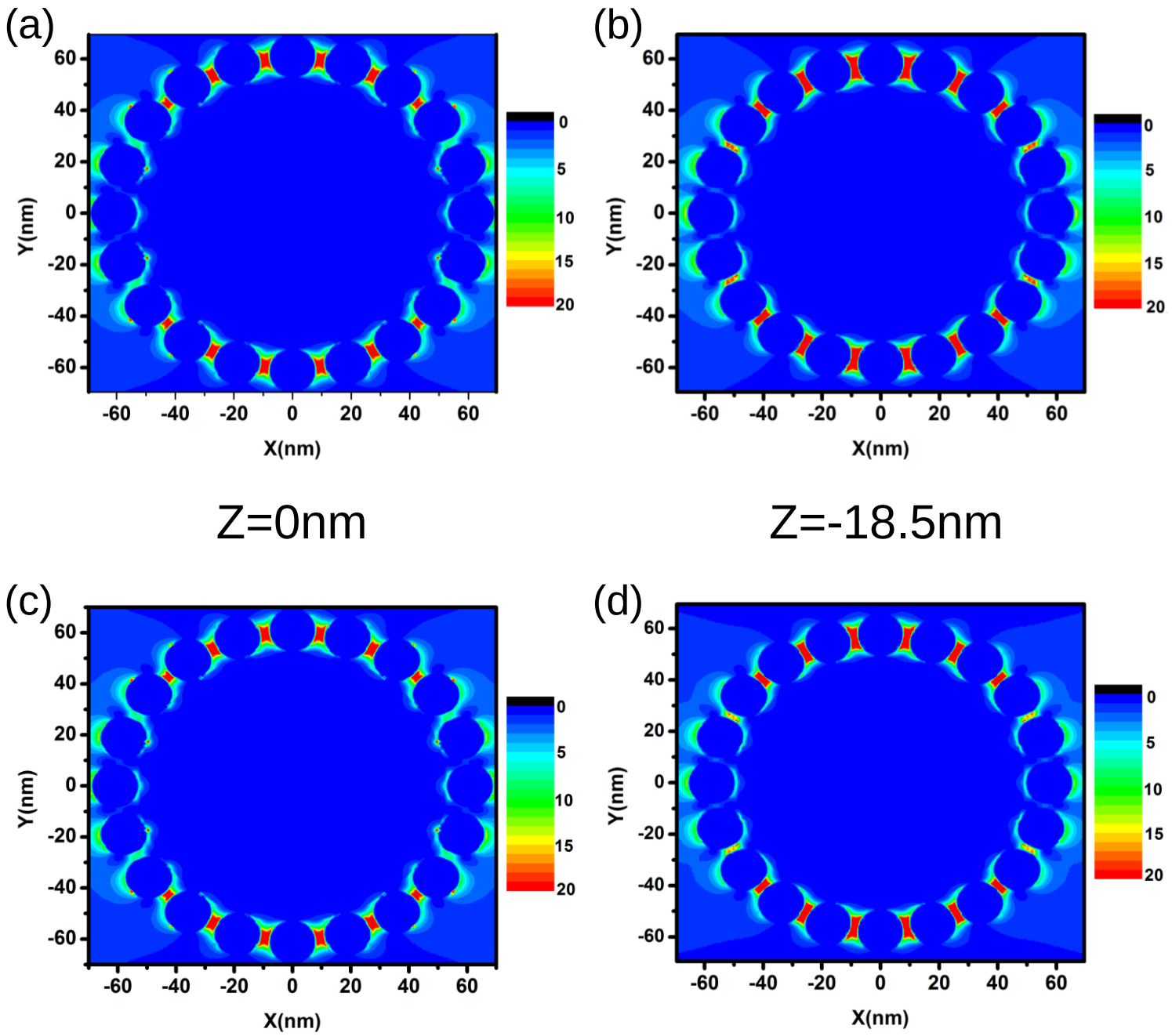


Figure S7. Simulated electromagnetic field distribution of the Fe_3O_4@Au NC at the x-y plane of z=0 nm and z=-18.5 nm in the aggregated status, respectively. a-b) Gap distance between NCs: 1 nm. c-d) Gap distance between NCs: 2 nm.