When the Imām says amen, you too say amen, for whoever says amen at the same time the angels say amen will have his previous sins forgiven

Abu Hurayrah (may Allah be pleased with him) reported that the Prophet (may Allah's peace and blessings be upon him) said: "When the Imām says amen, you too say amen, for whoever says amen at the same time the angels say amen will have his previous sins forgiven."

[Authentic hadith] [Narrated by Bukhari & Muslim]

The Prophet (may Allah's peace and blessings be upon him) ordered us to say 'amen' when the Imām says it because this is the time when the angels say 'amen', and whoever says it at the same time as the angels his previous sins will be forgiven.

http://www.sunnah.global/hadeeth/en/show/5844